

**KARPAGAM ACADEMY OF HIGHER EDUCATION***(Deemed to be University)**(Established Under Section 3 of UGC Act 1956)***Coimbatore – 641 021.****SYLLABUS****DEPARTMENT OF CHEMISTRY**

STAFF NAME: Dr.M.R.EZHILARASI

SUBJECT NAME: INORGANIC CHEMISTRY-II
(COORDINATION CHEMISTRY)

SUB.CODE:18CHP202

SEMESTER: II

CLASS: I M.Sc (CHEMISTRY)

Semester-II**18CHP202
4H 4C****INORGANIC CHEMISTRY- II (COORDINATION CHEMISTRY)**

Instruction Hours/week:L: 4 T:0 P:0 Marks: Internal:40 External: 60 Total:100**Course Objectives**

1. To understand the theories of bonding in coordination compounds.
2. To study the kinetics and mechanisms of reactions of complex compounds.
3. To understand the magnetic properties of coordination compounds.
4. To learn about the coordination compounds present in the biological systems and their functions.

Course Outcome

1. Learned how to name coordination compounds and to be able to draw the structure based on it's name.
2. Used Crystal Field Theory to understand the magnetic properties (and in simple terms the colour) of coordination compounds.
2. Described the stability of metal complexes by the use of formation constants and to calculate thermodynamic parameters from them.
4. Recognized the types of coordination compounds like metal carbonyls, carbocyclic pi complexes in coordination compounds
5. Familiar with some reactions and applications of coordination compounds.
6. Predicted the geometries of simple molecules

UNIT-I

Coordination Chemistry: Nomenclature, isomerism and methods of preparation of coordination complexes- types of ligands.

Bonding: Valence bond theory- Crystal field theory – Crystal field effects in tetrahedral, octahedral and square planar symmetries. Crystal field stabilization energy - weak and strong fields- spectrochemical series. Molecular orbital theory: based on group theoretical approach. M.O. diagram of Oh, Td & square planar symmetries involving pi bonding- experimental evidence for the presence of pi bonding. Magnetic behaviour of the transition metal ions in crystal field and molecular orbital theories.

UNIT-II

Electronic spectra of complexes: Term symbols for d configuration. Characteristics of d-d transition and selection rules. Weak and strong field limits. Orgel and Tanabe - Sugano diagrams. Jahn-Teller tetrahedral distortion and spin orbit couplings. Nephelauxetic effect - charge transfer spectra.

UNIT-III

Metal carbonyls: Methods of preparation, structure, bonding and reactions. Carbonylate ions. Carbonyl hydrides–Vaska's compound, complexes of molecular nitrogen and oxygen. Nitrosyl complexes, dinitrogen complexes. Complexes of unsaturated hydrocarbons- alkenes, allyl and pentadienyl complexes.

UNIT-IV

Carbocyclic pi complexes: Cyclopentadienyl and related complexes synthesis, bonding, structure and reaction. Arene complexes-complexes of biochemical importance: Cytochromes, Haemoglobin, Myoglobin, Cyanocobalamine, Chlorophyll- structure and functions.

UNIT-V

Reaction of coordination compounds: Substitution reactions in square planar and octahedral complexes – Trans effect – mechanism of redox reactions.

Homogeneous catalysis by coordination compounds – hydroformylation –carboxylation of methanol – hydrogenation of unsaturated organic compounds.

SUGGESTED READINGS:

Text Books:

1. Huheey, J. E., Keitler, E. A., & Keitler, R. L. (2002). *Inorganic Chemistry-Principles of Structure and Reactivity* (IV Edition). Singapore: Pearson Education.
2. Madan, R. L., & Tuli, G. D. (2005). *Inorganic Chemistry Questions & Answers*. New Delhi: S. Chand and Co.
3. Sarn, K. (2005). *Co-ordination Chemistry*. New Delhi: Rajat Publications.
4. Catherine, E. H., & Alan G. S. (2012). *Inorganic Chemistry* (IV Edition). England: Pearson Education Limited, Harlow.
5. Cotton, F.A., Wilkinson, G. & Gaus, P.L. (2013). *Basic Inorganic Chemistry* (III Edition). New Delhi: Wiley India (P) Ltd.
6. Lee, J.D. (2013). *Concise Inorganic Chemistry* (V Edition). Wiley India (P) Ltd., New Delhi.

Reference Books:

1. Agarwal, R. C. (1998). *Some Recent Aspects of Inorganic Chemistry*. Allahabad: Kitab Mahal.
2. Chakraborty, D. K. (2003). *Inorganic Chemistry*. New Delhi: New Age International Publishing Pvt. Ltd.
3. Cotton, F.A., Wilkinson, G., Murillo, C.A. & Bochmann, M. (2014). *Advanced Inorganic Chemistry* (VI Edition). New Delhi: Wiley India Pvt. Ltd.
4. Drago, R. S. (1965). *Physical Methods in Inorganic Chemistry*. New York: Rein Gold Publishing Corporation.
5. Miessler, G. L., Fischer, P.J. & Tarr, D.A. (2014). *Inorganic Chemistry* (V Edition). Pearson, New York.

**KARPAGAM ACADEMY OF HIGHER EDUCATION***(Deemed to be University)**(Established Under Section 3 of UGC Act 1956)***Coimbatore – 641 021.****LECTURE PLAN****DEPARTMENT OF CHEMISTRY**

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CLASS: I M.Sc (CHEMISTRY)

S.No	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
UNIT-I			
1	1	Co-ordination chemistry: Types of ligand, Nomenclature Isomerism, Structure determination of complexes	T1-332-365
2	1	Bonding: Valence bond theory- Octahedral complexes, Tetrahedral and square planar complexes	T1-375-390,T2-139-153,391-394
3	1	CFT, Important features,Splitting of d-orbitals in Octahedral complexes	T1-390-395
4	1	Square planar and tetrahedral complexes	T1-395-399
5	1	Factors influencing the magnitude of	T1-399&408,T2-P-

		CFT and its applications, Crystal field stabilization energy & Spectrochemical series	404-413
6	1	MO Theory-Octahedral complexes	T1-430-441,T2-P-413-418
7	1	Square planar and tetrahedral complexes, π bonding in MO theory	T2-418-425
8	1	Experimental evidence for π bonding & Comparison of VBT,MOT,CFT	T1-425-433&448-450
9	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit 1=9		
	UNIT-II		
1	1	Electronic spectra of complexes: Relative energies of the orbitals, Term symbols and the vector method, Term symbols for excited states	T3-20-28
2	1	Term symbols for d-configurations, Selection rules	T3-161-162,164-166
3	1	Weak and strong field limits	T1-403-407
4	1	Orgel diagram, Tanabe sugano diagram	T2-440-447
5	1	Jahn teller tetrahedral distortion, Spin orbit couplings, Nephelauxetic effect	T2-449-455 , 413,T4-39
6	1	Charge transfer spectra	T2-P-455-459
7	1	Recapitulation and discussion of important questions	

	Total No of Hours Planned For Unit II=7		
	UNIT-III		
1	1	Metal Carbonyl complexes: Introduction, Preparation ,properties ,structure and substitution reactions of carbonyl complexes	T2-630-633&686-688
2	1	Carbonylate ions and Carbonyl hydride complexes, Carbonyl halide (carbonyl fluoride)	T2-211-213&639-647
3	1	Vaska's compound, Nitrosyl complexes	T2-689-695& 650-653
4	1	β –diketones (Chelate complexes)	T4-P-187-188
5	1	Alkene and Alkyne complexes	T2-P-662-666
6	1	Alkyl and pentadienyl complexes	T2-P-666-668
7	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit III=7		
		UNIT-IV	
1	1	Carbocyclic pi complexes : Structure of cyclopentadienyl compounds, Covalent versus ionic bonding	T4-688-691,T2-673-680
2	1	Synthesis of cyclopentadienyl compounds, Arene complexes	T4-P-684-688, T2-P-680-683
3	1	Cycloheptatriene and tropylium complexes	T2-P-683-684
4	1	Cyclooctatetraene and cyclobutadiene complexes	T4-P-1122-1123,T2-P-684-686

5	1	Cytochromes, Haemoglobin	T4-798-800,T2-891-895, 902-908
6	1	Myoglobin, The physiology of myoglobin and haemoglobin, Cyanocobalamine(Vitamin B ₁₂)	T2-897-902 & T5-863-864
7	1	Chlorophyll structure and function	T4-P-125-128,T2-P-917-919
8	1	Recapitulation and discussion of important questions	
Total No of Hours Planned For Unit IV=8			
UNIT-V			
1	1	Reactions of co-ordination compounds: Substitution reactions in square planar complexes, Octahedral complexes	T2-538-557
2	1	Trans effect –Theories, mechanism , reactions and uses	T1-P527-542,T2-P-543-547
3	1	Redox reactions	T2-P-557-572
4	1	Hydroformylation , Carboxylation of methanol-mono acetic acid process, Wacker process, Synthetic gasoline	T2-P-711-717
5	1	Hydrogenation of unsaturated organic compounds (Alkene hydrogenation), Tolman catalytic loops, synthetic gas, Ziegler-Natta catalyst	T2-P-706-711, 781
6	1	Recapitulation and discussion of important questions	
7	1	Discussion of previous ESE question papers	

8	1	Discussion of previous ESE question papers	
	Total No of Hours Planned for unit V=8		
Total Planned Hours	40		

References:**TEXT BOOKS**

T1. Wahid U. Malik, G. D. Tuli, R.D. Madan, 2003, selected topics in inorganic chemistry, S.Chand & company, New Delhi

T2. Huheey.J.E, E.A. Keitler, & R.L. Keitler, 2012. Inorganic chemistry, Vol-IV, Pearson Education, Singapore.

T3. Drago, R.S, 1965, Physical methods in inorganic chemistry, Rein gold publishing corporation, New York.

T4. Cotton . F. A, & G.Wilkinson, 2003, Advanced inorganic chemistry, John Wiley & sons, New York

Lecture notes

UNIT-I

SYLLABUS

Coordination Chemistry: Nomenclature, isomerism and methods of preparation of coordination complexes- types of ligands.

Bonding: Valence bond theory- Crystal field theory – Crystal field effects in tetrahedral, octahedral and square planar symmetries. Crystal field stabilization energy - weak and strong fields- spectrochemical series. Molecular orbital theory: based on group theoretical approach. M.O. diagram of Oh, Td & square planar symmetries involving pi bonding- experimental evidence for the presence of pi bonding. Magnetic behaviour of the transition metal ions in crystal field and molecular orbital theories.

CO-ORDINATION CHEMISTRY

Definition of some terms:

I) simple salts:

When an acid react with alkali, neutralisation takes place and a simple salt is produced.



When dissolved in water, these salts ionize and produce ions in solution. Depending upon the extent of neutralisation of the acid or base, these may be normal, acid or basic salts.

Mixed salts contain more than one acidic or basic radical's e.g : NaKSO₄

II) Molecular or Addition compounds:

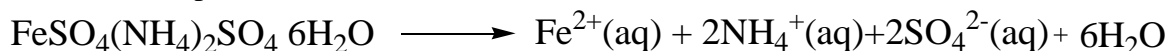
When solutions containing 2 or more salts in stoichiometric proportions are allowed to evaporate, we get crystals of compounds known as molecular or addition compounds.

These are of 2 types depending on their behavior in aqueous solution.

(i) Double salts or Lattice compounds

The addition compounds having the following characteristics are called double salts or lattice compounds.

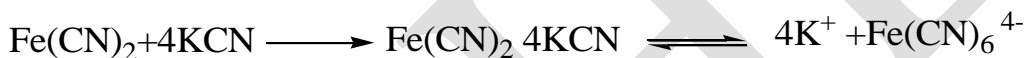
- a) They exist as such in crystalline state.
b) When dissolved in water, these dissociate in to ions in the same way in which the individual components of the double salts do.



Potash alum

(ii) Coordination (or complex) compounds:

It has been observed that when solution of $\text{Fe}(\text{CN})_2$ and KCN are mixed together and evaporated, potassium ferrocyanide, $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$ is obtained which in aqueous solution does not give test for the Fe^{2+} and CN^- ions, but gives the test for K^+ ions and ferrocyanide ion, $\text{Fe}(\text{CN})_6^{4-}$.



Thus we see that in the molecular compound like $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$, the individual compounds lose their identity. Such molecular complexes are called coordination (or complex) compounds.

III) Ligands :

The neutral molecules or ions which are attached with the central metal ions called ligands. Eg: In the complex ion $[\text{Fe}(\text{CN})_6]^{3-}$, the six CN^- ions are the ligands.

IV) Coordination number (C.N) or ligancy

It is the total no of the atoms of the ligands that can coordinate to the central metal ion. Numerically coordination no represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands thus in $[\text{Fe}^{III}(\text{CN})_6]^{3-}$. C.N of Fe^{3+} is six while in $[\text{Ni}^{II}(\text{NH}_2\text{-CH}_2\text{-H}_2\text{N})_3]^{2+}$ C.N of Ni^{2+} is also six, since each ethylene diamine molecule.

* $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-H}_2\text{N}$ * has 2 donor atoms. viz nitrogen atoms denoted by asterisks.

V) Coordination sphere:

The central metal ion and the ligands that are directly to it are enclosed in a square bracket which Werner has called coordination sphere or first sphere of attraction. The anions being outside the square bracket form the second sphere of attraction.

Classification of ligands:

The following 2 ways have been used to classify the ligands.

1. Classification based on donor and acceptor properties of the ligands.

i) Ligands having one (or more) lone pair (or pairs) of electrons.

Such ligands are further classified as:

a) ligands which contain vacant Π -type orbital that can receive back donated Π electrons from the metal ion in low oxidation state.

Ex: Co, No, CN, isocyanides, $R-N=C$, R_3P , R_3AS , α, α -dipyridyl, O-phenanthroline and unsaturated organic molecules.

b) ligands which do not have vacant orbital's to receive back donated electrons from the metal, eg: H_2O , NH_3 , F.

ii) ligands having no lone pairs of electrons but have Π -bonding electrons e.g ethylene, benzene, cyclopentadienyl ion.

2. Classification based on the number of donor atoms present in the ligands:

The ligands of this class may be of the following types:

i) Monodentate or unidentate ligands:

The ligands which have only one donor atom and hence can coordinate to the central metal ion at one site only are called monodentate or unidentate ligands. These ligands may be neutral molecules, negatively charged ions or positively charged ions. e.g:

a) Neutral monodentate ligands:

The names of neutral ligands are not systematic,

e.g: H_2O (aquo), NH_3 (ammine), CO (carbonyl), CS (thiocarbonyl), NO (nitrosyl), NS (thionitrosyl).

b) Negative monodentate ligands:

If the names of the anions end in -ide, -ite, or ate, the ending of the name of the ligands used are -ido, -ito, and -ato respectively.

Eg : $CH_3 COO^-$ (acetate), F^- (fluoro), Cl^- (chloro), Br^- (Bromo), I^- (iodo), CN^- (cyano) etc.

c) Positive monodentate ligands:

Egs of positively charged monodentate ligands are NO^+ (nitrosylium) and $NH_2NH_3^+$ (hydrazonium).

Quite obviously the names of these ligands have the suffix -ium.

Bridging ligands:

The ligand forms 2 σ -bonds with two metal atoms and thus acts a bridge between the metal atoms.

Such a ligands is called bridging ligand and the resulting complex is known as bridged complex.

Eg: OH^- , F^- , Cl^- , NH_2^- , CO , O^{2-} , SO_4^{2-} etc.

ii) Bidentate, tridentate..... polydentate ligands:

The ligands having 2,3, 4,5 or 6 donor atoms called, bi,tri,tetra, (or quadri), penta and hexa (or sexi) dentate ligands respectively.The Bidentate, tridentate etc are called polydentate or multidentate ligands.The polydentate ligands many further be subdivided according to the nature of their donor atoms.

For eg: ethylene diamine, $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ is a Bidentate ligand with 2 neutral donors. Viz N atoms.

Whereas oxalate ion $\left[\begin{array}{c} \text{O}=\text{C}-\text{O}^- \\ | \\ \text{O}=\text{C}-\text{O}^- \end{array} \right]$ is bidentate having 2 acidic donors viz O^- .

Glycinato ion, $\left[\begin{array}{c} \text{H}_2\text{N}-\text{C} \begin{array}{l} \text{H}_2 \\ | \\ \text{C}=\text{O} \end{array} -\text{O}^- \end{array} \right]$ is again a bidentate with one neutral donor Viz N-atom and a acidic donor vic O^- .

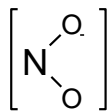
Symmetrical and unsymmetrical bidentate ligands:

- Bidentate ligands may be symmetrical or unsymmetrical ligands.
- In symmetrical bidentate ligands the 2 coordinating atoms are the same, while in unsymmetrical bidentate ligands the 2 coordinatings atoms are different.
- Thus the symmetrical and unsymmetrical bidentate ligands are generally represented as (AA) and (AB) respectively, where A and B are the donor atoms.

Ambidentate ligands:

These are the ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to the metal ion at a given time. Such ligands are called Ambidentate ligands.

e.g:



Nitro (M-NO₂),

Nitro (M-ON=O).

CN⁻ ion

Cyano (MCN),

Isocyano (MCVC).

NCS⁻ ion

thiocyanate (MSCN),

Isothiocyanate (MNCS).

NCO⁻ ion

MOCN, MNCO

SeCN⁻ ion

MSeCN, MNCS_e.

R₂SO

S bonded or O bonded.

S₂O₃⁻ ion

thiosulphato-S (MSSO₃),

thiosulphato-O (MOSO₂S)

Some common Polydentate Ligands:

Type of ligand	Name of ligand	Structure of ligand	Abbreviation
Bi-dentate	Carbonato	$\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{O}-\text{C}-\text{O}- \\ * \quad * \end{array} \right]^{2-}$	CO ₃ ²⁻
	Acetylacetonato	$\left[\begin{array}{c} \text{O}^- \quad \text{O}^- \\ \quad \\ \text{H}_3\text{C}-\text{C}=\text{C}-\text{C}=\text{CH}_3 \\ \\ \text{H} \end{array} \right]^-$	(acec) ⁻
Tridentate	Diethylenetriamine	$^* \text{NH}_2(\text{CH}_2)_2\text{-NH}(\text{CH}_2)_2\text{-NH}_2^*$	Dien
	Imido-di-acetato	$\left[\begin{array}{c} \text{COO}-\text{CH}_2-\text{NH}-\text{CH}_2-\text{COO} \\ * \quad * \quad * \end{array} \right]^{2-}$	(IDA) ²⁻

Tetra dentate	Triethylene tetramine Nitrilo triacetate	$\text{H}_2\text{N}^*-(\text{CH}_2)_2-\text{N}^*-(\text{CH}_2)_2-\text{N}^*-(\text{CH}_2)_2-\text{NH}_2^*$ $\left[\begin{array}{c} \text{CH}_2 \text{COO}^* \\ \\ \text{N} \\ \\ \text{CH}_2 \text{COO}^* \\ \\ \text{CH}_2 \text{COO}^* \end{array} \right]^{3-}$	Trien (NTA) ³⁻ (NTA) ³⁻
Penta dentate	Ethylene diamine triacetato	$\left[\begin{array}{c} \text{OOC}-\text{H}_2\text{C}^* \\ \\ \text{OOC}-\text{H}_2\text{C}^* \\ \\ \text{N}^*-(\text{CH}_2)_2 \\ \\ \text{N}^*-\text{CH}_2-\text{COO}^* \\ \\ \text{H} \end{array} \right]^{3-}$	-
Hexa dentate	Ethylene diamine tetra acetate	$\left[\begin{array}{c} \text{OOC}-\text{H}_2\text{C}^* \\ \\ \text{OOC}-\text{H}_2\text{C}^* \\ \\ \text{N}^*-(\text{CH}_2)_2 \\ \\ \text{N}^*-\text{CH}_2-\text{COO}^* \\ \\ \text{CH}_2 \text{COO}^* \end{array} \right]^{4-}$	(EDTA) ⁴⁻ Y ⁴⁻

Nomenclature of coordination compounds:

The first comprehensive system of nomenclature was suggested by A. Werner. Though this has been modified by the inorganic nomenclature committee of the international union of pure and applied chemistry (IUPAC), the fundamental rules suggested by Werner essentially remain the same. Trivial names for certain coordination compounds still persist e.g. many authors still prefer to call the ions viz [Fe^{II}(en)₆]⁴⁺ and [Fe^{III}(CN)₆]³⁻ ferrocyanide and ferric cyanide instead of hexacyanoferrate (II) and hexacyano ferrate (III) ions respectively as suggested by IUPAC system. On the basis of the nature of the cation and anion of the complexes, these are classified as: cationic complexes eg [Cr(H₂O)₄Cl]⁺, [Cu(NH₃)₄]²⁺ etc. anionic complexes eg [Cr(en)I₄]⁻, [Pt(NH₃)Cl₅]⁻ etc. ionic complexes: these contain simple or complex cation and simple or complex anion, eg K₃⁺[PtCl₆]²⁻ Neutral complexes; these are non ionic or molecular complexes e.g. [Ni(CO)₄]⁰. For naming all the types of complexes mentioned above the following rules are observed.

1. Naming of the Ligands

In all the types of complexes mentioned above the ligands are named first and the central atom is named last. The ligands are named according to the following rules.

i) Order of Naming Ligands:

- If the coordination sphere of a given complex compound contains various types of ligands. The ligands are named in alphabetical order.
- The prefixes di, tri etc are not to be considered while determining this alphabetical order.
- For example $[\text{Co}(\text{NH}_3)_4(\text{NO})_2\text{Cl}]^+$ ion is named as tetra ammine chloronitro cobalt (III) ion.

ii) Naming of the negative ligands:

- In general, if the anion name ends in -ide, -ite, or -ate, the final -e is replaced by o giving -ido, -ito, and -ato respectively.
- Eg: SO_3^{2-} (sulphito), SO_4^{2-} (sulphato), CH_3COO^- (acetate), S^{2-} (thio or sulphido), NO_3^- (nitrate), NH_2^- (imido) NH_2^- (amino or amine), N_3^- (azido), NHOH^- (hydroxylamido).
- Some exceptions to this rule are: F^- (fluoro), Cl^- (chloro), CN^- (cyano), O^{2-} (oxo), OH^- (hydroxo), O_2^{2-} (Peroxo), H_2O^- (perhydroxo).

iii) Naming of the neutral ligands:

- For neutral ligands, the names are not systematic.
- Eg of neutral ligands: H_2O (aquo), NH_3 (ammine), CO (carbonyl), CS (thiocarbonyl), NO (nitrosyl), NS (thionitrosyl).
- First H_2O (aquo) then NH_3 (ammine) second other neutral coordinated ligands in the order, B, Si, C, Sb, As, P, N, H, Te, Se, S, At, I, Br, Cl, O, F, third :neutral organic ligands in alphabetical order.

iv) Naming of the positive ligands:

- Positively charged ligands have suffix ium e.g NH_2NH_3^+ is called hydrazinium and NO^+ is nitrosylium.

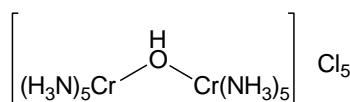
v) Indication of the number of ligands:

- the number of simple ligands such as Cl^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$ etc is indicated by using before them the greek prefixes; di, tri, tetra, penta, hexa etc.
- In case of chelating ligands like ethylenediamine, trialkyl phosphine which contain the prefixes di, tri etc in their ligand names, the prefixes, bis (for two), tris (for three), tetrakis (for four), pentakis (for five), hexakis (for six) etc are used before their names.
- The ligands to which these prefixes refer are often placed in parentheses.
For ex:
- $[\text{Co}(\text{NH}_3)_2(\text{en})_2]\text{Cl}_3$ -diammine -bis(ethylene diamine) cobalt (III)chloride.

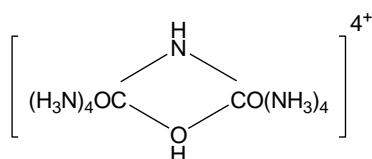
vi) Naming of the bridging ligands of the bridged polynuclear complexes:

- The complexes having 2 or more atoms are called polynuclear complexes.
- In these complexes the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens and by adding the prefix μ before its name.
- The greek letter μ should be repeating before the name of each different bridging group.
- Two or more bridging groups of the same kind are indicated by di- μ , tri- μetc.

Examples:



μ -hydroxo-bis(penta-amine chromium (III) chloride.



μ -amido μ -hydroxoocta ammine dicobalt (III) ion

viii) Naming of Ambidentate ligands:

The ligands which can be coordinated to the central metal ion through either of the two donor atoms are called Ambidentate ligands.

- Thiocyanate for -SCN
- Isothiocyanate for -NCS
- Nitro for -NO₂
- Nitrito for -ONO

$[\text{Co}(\text{NH}_3)_5 - \text{ONO}]\text{Cl}_2 \longrightarrow$ Nitro- O or Nitrito complex

$[\text{Co}(\text{NH}_3)_5 - \text{NO}_2]\text{Cl}_2 \longrightarrow$ Nitro- N or Nitrate complex

$[\text{Pd}(\text{diph})(\text{SCN})_2] \longrightarrow$ Thiocyanate -S-complex

$[\text{Pd}(\text{diph})(\text{NCS})_2] \longrightarrow$ Thiocyanate-N-complex

$\text{K}_2 \left[\text{Ni} \left(\begin{array}{c} \text{S}-\text{C}=\text{O} \\ | \\ \text{S}-\text{C}=\text{O} \end{array} \right)_2 \right] \longrightarrow$ Potassium bis(N,N-diamine ethylamino ethyl sulphide-N',S)-platinum(II)

$\left[\begin{array}{c} \text{Cl} \quad \text{NH}_2-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{Pt} \\ \diagdown \quad \diagup \\ \text{Cl} \quad \text{SH}-\text{CH}_2 \\ | \quad | \\ \text{C}_2\text{H}_4 \quad \text{N}(\text{CH}_3)_2 \end{array} \right] \longrightarrow$ Dichloro(N,N-dimethylamino ethylamino ethyl sulphide-N',S)-platinum(II)

2. Naming of the central metal ion and mononuclear complexes:

Different rules are used for naming different complexes.

i) Anionic complexes:

- In naming anionic complexes like $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$, $[\text{Cr}(\text{en})\text{I}_4]^-$ etc ligands are named first and then the central metal ion.
- To name the central metal ion the suffix “ate” is attached to its name and in order to indicate the oxidation state of the neutral ion this suffix is followed by roman numeral (such as I, II, III, etc).

Examples:

$[\text{Cr}^{\text{III}}(\text{en})\text{I}_4]^-$ -Tetra iodo (ethylene diamine) chromate (III) ion.

$[\text{Pt}^{\text{IV}}(\text{NH}_3)\text{Cl}_5]^-$ - pentachloro mono-ammine platinate (IV) ion.

ii) Cationic and neutral complexes:

- In case of cationic and neutral complexes like $[\text{Cr}(\text{H}_2\text{O})\text{Cl}_2]^+$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Ni}(\text{CO})_4]$ etc, the ligands are named first and then the central metal ion followed by a roman numeral in parentheses to indicate its oxidation state.
- The suffix ate is not attached to the name of the metal in case of these complexes.

e.x : $[\text{Cr}^{\text{III}}(\text{NH}_3)_4\text{Cl}_2]^+$ - dichloro-tetra aquo chromium (III) ion.

$[\text{Ag}^{\text{I}}(\text{NH}_3)_2]^+$ - Diammine silver (I) ion.

iii) Ionic complexes:

In ionic complexes like $K_2[Pt^{IV}Cl_6]^{2-}$, $[Pt^{IV}(NH_3)_4Br_2]^{2+}Br_2^-$, $[Pt^{II}(Py)_4]^{2+}$, $[Pt^{II}Cl_4]^{2-}$ etc. the cation is named first and then the anion as we do in naming a simple salt like NaCl.

Names of some mononuclear ionic complex compounds:

Composition	Cation and anion type	Name
$K_2[Pt^{IV}Cl_6]$	Simple cation, K^+ and complex anion, $[Pt^{IV}Cl_6]^{2-}$	Potassium hexachloro palatinate (IV)
$NH_4[Cr^{III}(SCN)_4(NH_3)_2]$	Simple cation, NH_4^+ and complex anion, $[Cr^{III}(SCN)_4(NH_3)_2]^-$	Ammonium tetra thiocyanate diamine chromate(III)
$[Pt^{II}(Py)_4]$, $[Pt^{II}Cl_4]$	Complex cation $[Pt^{II}(Py)_4]^{2+}$ and complex anion $[Pt^{II}Cl_4]^{2-}$	Tetrapyridine platinum(II) tetrachloro palatinate (II)
$[Pt^{IV}(NH_3)_4Br_2]Br$	Complex cation, $[Pt^{IV}(NH_3)_4Br_2]^{2+}$ and simple anion Br^-	Dibromo -tetra ammine platinum IV bromide

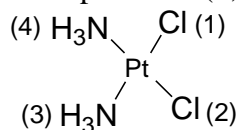
3. Metal to Metal bonding:

- In complexes containing metal to metal bonds, the prefix bi- is used before the name of the metals forming a metal to metal bond.
- E.g the name of the complex having the formula,

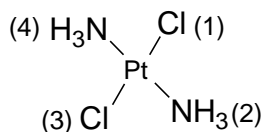
$$\left[\begin{array}{c} (CH_3NH_2)_4 Pt-Pt(NH_2CH_3)_4 \\ Cl \quad Cl \end{array} \right] 2Cl^-$$
- Is sym-dichloro octakis (methyl-amine) bi-platinum (II) chloride.

4. Geometrical isomers:

- Geometrical isomers are named either by using the prefixes cis for adjacent positions (90° apart) and trans for opposite (180° apart) positions before the name of the ligands or by numbering system.
- In square planar complexes the group at positions (1,2) and (3,4) are cis to each other while those at positions (1,3) and (2,4) are trans to each other.



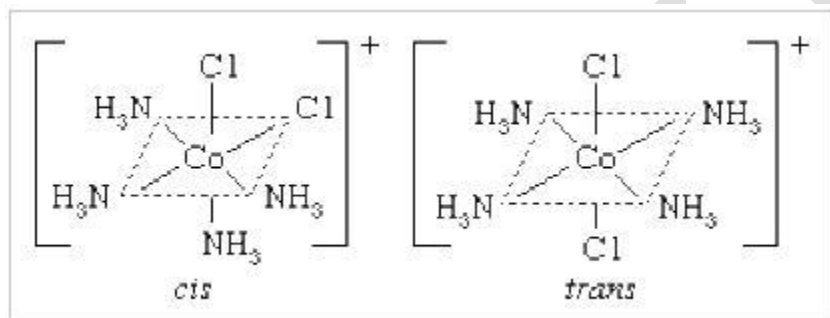
Cis-diamine dichloro platinum (II) or 1,2-dichlorodiammine platinum (II)



Trans- diamine dichloro platinum (II) or diamine 1,2-dichloro platinum (II)

- In mono nuclear octahedral complexes of Ma b₄ type (1,2), (1,3), (1,4), (1,5), (6,2), (6,3), (6,4), (6,5), (2,3), (3,4), (4,5), and (5,2) are cis positions and (1,6), (2,4) and (3,5) are trans positions.
- In mono nuclear complexes of Ma₃ b₃ type (1,2,3) are cis (1,2,6) are trans positions thus,

Figure:



Cis-dichlorotetraammine cobalt (III) ion or 1,2-dichlorotetraammine cobalt (III)ion

Trans- dichlorotetraammine cobalt (III) ion or 1,6-dichlorotetraammine cobalt (III)ion

5) Optical isomers:

- Dextro and levorotatory complexes are respectively designated either by (+) or (-) by d or l, e.g
- (+) or d-K₃[Ir(C₂O₄)₃]-Potassium (+), or d-trioxalato iridatr(III)
- If the ligands molecules of a complex are optically active, the configuration of the whole ion is replaced by D or L and that of the ligand molecules by d or l e.g
D-[Co (l-pn)₃]⁺

Methods of preparation of coordination complexes:

i) Solubility:

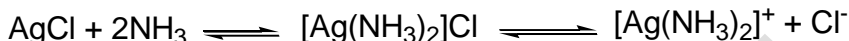
Complex formation is often indicated by the fact the solubility of a sparingly soluble salt is increased when one of its ions forms a complex in solution. E.g

i) when KCN is added to a solution of AgCN which is sparingly soluble, the solubility of AgCN is increased due to the formation of a soluble complex ion, $[\text{Ag}(\text{CN})_2]^-$



Sparingly soluble soluble complex ion(soluble)

ii) Addition of NH_3 to insoluble AgCl gives very soluble $[\text{Ag}(\text{NH}_3)_2]^+$



insoluble

soluble

ii) Change in colour:

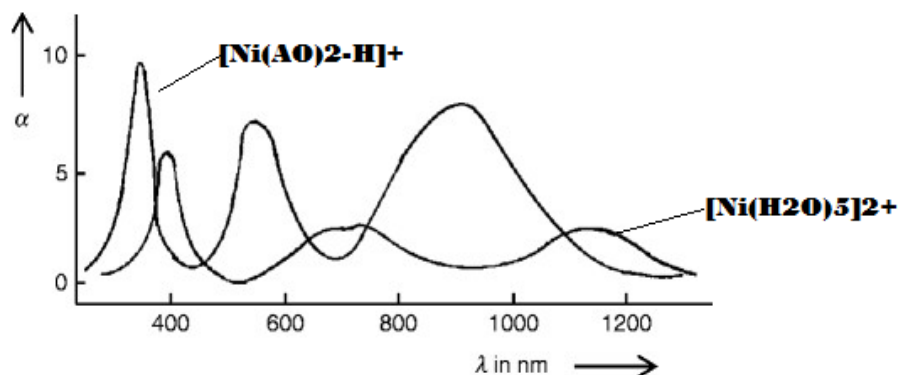
Sometimes a change in colour is an indication of complex formation. E.g addition of NH_3 to $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ion leads to an intense blue colour due to the formation of the complex ion, $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

iii) P^{H} Measurements

Generally the ligands are either weak bases or acids. The formation of a complex is accompanied by the displacement of one or more, usually weak, acidic, protons of the ligands by the metal ion. Thus increases the concentration of H^+ , $[\text{H}^+]$ in the complex formation and hence causes a drop in the value of P^{H} . Thus the change in P^{H} value can be used as an indication of the extent of complex formation.

iv) Visible absorption spectral studies:

- The absorption of the light in the visible region (400-800 mμ) by a metal ion depends on the electron transitions within the ion and also on the type and strength of ligands to metal bonding.
- Thus the metal containing d-electrons (except those having 10e⁻s in d-orbital) give variable colour depending on the nature of the ligands attached with the metal ion.
- In many cases the intensity of absorption is increased and the absorption shifts to higher energies (lower mμ), when coordinated water molecules are replaced by ligands more basic than water.
- In this figure the visible spectrum shown by dotted lines is that of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion while that shown by solid lines is that of α-amineoxime complex of Ni^{2+} , represented as $[\text{Ni}(\text{AO})_2\text{-H}]^+$.
- The absorption has shifted to higher energies (i.e lower mμ) and has become more intense.



visible spectra of $[\text{Ni}(\text{H}_2\text{O})]^{2+}$ and $[\text{Ni}(\text{AO})_2\text{-H}]^+$

v) Change in chemical properties:

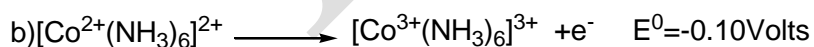
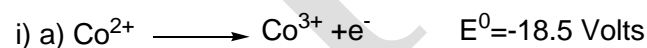
When a metal ion combines with a ligand to form a complex, its usual chemical properties are lost in the solution. Thus, the loss of the normal chemical properties of the metal ion in solution is an indication of the complex formation. e.g., when CuSO_4 is treated with excess KCN, the complex $\text{K}_3[\text{Cu}^+(\text{CN})_4]$ (soluble complex) is formed. This complex gives none of the tests of Cu^+ .

vi) polarographic method:

polarographic measurements provide certain information which can be used for the detection of complex formation, determination of coordination number and stability constant.

vii) Change in oxidation potential:

There is a decrease in ionic activity of the metal and hence an increase in its oxidation potential, when it combines with ligands to form a complex e.g:



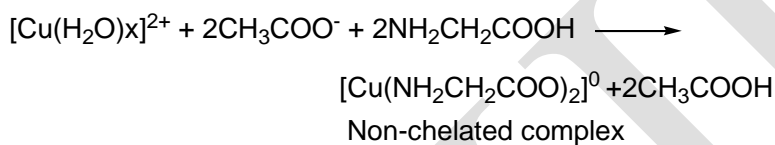
viii) Magnetic susceptibility:

A measurement of the magnetic susceptibility sometimes indicates the formation of a complex, nature of bonding and stereochemistry. e.g: Ni(II) square planar complexes like $[\text{Ni}(\text{Big})_2]^0$ (dsp^2 hybridisation) are diamagnetic due to the absence of unpaired electrons while Ni(II) tetrahedral

complexes like $[\text{NiCl}_4]^{2-}$ (sp^3 hybridisation) are para magnetic due to the presence of two unpaired electrons.

ix) Conductance measurements:

There is a decrease or increase in the value of electrical conductance of the solution in which complex formation occurs. This is due to the disappearance or production of ions of comparatively higher mobility. e.g : the addition of 2 moles of glycine, $\text{NH}_2\text{CH}_2\text{COOH}$ to one mole of aqueous copper acetate solution decrease the solution conductivity because of the formation of a non-ionic chelated complex.



This method can also be used to give useful information about the total no of ions given by a complex in solution and charge type on each ion. This point has been discussed for CO (III) Ammine under Werner's theory.

X) Dipole moment measurements:-

Dipole moment measurement is often used to distinguish between cis and trans-isomers of a complex.e.g:- $[\text{Pt}^{\text{II}}(\text{R}_3\text{P})_2\text{Cl}_2]^0$ has been isolated in α - and β -forms. $\alpha = 0$. Collinear pt-cl and pt-p bond α -trans, β -high dipole moment,&it is cis. There are many other techniques such as infrared spectra, nuclear magnetic resonance, electron spin resonance etc.

Valance Bond Theory (VBT)

This theory is mainly due to Pauling. It deals with the electronic structure of central metal ion in its ground state, kind of bonding, geometry (ie shape) and magnetic properties of the complexes.

This is based on the following assumptions:-

- i) The central metal atom or ion makes available a number of empty s,p and d atomic orbitals equal to its coordination number. These vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These are vacant, equivalent in energy and have definite geometry. The most commonly encountered hybridizations in complexes are given in table

- ii) The ligands have at least one σ -orbital containing a lone pair of electrons.
- iii) Vacant hybrid orbitals of the metal atom or ion overlap with the filled (containing lone pair of electrons) σ -orbitals of the ligands to form ligand \rightarrow metal σ -bond (represented as $M \rightarrow L$). This bond which is generally known as coordinate bond is a special type of covalent bond and shows the characteristics of both the overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation.

Table:- Important type of hybridization occurring in the first row transition metal complexes.

- i) C.N = coordination number of the central metal, M indicated by black circles.
- ii) L = Ligands indicated by white circles, These may be the same or different

C.N	Types of hybridisation	Geometry of the hybrid orbitals or complex	Examples of complexes
2	$sp(4s\ 4p)$	Linear or diagonal	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	$sp^2(4s\ 4p^2)$	Trigonal planar	$[HgI_3]^-$
3	$sp^3(4s\ 4p^3)$	Tetrahedral	$[Ni(CO)_4]^0$, $[Zn(NH_3)_4]^2$ $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$, $[MnX_4]^{2-}$, $[NiX_4]^{2-}$ $X = Cl^-, Br^-, I^-$
4	$dsp^2(3dx^2-y^2\ 4s\ 4p_x\ 4p_y)$	Square planar	$[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
5	$dsp^3(3dz^2\ 4s\ 4p^3)$	Trigonal bipyramidal	$[CuCl_5]^{3-}$, $[Fe(CO)_5]^0$
5	$sp^3d(4s\ 4p^3\ 4dx^2-y^2)$	Square pyramidal	$[SbF_5]^2$, IF_5
6	$d^2sp^3(3dx^2-y^2\ 3dz^2\ 4s\ 4p^3)$	Inner orbital octahedral	$[Cr(NH_3)_6]^{3+}$ $[Mn(CN)_6]^{3-}$

	$sp^3d^3(4s\ 4p^3\ 4dx^2-y^2\ 4dz^2)$	Outer orbital octahedral	$[FeF_6]^{3-}, [Co(H_2O)]^2$
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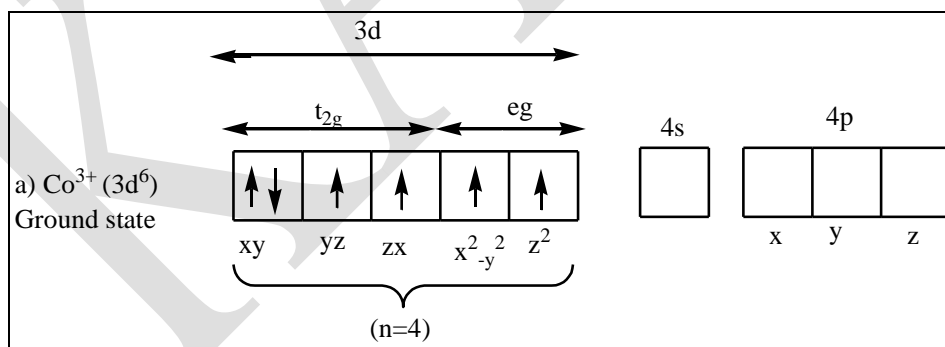
4) Octahedral Complexes:-

$[(n-1)d^2, ns.np^3 \text{ or } ns.np^3.nd^2\text{-hybridisation}]$

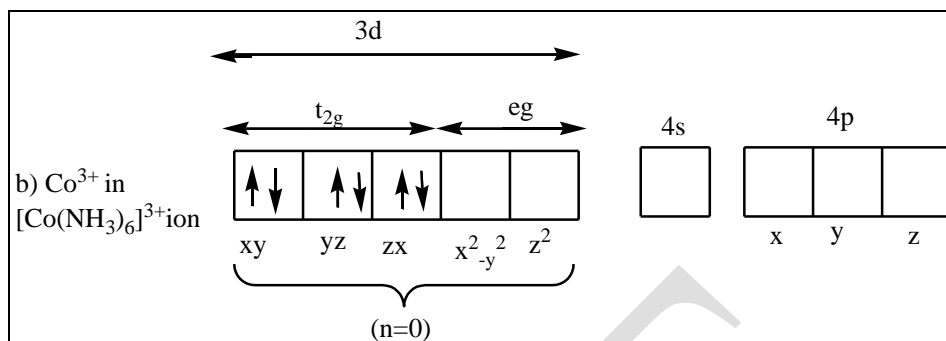
Since d_z^2 and $d_{x^2-y^2}$ orbitals lie directly in the path of the ligands, it is these orbitals which are used in the $(n-1)d^2\ ns.np^3$ or $ns.np^3.nd^2$ - octahedral hybridization. These orbitals are generally referred to as eg-set of orbitals. Let us consider the formation of $[Co^{111}(NH_3)_6]^{3+}$ and $[Co^{111}F_6]^{3-}$ ions. Both of these ions are octahedral (complexes) ions. Since the C.N of the central metal ion is 6 in each case and are of the same metal ion, Co^{3+} . $[Co(NH_3)_6]^+$ contains strong(er) ligands while $[CoF_6]^{3-}$ has weak(er) ligands.

i) $[Co^{111}(NH_3)_6]^{3+}$ ion.

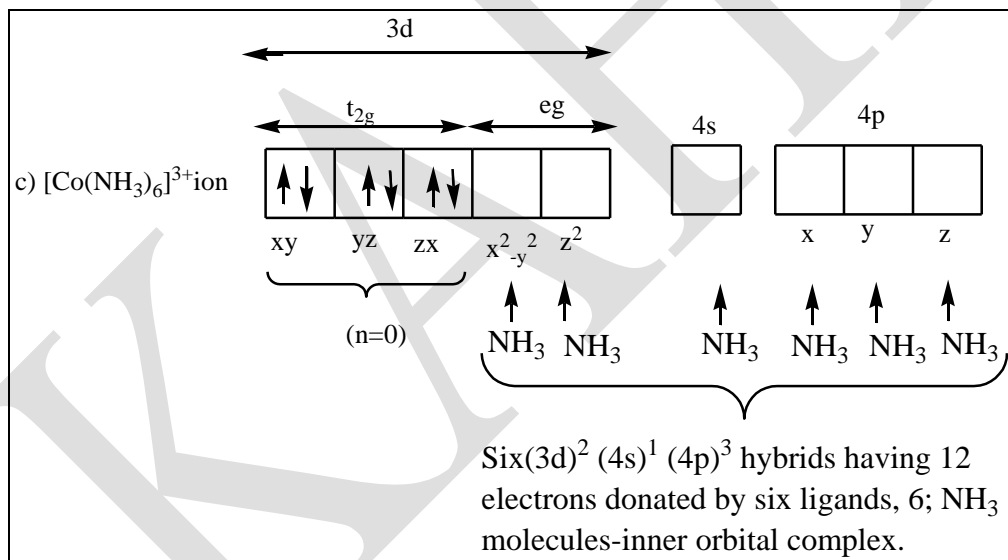
- Pauling originally called such complexes covalent complexes, since according to him the metal-ligand bonds in such complexes are primarily covalent.
- He further says that in covalent complexes electrons in the 3d-orbitals of the (namely 3d x^2-y^2 and 3d d_z^2 orbitals) which are occupied by the ligand electronics to form six $(3d)^2\ (4s)(4p)^3$ hybrids.
- In this complex ion co is present as co^{3+} ion whose electronic configuration $(3d^6\ 4s^0\ 4p^0)$ is shown at (a): (n=no. of unpaired electrons).



- In order to accommodate the six electron pairs donated by six ligands (6: NH_3 molecules), six vacant hybrid orbitals namely $eg^2\ sp^3$ must be made available.
- It can be done by transferring the two unpaired electrons (one being in $3d_{x^2-y^2}$ and the other in $3d_{z^2}$ orbital) to the $3d_{yz}$ and $3d_{zx}$ orbitals.
- Thus in $[co^{111}(NH_3)]^{3+}$ ion co^{3+} has the configuration shown at (b)



- This six pairs donated by six NH_3 molecules will be entering the hybrid orbitals formed by combining two 3d orbitals (namely $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals), one 4s and three 4p (ie $4p_x, 4p_y$ and $4p_z$ orbitals) orbitals.
- Thus the configuration of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion will be shown at (c).
- xx represents an electron pair denoted by each NH_3 molecule.
- The 2 electrons of this pair have opposite spins.



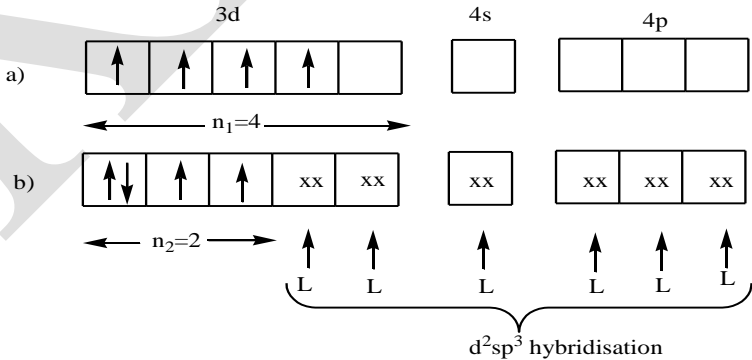
- Evidently, since $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion has unpaired electron, it should be diamagnetic.
- Actually this ion has been found diamagnetic.
- Here it may be noted that the d-orbitals used in the formation of octahedral d^2sp^3 hybrids (six hybrids) are from a lower shell than the s- and p-orbitals, since d orbitals are 3d-orbitals while s and p orbitals are 4s and 4p orbitals. ie for 3d orbitals, $n=3$ and for 4s- and 4p-orbitals, $n=4$ (n =principal quantum number).
- Complexes using the inner d-orbitals (which are 3d orbitals, for the first row transition elements) are called “inner orbital” complexes by Huggin.

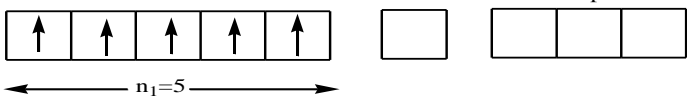
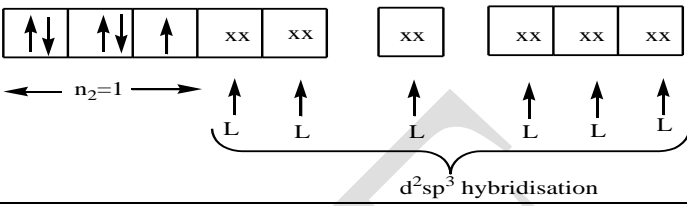
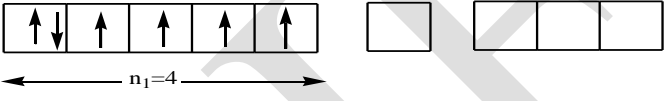
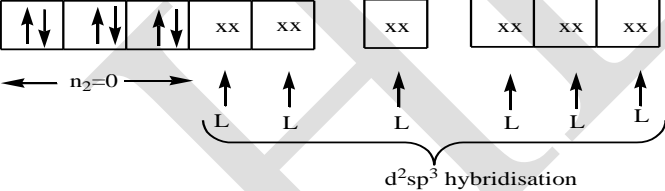
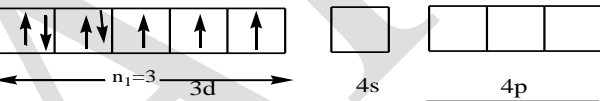
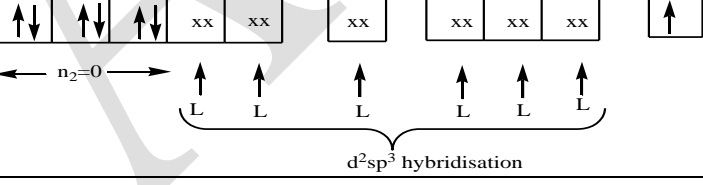
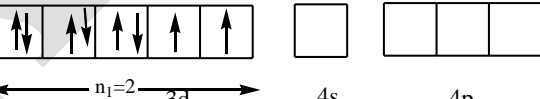
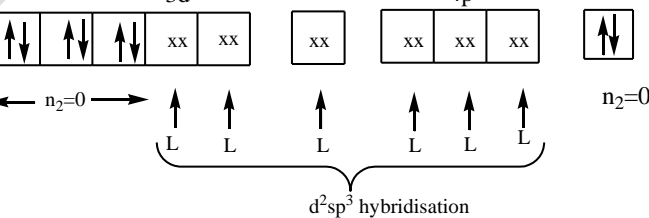
- Thus, in general, the complexes which use two (n-1)d[namely(n-1)d_z² and (n-1) d_{x²-y²}² orbitals], one ns and three np orbitals in their octahedral hybridization scheme are the “inner orbital” complexes.
- In our present case the scheme of octahedral hybridization is (3d)² (4s) (4p)³.
- The information of the inner-orbital octahedral complexes of d⁴ d⁵ d⁶ d⁷ and d⁸ ions of 3d series elements on the basis of VBT has been explained by the shown in table.
- In this table i) the electronic configuration shown at (a) is that of the free metal ion while that shown at (b) is that of the same metal ion in the complex.
- ii) n₁ and n₂ are the number of unpaired electrons in the free metal ion and the complex respectively.
- Crosses represent the electrons denoted by the ligands which have been denoted by L.
- It will be seen from the table number of unpaired electrons, n₂, in the complex is less than that in the free metal ion, i.e. n₂ < n₁ in each case.
- It is for this reason (namely (n₂ < n₁)) that the value of the experimental magnetic moment, μ_{exp}, for these complexes is less than as value of the free metal ion calculated from “spin-only” formula;

I.e., $\mu_s = \sqrt{n(n+2)} \text{ B.M}$

$\mu_{\text{exp}} < \mu_s$

Formation of inner orbital octahedral complexes (d⁴, d⁵, d⁶, d⁷ and d⁸ ions of 3d series element on the basis of VBT.

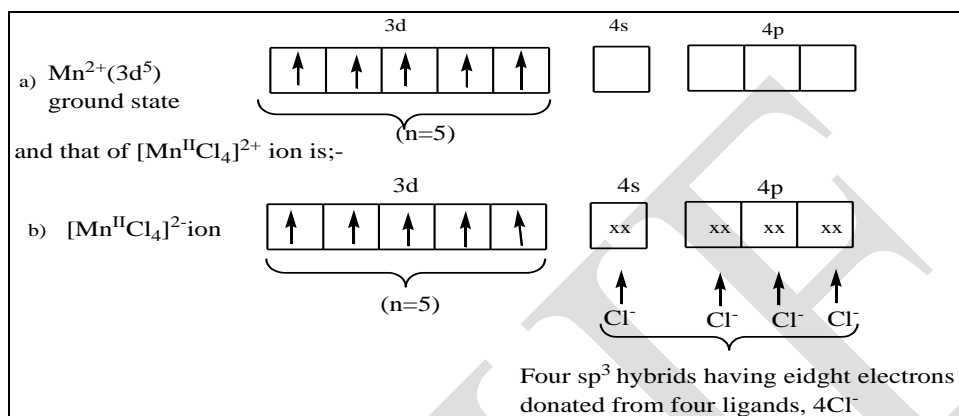
d ^x ion	Inner orbital Octahedral complexes(d ² sp ³ hybridisation)
d ⁴	

d⁵	<p>a) </p> <p>b) </p>
d⁶	<p>a) </p> <p>b) </p>
d⁷	<p>a) </p> <p>b) </p>
d⁸	<p>a) </p> <p>b) </p>

B) Tetrahedral Complexes:- (SP³- hybridisation)

The formation of tetrahedral complexes can be explained by considering the formation of $[\text{Mn}^{II}\text{Cl}_4]^{2-}$ complex ion.

The configuration of Mn^{2+} ion is:



The hybridisation scheme given at (b) above clearly shows the presence of five unpaired electrons in $[\text{MnCl}_4]^{2-}$ ion. Experiments also show that this ion is paramagnetic corresponding to five unpaired electrons ($\mu_s=5.92\text{BM}$, $\mu_{\text{exp}}=5.95\text{BM}$).

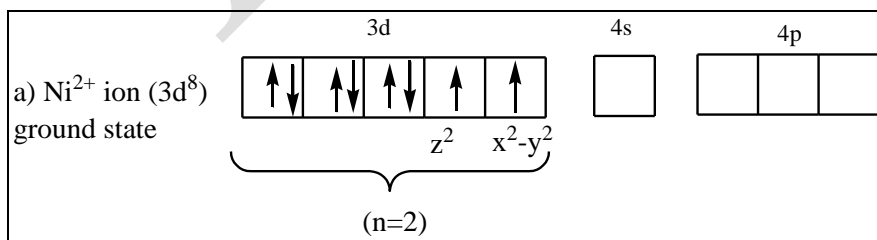
C) Square planar complexes:-

$[(n-1) d_{x^2-y^2} ns, np^2\text{-hybridisation}]$

In the formation of four $d-sp^2$ hybrid orbitals, $d_{x^2-y^2}$ orbital should be lower shell than the s- and p-orbitals. If these four hybrid orbitals are in the xy plane, the two p-orbitals involved in the formation of four dsp^2 -hybrids should be p_x and p_y orbitals.

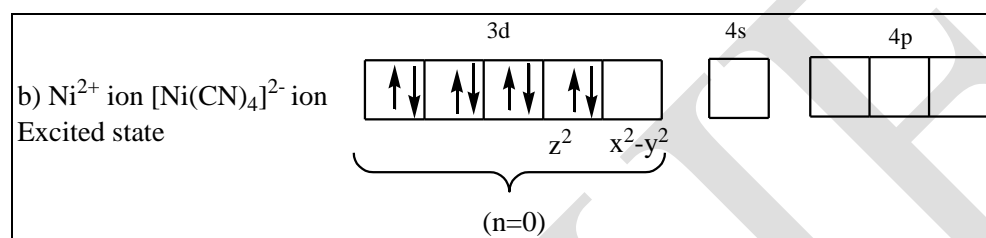
i) $[\text{Ni}^{II}(\text{CN})_4]^{2-}$ ion.

Evidently in this complex ion Ni is present as Ni^{2+} whose electronic configuration is shown at given below:-

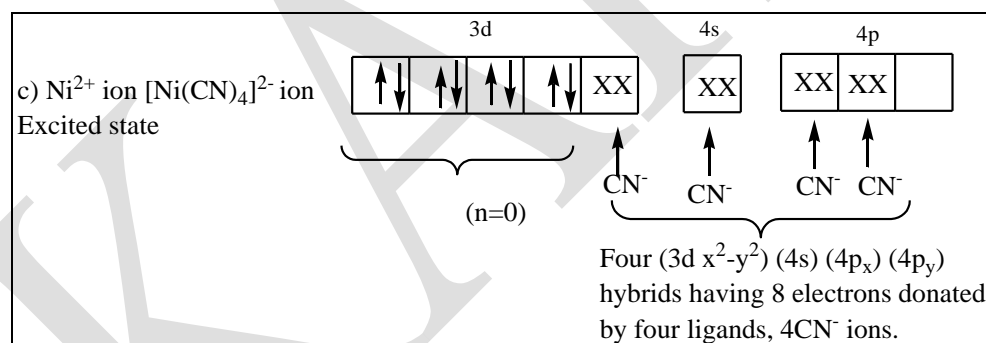


Since the coordination number of Ni in $[\text{Ni}(\text{CN})_4]^{2-}$ ion it can also be assumed that the complex ion is formed by sp^3 -hybridisation $[(4s)(4p)^3]$. This type of hybridisation will give two unpaired electrons in this complex ion and consequently the ion should be paramagnetic corresponding to two unpaired electrons having μ_{exp} value equal to 2.83 BM. Actually the complex ion has $\mu_{\text{exp}} = 0$ which indicates that it is diamagnetically, i.e. it has no unpaired electrons.

This situation can be obtained by sending one $3d_{x^2-y^2}$ orbital electron to $3d_z^2$ orbital. So that all the electrons get paired and we get the electronic configuration of Ni^{2+} ion as shown at (b)



Now $3d_{x^2-y^2}$, $4s$ and 2 $4p$ orbitals (namely $4p_x$ and $4p_y$ orbitals) on hybridising give four $(3d_{x^2-y^2})$ $(4s)$ $(4p_x)$ $(4p_y)$ hybrid orbitals which are used in the formation of $[\text{Ni}(\text{CN})_4]^{2-}$ ion as shown at (c) below



Evidently the complex ion, $[\text{Ni}(\text{CN})_4]^{2-}$, has no unpaired electrons and value of μ_{exp} should be zero. Actually the value of μ_{exp} has been found to be equal to zero.

Limitations of VBT:-

a) Octahedral, square planar and tetrahedral complexes of d^1, d^2, d^3 and d^9 ions have the same no/- of unpaired electrons and hence cannot be distinguished from each other merely on the basis of the no/- of unpaired electrons.

b) similarly outer orbital octahedral and tetrahedral complexes of all the ions viz d^1 and d^9 which have the same no/- of unpaired electrons cannot be distinguished from each other. It is firmly established that both the colour and the magnetic moments of transition metal complexes are due to their possessing d-orbital electrons. There must be a quantitative connection between spectra and magnetic moment. Unfortunately this connection is not revealed by the VBT which does not consider the splitting of the d-orbitals of the central metal ion and consequently these properties could not be explained by this theory.

iii) VBT does not explain the behavior of complexes having d^8 central ion (e.g Ni^{2+} , Pb^{2+} , Au^{3+} etc) in the forming the expected 5 coordinate complexes.

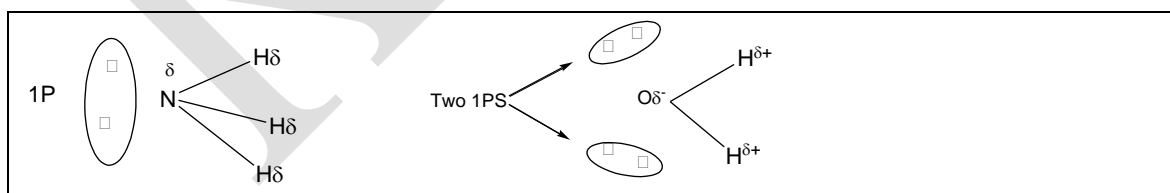
iv) VBT cannot explain why square planar complexes of Cu^{2+} ion (d^9 system) like $[Cu(NH_3)_4]^{2+}$ are not reducing agents like inner orbital octahedral cases promotion of a non bonding d-electron to some higher energy level is required.

v) Too much stress has been laid on the metal ion while the importance of ligand is not properly stressed.

vi) VBT cannot explain reaction rates and mechanism of reactions.

Crystal Field Theory (CFT)

This theory advanced by Brethe and VanVleck was originally applied mainly in ionic crystals and is, therefore called Crystal Field Theory (CFT). It was not until 1952 that Orgel popularized its use for Inorganic Chemist. This theory regards the ligand atoms of ionic ligands such as F^- , CN^- , or OH^- as negative point charges (also called point charges) and if the ligands are neutral molecules, these are regarded as point dipoles or simply dipoles, since such ligands are dipolar, e.g: NH_3 and H_2O shown below.



Such ligands approach the central metal ion with negative poles (ie ends) closest to the central metal ion. Actually, even if the ligands are not negatively charged (ie neutral ligands), they are polarised by the positive charge of the cation and thus appear negatively charged. Thus in octahedral complexes having neutral molecules as ligands, the central metal ion is surrounded by dipoles.

Important Features of CFT:-

- i) CFT regards a complex as a combination of a central ion surrounded by other ions or molecules with electrical dipoles (ie ligands). It considers these ligands as point charge or point dipoles.
- ii) In its simplest treatment CFT does not consider covalent bonding in complexes, but ligand field arises from the electrostatic attraction between the nucleus of the metal cation and the partial negative charge invariably present on the ligands. The interaction between the electrons of the cation and those of the ligands is entirely repulsive. It is these repulsive forces that are responsible for causing the splitting of the d-orbitals of the metal cation. The bonds between the metal and the surrounding ligands are thus purely ionic.
- iii) CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons ie it does not consider any orbital overlap.
- iv) CFT gives a representation of bonding that is purely an electrostatic or coulombic interaction between positively charged (ie cation) and negatively charged (ie anions or dipole molecules which act as ligands) species.

Crystal Field Splitting of d-Orbitals:-

A) Splitting of d-orbital's in octahedral complexes:-

On the basis of the orientation of the lobes of the five-d-orbitals with respect to coordinates these have been divided into 2 groups:-

- i) The group has the orbitals which have their lobes along the axes and hence are called axial orbitals. Quite obviously these are d_{z^2} and $d_{x^2-y^2}$ orbitals. Group theory calls these eg orbitals in which e refers to doubly degenerate set.
- ii) This group includes the orbitals whose lobes lie between the axes and are called non-axial orbitals. Group theory calls these t_{2g} orbitals where t refers to triply degenerate set. In case of a free metal ion all the five d-orbitals are degenerate. Ie these have the same energy. Now let us consider the octahedral complex, $[ML_6]^{n+}$ in which the central metal cation, M^{n+} is placed at the centre of the octahedron and is surrounded by ligands which reside at the six corners of the octahedron as shown in fig.

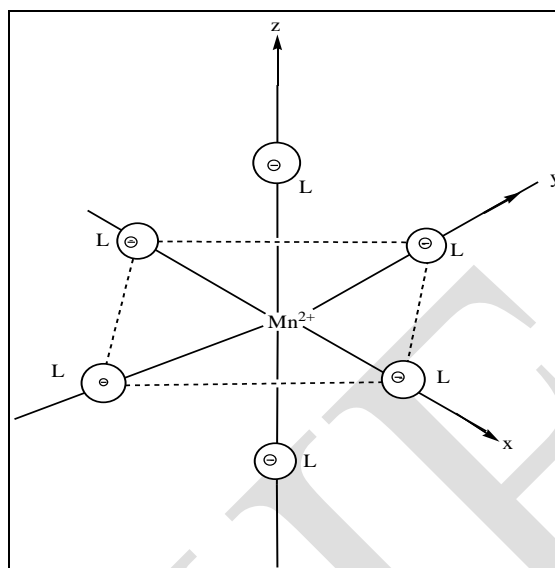
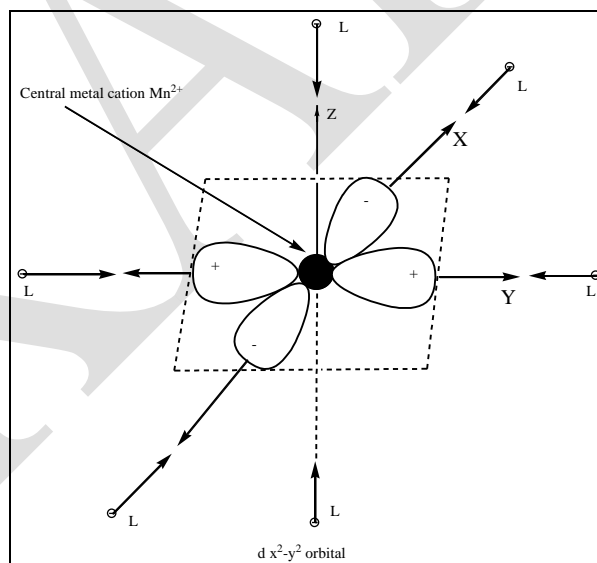
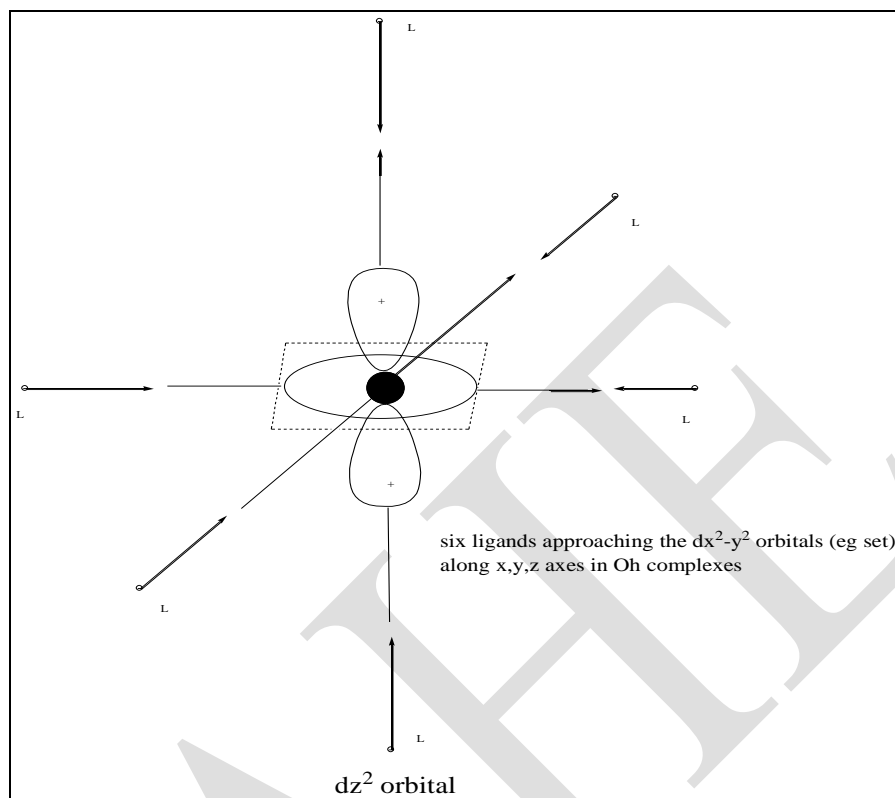


Fig:- Position of the central metal cation, M^{n+} and six ligands, L 's in an octahedral complex, $[ML_6]^{n+}$

- The three axes Viz x , y and z axes which point along the corners have also been shown.



- Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation, M^{n+} from both the ends of the axes.



In this process the electrons in d-orbitals of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. This repulsion will raise the energy of all the five d orbitals. If all the ligands approaching the central cation are at an equal distance from each of the d-orbitals (ie the ligand field is spherically symmetrical), the energy of each of five d-orbitals will still remain degenerate, although they will have now higher energy than before. This is only a hypothetical situation. Since the lobes of the two eg orbitals (ie d_{z^2} and $d_{x^2-y^2}$ orbitals) lie directly in the path of the approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in three t_{2g} orbitals (ie, d_{xy}, d_{yz}, d_{zx} orbitals).

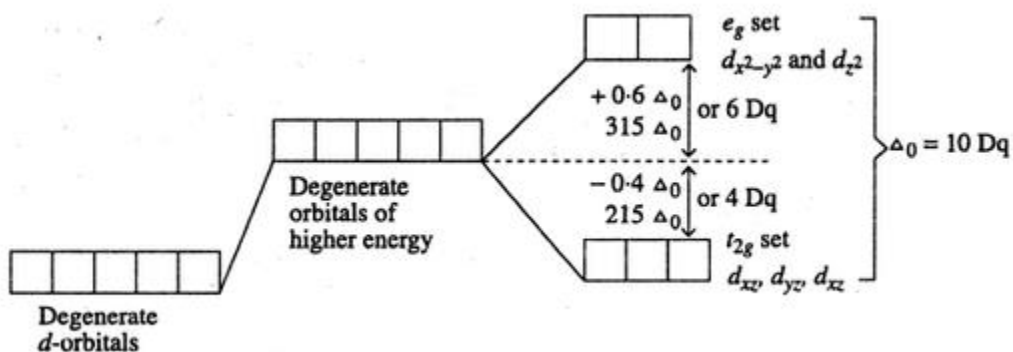
Whose lobes are directed in space between the path of the approaching ligands. Ie, the energy of eg orbitals is increased while that of t_{2g} is decreased. Thus we find that under the influence of approaching ligands the five d-orbitals which were originally degenerate in the free metallic cation are now split into two levels viz.

- i) T_{2g} level which is triply degenerate and is of lower energy, and
- ii) E_g level which is doubly degenerate and is of higher energy.

In other words the degeneracy of the five d-orbitals is removed under the influence of the ligands. “The separation of five d-orbitals of the metal ion into two sets having different energies is called crystal field splitting or energy level splitting”. This concept of crystal field splitting makes in basis of CFT. “The energy gap between t_{2g} and e_g set is denoted by Δ_0 or $10Dq$ where 0 in Δ_0 indicates an octahedral arrangement of the ligands round the central metal cation.

This energy difference arises because of the difference in electrostatic field exerted by the ligands on t_{2g} and e_g sets of orbitals of the central metal cation. Δ_0 or $10Dq$ is called crystal field splitting energy.

With the help of simple geometry it can be shown that the energy of t_{2g} orbital is $0.4 \Delta_0$ ($=4 Dq$) less of hypothetical degenerate d-orbitals and hence that of e_g orbitals is $0.6 \Delta_0$ ($=6Dq$) above that of the hypothetical d – orbitals. Thus, we find that t_{2g} set loses an energy equal to $0.4 \Delta_0$ ($=4Dq$) while e_g set gains an energy equal to $0.6 \Delta_0$ ($=6 Dq$). In fig the loss and gain in energies of t_{2g} and e_g orbitals is shown by negative and positive signs respectively.



Crystal field splitting of d orbitals in an octahedral complex

- Five degenerate d-orbitals of free metal cation which are free from any ligand field.
- Hypothetical degenerate d-orbital at a higher energy level under spherically symmetrical ligand field.
- Splitting of d orbitals under the influence of approaching ligands into t_{2g} and e_g sets.

B) splitting of d-orbitals in tetrahedral, tetragonal and square planar complexes:

1. Tetragonal Structure:

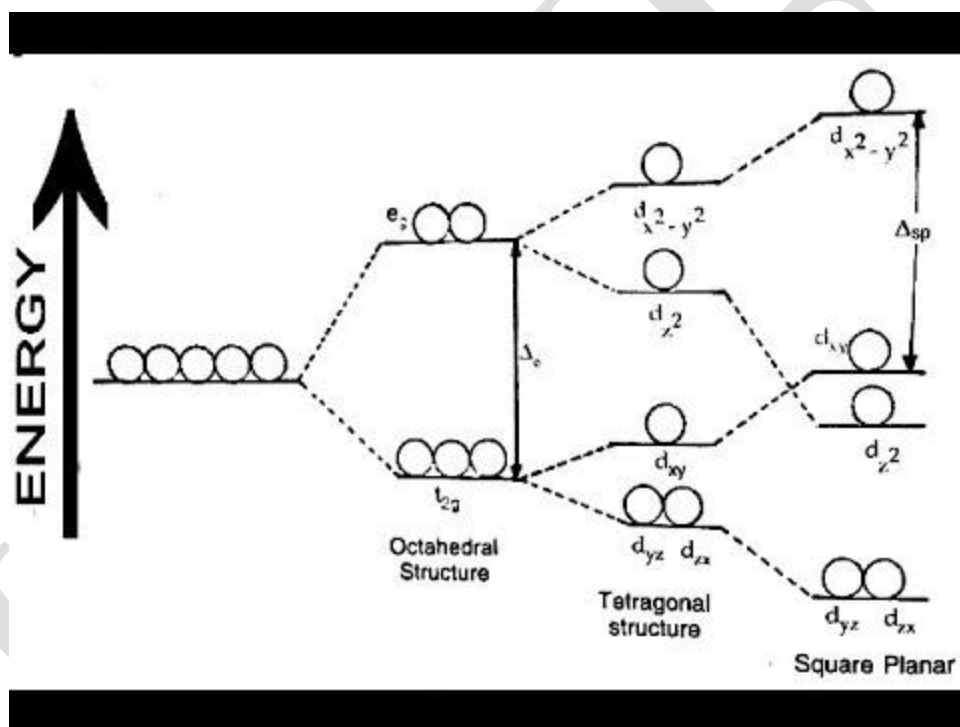
If the two trans ligands lying on the z-axis of an octahedron are removed away from the central cation so that distance from the metal cation is slightly greater than it is for the other four ligands lying in the xy plane, we get a tetragonally distorted octahedron. Such a structure is called tetragonal structure.

In a tetragonal geometry since the distance of the 2 ligands on z-axis is increased from the central metal cation by removing them away, d orbitals along the z-axis (ie $d_{x^2-y^2}$ orbital) and in xz (ie d_{xz}) and yz (ie d_{yz}) planes experience less repulsion from the ligands than they do in an octahedral geometry and those in the xy plane (ie d_{xy} and $d_{x^2-y^2}$ orbitals) experience relatively greater repulsion.

Consequently the energy of the orbitals experiencing less repulsion decreases while that of the orbitals experiencing greater repulsion increases (fig). Note that d_{xz} and d_{yz} orbitals are degenerate.

Thus under the influence of the ligands in tetrahedral complex the order of the energy of various d-orbitals is:

$$d_{yz} = d_{zx} < d_{xy} < d_{z^2} < d_{x^2-y^2}$$



Crystal field splitting of d-orbitals of the central metal cation of tetrahedral, tetragonal and square planar complexes. Splitting in octahedral complexes is also given for comparison.

2. Square planar complexes:

If the 2 trans ligands on the z-axis are completely removed, we get a square planar geometry. This is accompanied by a further rise in the energies of $d_{x^2-y^2}$ and d_{xy} orbitals and a further fall in the energies of d_{z^2} , d_{xz} and d_{yz} orbitals as shown in fig.

Thus in square planar geometry the order of energy of different d orbitals is:

$$d_{yz} = d_{zx} < d_{z^2} < d_{xy} < d_{x^2-y^2}$$

From this order we can see that planer complexes of d7,d8 and d9 should have 1,0 and 1 unpaired electrons respectively.

The crystal field splitting in square planer complex is denoted by Δ_{sp} , which represents the total square planer spitting from the lowest dxz, dyz pair to the highest dx^2-dy^2 and is given by

$$\begin{aligned}\Delta_{sp} &= [E(dx^2-dy^2) - E(dxz, dyz)] \\ &= [E(dx^2-dy^2) - E(dxy)] + [E(dxy) - E(dz^2)] + [E(dz^2) - E(dxz, dyz)] \\ &= \Delta_1 + \Delta_2 + \Delta_3\end{aligned}$$

The value of Δ_{sp} has been found larger than Δ_0 because of the reason that dxz and dyz orbitals interact with only 2 ligands in square planer complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to $1.3\Delta_0$. Thus

$$\begin{aligned}\Delta_{sp} &= (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_0 \\ \Delta_{sp} &= 1.3 \Delta_0\end{aligned}$$

3. Tetrahedral complexes:

In order to understand the splitting of d orbitals in tetrahedral complexes it is convenient to picture a tetrahedral placed inside a cube (Fig).

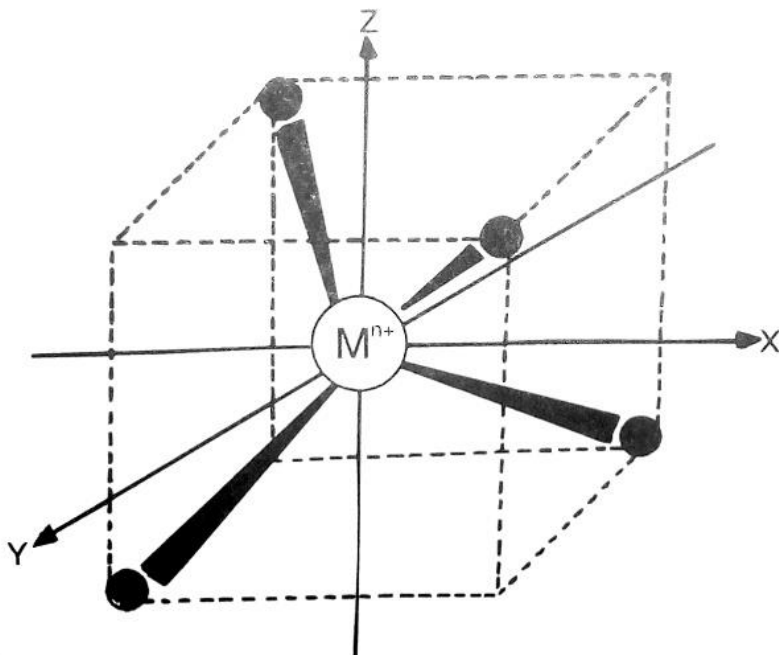


Fig- A tetrahedral placed in a cube the centre of the cube is the centre of the tetrahedral at which is placed central metallic cation M^{n+} . Four corners of the cube are the four corners of the tetrahedral at which are placed the four negative ligands which have been shown by circles with negative signs .

Now since the lobes of t_2g orbitals (dxy, dyz & dxz) are lying between the axes, i.e. are lying directly in the path of the ligands, this orbital will experience greater force of repulsion from the ligands than those of e_g orbitals (dx^2-dy^2) whose lobes are lying along the axes, i.e. are lying in space between the ligands.

Thus the energy of t_{2g} orbitals will be increase while that of e_g orbitals will be decreased.

The energy different between t_{2g} and e_g sets for tetrahedral complex is represented as Δ_t .

It has been shown that, $\Delta_t < \Delta_o$ for the same metal and ligand and the same inter nuclear distance.

It has been shown that $\Delta_t = 0.45 \Delta_o$

Thus the energy level of the t_{2g} set is raised by $0.4 \Delta_t = 0.18 \Delta_o$ while that of e_g set is lowered by $0.6 \Delta_t = 0.27 \Delta_o$

The relation namely $\Delta_t = 0.45 \Delta_o$ also shows that, other things being about equal, the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex.

Since Δ_t is relatively small orbitals splitting, spin-paring in tetrahedral is rather unlikely.

Since $\Delta_t < \Delta_o$ crystal field splitting favours the formation of octahedral complexes.

Factors influencing the magnitude of Δ_o :

A mass of experimental data show that the magnitude of Δ_o depends on the following

1. Nature of the metal cation:

The influence of this factor can be studied under the following four headings.

i) Different charges on the cation of the same metal. The cations from atoms of the same transition series and having the same oxidation state have all most the same value of but the cation with a higher oxidation state has a larger value of then to that lower oxidation state , eg

a) Δ_o for $[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 10,400 \text{ cm}^{-1}$ ----- $3d^6$

Δ_o for $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+} = 13,700 \text{ cm}^{-1}$ ----- $3d^5$

b) Δ_o for $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]^{2+} = 9,300 \text{ cm}^{-1}$ ----- $3d^7$

Δ_o for $[\text{Co}^{\text{III}}(\text{H}_2\text{O})_6]^{3+} = 18,200 \text{ cm}^{-1}$ ----- $3d^6$

This effect is probably due the fact that the central ion with the higher oxidation state (ie with higher charges) will polarize the ligands more effectively and thus the ligands would approach such a cation more closely then they can do the cation of lower oxidation state, resulting in larger splitting.

ii) Different charges on the cation of different metals

Two different cations having the same number of d-electrons and the same geometry of the complex but with different charge can also be compared.

The cation with a higher oxidation state has a larger value of Δ_o do than that with a lower oxidation state. For example, the behavior towards the same ligand of V(II) and Cr(III), which are both d^3 ions can be compared.

It is observed that the value of Δ_o in $[V^{II}(H_2O)_6]Cl$ is less than that in $[Cr^{III}(H_2O)_6]^{3+}$, as is shown below

Δ_o for $[V^{II}(H_2O)_6]^{2+} = 12,400 \text{ cm}^{-1}$ -----3d3

And Δ_o for $[Cr^{III}(H_2O)_6]^{3+} = 17,400 \text{ cm}^{-1}$ -----3d3

This fact can be explained in terms of the charge on the cation

The Cr^{3+} ion, which has greater positive charge than V^{2+} ion, exerts a greater attraction for water molecule(ligands) than does the V^{2+} ion. Hence the water molecule approaches the Cr^{3+} ion more closely than they approach the V^{2+} ion and so exert a stronger crystal field effect on the d-electron of Cr^{3+} ions.

iii) Same charges on the cation but the number of d-electrons is different. In case of complexes having the cation with the same charges, but with different number of d-electrons in the central metal cation the magnitude of Δ_o decreases with the increase of the number of d-electrons, eg

Δ_o for $[Co^{II}(H_2O)_6]^{2+} = 9,300 \text{ cm}^{-1}$ -----3d7

and Δ_o for $[Ni^{II}(H_2O)_6]^{2+} = 8,500 \text{ cm}^{-1}$ -----3d8

From the combination of (i),(ii) and (iii) mentioned above it can be concluded that

a) for the complexes having the same geometry and the same ligands but having the different number of d-electrons, the magnitude of Δ_o decreases with the increases of the number of d-electrons in the central metal cation.(no. of d –electrons $\propto 1/\Delta_o$).

b) In case of complexes having the same number of d-electrons the magnitude of Δ_o increases with increasing of the charges(ie. Oxidation state) on the central metal cation(oxidation state $\propto \Delta_o$). iv) Quantum number(n) of the d-orbitals of the central metal ion Δ_o increases about 30% to 50% from 3dn to 4dn and by about the same amount again from 4dn to 5dn complexes. eg

Δ_o for $[Co^{III}(NH_3)_6]^{3+} = 23,000 \text{ cm}^{-1}$ -----3d6

Δ_o for $[Rh^{III}(NH_3)_6]^{3+} = 34,000 \text{ cm}^{-1}$ -----4d6

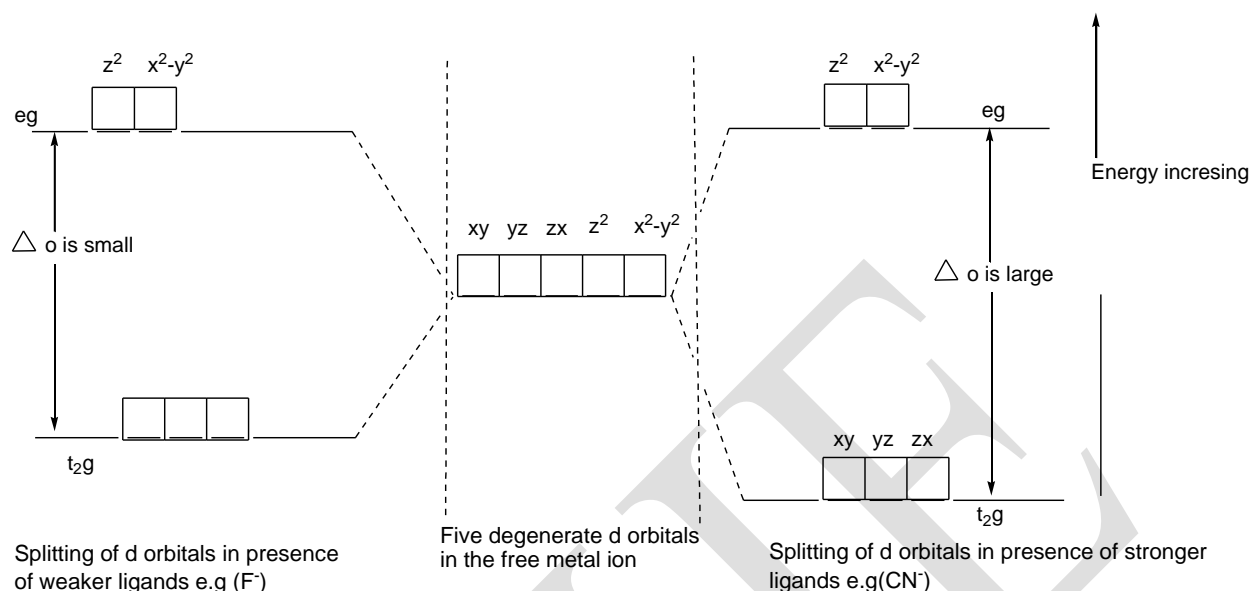
Δ_o for $[Ir^{III}(NH_3)_6]^{3+} = 41,000 \text{ cm}^{-1}$ -----5d6

Presumably the 5d and 4d valence orbitals of the central ion are better than the 3d-orbitals in O-bonding with the ligands.

2. Stronger and Weaker ligands and spectrochemical series

The magnitude of Δ_o varies from stronger ligands to weaker ligands. Stronger ligands are those which exert a stronger field on the central metal ion and hence have higher splitting power while the weaker ligands are those which have a weaker field on the central metal cation and consecutively relatively lower splitting power.

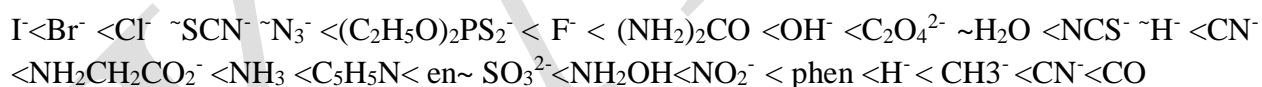
The stronger ligands (eg CN^-) give larger value of Δ_o and weaker ligands (eg F^-) yields a smaller value of Δ_o , fig



CFT splitting of 5d orbitals in stronger and weaker octahedral field

Fig shows that not only Δ_o , which represents the energy difference between the t_{2g} and e_g sets of orbitals, is smaller in the weaker field complex than in the stronger field, but also that both the t_{2g} and e_g levels of the weaker field are correspondingly closer to the level of the degenerate five d orbitals of the free isolated metallic ion than are those, respectively, of the stronger field.

The common ligands can be arranged in the order of their increasing splitting power to cause of d-orbitals splitting. This series is called spectrochemical series and is given below.



(The binding atoms are in thick type and two positions have been given for H⁻ ion).

This series shows that the value, of Δ_o in the series also increases in the same order, ie from left to right. The above order, independent of the nature of central metal ion and the geometry of the complex.

Application of CFT

i) Colour of transition metal complexes

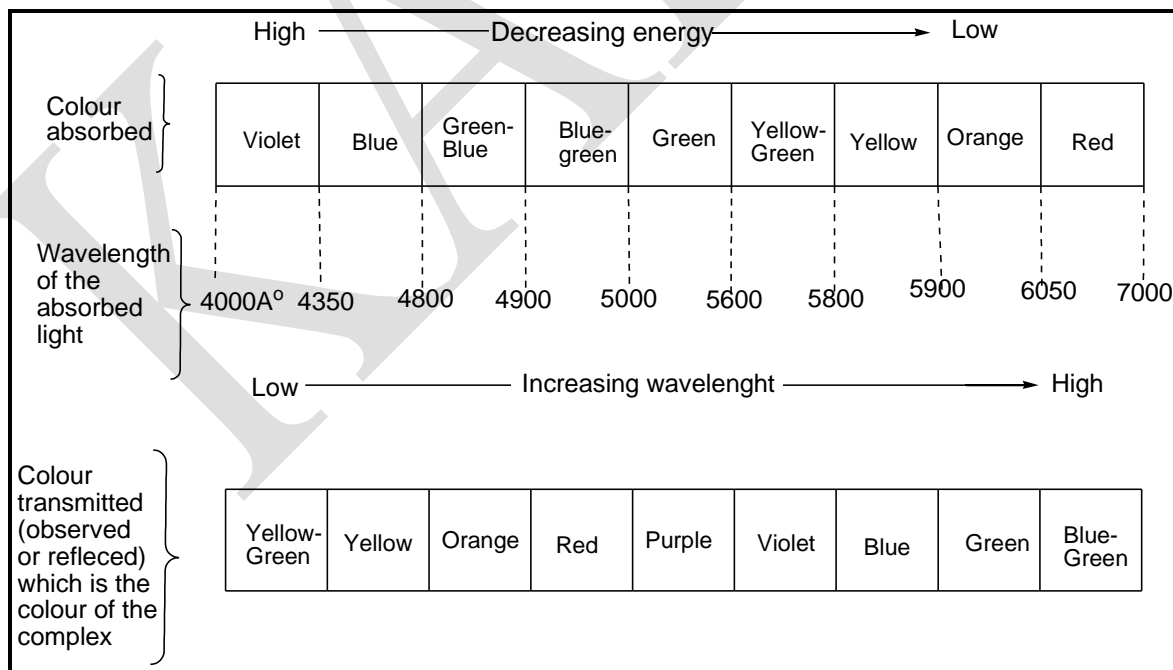
One of the major successes of the CFT is that it can provide an explanation for the observed colours of transition metal complexes.

When on while light is allowed to fall on a complex, the following things may occur:

- i) The complex may absorb the whole of white light. In this case complex appears black.
- ii) The complex may reflex (or transmit) the whole light. In this case it appears white.
- iii) The complex may absorb some of it and may reflex the remaining light. In this case the complex has some colour. ie it is coloured. The absorption of light by the coloured complexes takes place in the visible region of the spectrum which extends from 4000 Å to 7000 Å in wavelength. The colour of the absorbed light is different from that of the transmitted light. The relation between the colours of the absorbed and reflected light is shown in Fig.

The colour of the transmitted light is called the complementary colour of that of the absorbed light as is, in fact the colour of the complex. Thus: Hydrated cupric sulphate containing $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions is blue (colour of the transmitted light) because it absorbs yellow light. Copper ammonium sulphate containing $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions is violet, because it absorbs yellow green light.

iii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs green light in the visible region and hence it is purple which is the colour of the transmitted light.



Relation between the colours of the absorbed light (visible spectrum) and those of the transmitted light.

The complex ions which absorb light in the infra-red ($\lambda < 7000 \text{ \AA}$) or ultra-violet ($\lambda < 4000 \text{ \AA}$) regions of the spectrum are colourless. e.g: i) anhydrous cupric sulphate is colourless, since it absorbs light in the infra-red region.

ii) $[\text{Cu}(\text{CN})_4]^{2-}$ ion absorbs light in the ultra-violet region and hence is colourless. With the help of visible absorption spectrum of a complex ion it is possible to predict the colour of the complex.

For example $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion shows absorption maxima at a wavelength about 5000 \AA , Fig(2) Which corresponds to the wave number, $\gamma = 20000 \text{ cm}^{-1}$ as shown below.

Since $1 \text{ \AA} = 10^{-8} \text{ cm}$, wave length, $\lambda = 5000$, $\text{ \AA} = 5000 \times 10^{-8} \text{ cm}$.

Consequently wave number

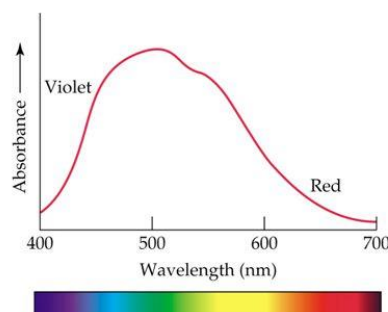
$$\begin{aligned}\bar{\nu} &= \frac{1}{\lambda \text{ (in cm)}} = \frac{1}{5000 \times 10^{-8}} \\ &= 1/5 \times 10^{-5} \text{ cm}^{-1} = 0.2 \times 10^5 \text{ cm}^{-1} \\ &= 20000 \text{ cm}^{-1}\end{aligned}$$

Light of this wavelength ($= 5000 \text{ \AA}$) is green (Fig 1) and is absorbed by the complex ion. thus the transmitted light is purple which is, in fact the colour of the ion.

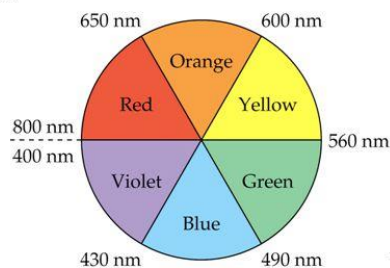
Hexaquo-titanium (III) Solutions Appear Violet Due to Absorption of Yellow and Green Light



(a)



(b)



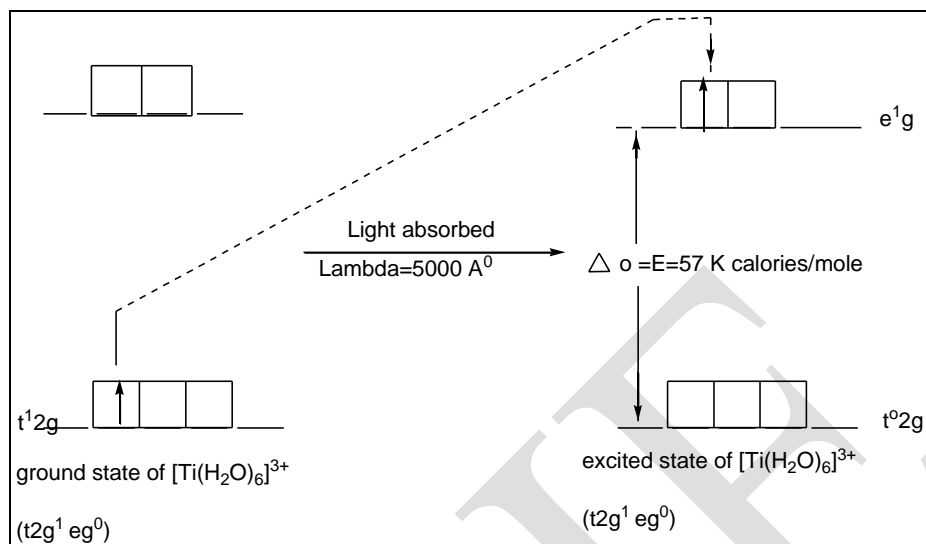
Visible absorption spectrum of $[\text{Ti}^{III}(\text{H}_2\text{O})_6]^{3+}$ ion. Peak of the curve shows the maximum absorption.

Now let us see what happens to the single d-electron of Ti^{3+} ion in t_{2g} orbital ($\text{Ti}^{3+} \rightarrow t_{2g}^1 e_g^0$), when the complex ion absorbs light in the visible region at 5000 \AA .

The energy (in kcal/mole) associated with this absorbed light of wave number, γ of 20000 cm^{-1} is equal to $20000 \times 2.85 \times 10^{-3} = 57 \text{ kcal/mole}$, since $1 \text{ cm}^{-1} = 2.85 \times 10^{-3} \text{ kcal/mole}$.

This energy ($=57 \text{ kcal/mole}$) is equal to the energy difference, Δ_o between t_{2g} and e_g levels and hence is sufficient to excite the single d-electrons in t_{2g} orbital to e_g orbital. This type of electronic transition from t_{2g} to e_g level is called d-d or ligand field transition. Fig (3).

Thus the colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is attributed to d-d electro-transition.



Fig(3); Absorption of light by $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion involving a shift of an electron from t_{2g} level to e_g level. this transition: $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$, gives the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion its purple colour.

2. Number of unpaired electrons and magnetic properties of oh complexes:

- CFT is helpful in determining the no. of unpaired electrons is given HS and LS octahedral complex and consequently, with the help of "spin-only" formula BM, we can find the value of "spin-only" moment, μ_s of a given HS and LS oh-complex.
- Value of μ_s calculated from the spin only formula given above and those of μ_J and μ_{s+L} calculated from the following equations for HS Oh complexes of some of the d_1^0 and trivalent ions of the 3d series element.

Equation:

$$\mu_J = g\sqrt{J(J+1)}\text{BM}$$

where g which is Lande splitting factor is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$\mu_{s+L} = \sqrt{4S(S+1) + L(L+1)}\text{BM}$$

Crystal field stabilization energies CFSE'S and their uses:

- According to CFT, under the influence of the six approaching towards the central metal ion during the formation of an octahedral complex, the d-orbital of the central metal ion are split in to two sets viz t_{2g} (lower energy set) and e_g (higher energy set) sets.
- The energy gap between these two set is equal to Δ_o (or $10 Dq$).
- The energy of t_{2g} set is lowered by $2/5\Delta_o$ ($=0.4\Delta_o$) or $4 Dq$ while that of e_g set is raised by $3/5\Delta_o$ ($=0.6\Delta_o$) or $6 Dq$ relation to the energy of hypothetical degenerate orbitals.
- Thus each electron occupying t_{2g} orbitals decreases the energy of d-orbitals by $0.4 \Delta_o$ ($=-4 Dq$) while that going into e_g orbitals increases its energy by $+0.6 \Delta_o$ ($=+6Dq$).+ and – sign indicate respectively the decrease and increase in the energy of d-orbitals caused by their splitting under the influence of six ligands. Now consider a d^{p+q} ion with p electrons in t_{2g} and q electrons in e_g orbitals. Quite obviously.

Gain in energy due to q e's in e_g orbitals (in terms of Δ_o) $= +0.6 \Delta_o \times q$

And lose in energy due to p e's in t_{2g} e's (in terms of Δ_o) $= -0.4 \Delta_o \times p$

Net change in energy for d^{p+q} ion (in terms of Δ_o) $= [-0.4 p + 0.6 q] \Delta_o$ —(1)

This change in energy in terms of Dq will be given by utilizing the relation.

$\Delta_o = 10 Dq$ thus;

Change in energy (in terms of Dq) $= [-0.4p + 0.6] \times 10Dq$

$$= [-4p + 6q] \times Dq \text{ —(2)}$$

- This change in energy is called crystal field stabilization energy (CFSE), since it stabilises d-orbitals by lowering their energy which results from their splitting into t_{2g} and e_g orbitals.
- This may seen from equations (1) and (2) that for d^0 (low-spin and high-spin), d^5 (high spin) and d^{10} (low spin and high spin) ions of an oh. complexes there is no net change in their energy due to their splitting into t_{2g} and e_g orbitals, ie no stabilization results from the splitting of d-orbitals of these ions.
- e.g :
- For a d^{10} ion with $t_{2g}^6 e_g^4$ configuration, the net change in energy ($p=6, q=4$)

$$= [-0.4 \times 6 + 0.6 \times 4] \Delta_o = 0$$
- ii) for d^5 (high-spin) ion with $t_{2g}^3 e_g^2$ configuration, the net change in energy ($p=3, q=2$).

$$= [-0.4 \times 3 + 0.6 \times 2] \Delta_o = 0$$
- If p = mean pairing energy which is the energy required to pair two electrons against electron-electron repulsion in the same orbital and m = no. of paired electrons, then
- CFSE for d^{p+q} ion (in terms of Δ_o)

$$= [-0.4p + 0.6 q] \Delta_o + mp \text{ —(3)}$$
- As a illustration let us use equation 3 to calculate CFSE values for d^3 , d^4 and d^7 ions. in oh. complexes

i) d^3 ion.

We know that the distribution of 3 d-electrons in t_{2g} and e_g levels in both the fields (ie strong and weak) is $t_{2g}^3 e_g^0$ and $m=0$, thus $p=3$, $q=0$ and $m=0$ hence

CFSE for both the fields (low spin and high spin)

$$= [-0.4 \times 3 + 0.6 \times 0] \Delta_o + 0 \times P$$

$$= -1.2 \Delta_o = -12 Dq$$

ii) d^4 ion

a) For weak field (high spin complex) $d^4 = t_{2g}^3 e_g^1$

thus $p=3$, $q=1$ and $m=0$ and hence

$$\text{CFSE for weak field} = [-0.4 \times 3 + 0.6 \times 1] \Delta_o + 0 \times P$$

$$= -0.6 \Delta_o = -6 Dq$$

b) For strong field (low spin complex) $d^4 = t_{2g}^4 e_g^0$

Thus $p=4$, $q=0$ and $m=1$ and hence

$$\text{CFSE for energy field} = [-0.4 \times 4 + 0.6 \times 0] \Delta_o + 1 \times P$$

$$= -1.6 \Delta_o + P = -16 Dq + P$$

iii) d^7 ion

a) For weak field (high spin complex) $d^7 = t_{2g}^5 e_g^2$

thus $p=5$, $q=2$ and $m=2$ and hence

$$\text{CFSE for weak field} = [-0.4 \times 5 + 0.6 \times 2] \Delta_o + 2P$$

$$= -0.8 \Delta_o + 2P = -8 Dq + 2P$$

b) For strong field (low spin complex) $d^7 = t_{2g}^6 e_g^1$

thus $p=6$, $q=1$ and $m=3$ and hence

$$\text{CFSE for strong field} = [-0.4 \times 6 + 0.6 \times 1] \Delta_o + 3P$$

$$= -1.8 \Delta_o + 3P = -18 Dq + 3P$$

Uses of CFSE values:

i) Crystal structure of spinels:

Mixed oxides of the general formula $A^{2+}B_2^{3+}O_4^{2-}$ are called spinels after the name of the mineral spinel, $MgAl_2O_4$. A^{2+} and B^{3+} are divalent and trivalent metallic cations may be different or the same.

In spinels oxygen atoms are arranged in a cubic close-packed lattice. In such lattices each oxygen atom has 12 other oxygen atoms equidistant from it and the holes between oxygen atoms are of two types.

i) Octahedral holes which are so called because these are surrounded by six oxygen atoms. There is one of such holes for each oxygen atom.

ii) Tetrahedral holes which are so called since these are surrounded by four oxygen atoms.

There are two such holes for each oxygen atom. These are smaller than the oh-holes. There are twice as many tetrahedral holes as there are octahedral holes. The cations occupy the oh-holes and tetrahedral holes, since these are large enough to be filled by cations.

There are 2 main types of spinels: i) inverse and ii) normal.

In normal spinel all the A^{2+} cations occupy one of the eight available tetrahedral holes and all B^{3+} cations occupy half of the available octahedral holes.

In inverse spinels all the A^{2+} and half of the B^{3+} cations are in oh and the other half of the B^{3+} cations are in tetrahedral holes.

These inverse spinels are, therefore, represented as $B^{3+} [A^{2+} B^{3+}] O_4^{2-}$ to distinguish them from the normal spinels which are represented as $A^{2+} [B^{3+}] O_4^{2-}$.

The species enclosed in square brackets occupy the octahedral holes.

Eg: - Ti^{4+} , $Zn^{2+} O_4^{2-}$, $Sn^{4+} Co_2^{2+} O_4^{2-}$

ii) Stabilization of oxidation states:-

CFSE values also explain why certain oxidation states are preferentially stabilized by coordination with certain ligands.

Although H_2O molecule which is weak ligand should be expected to coordinate with Co^{2+} and Co^{3+} ions to form the high spin octahedral complexes. $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}$

respectively, experiments show that H_2O stabilises Co^{2+} ion and not Co^{3+} ie $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is more stable than $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$.

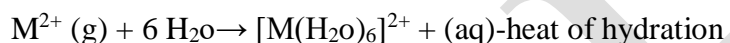
This is because of the fact that Co^{2+} (d^7) has a much higher value of CFSE in weak oh-configuration ($\text{CFSE}=0.8 \Delta_0$) than Co^{3+} (d^6) in the same configuration ($\text{CFSE}=0.4 \Delta_0$).

iii) Stereochemistry of complexes:-

CFSE values also predict why Cu^{2+} ion forms square planar complexes rather than tetrahedral complexes or octahedral complexes on both fields. This is because of the reason that Cu^{2+} ion (d^9 system) has a much higher CFSE value in a square planar configuration ($\text{CFSE}=1.22 \Delta_0$) than in octahedral ($\text{CFSE}=0.6 \Delta_0$) or tetrahedral configuration ($\text{CFSE}=0.18 \Delta_0$).

iv) Heats of hydration of divalent ions of first row transition elements:-

The heat of hydration is the heat evolved in the hydration process.



Minus sign indicates that heat of hydration is evolved in hydration process.

We know that on passing from Ba^{2+} to Mg^{2+} (alkaline earth metals) in II A group of the periodic table there is a decrease in the ionic radii. The decrease in ionic radii values brings the ligands viz H_2O molecules closer to the metal cation, M^{2+} , resulting in the increased electrostatic attraction between the cation and the ligands. Consequently the values of heat of hydration increase steadily from Ba^{2+} to Mg^{2+} .

Limitations of CFT:

i) CFT consider only the metal ion d-orbitals and gives consideration at all to other metal orbitals such as S, p_x , p_y , and p_z orbitals and the ligand -orbitals. Therefore, to explain all the properties of the complexes dependent on the - ligand orbitals will be outside the scope of CFT. CFT does not consider the formation of -bonding in complexes.

ii) CFT is unable to account satisfactorily for the relative strengths of ligands e-g it gives no explanation as to why H_2O appears in the spectro chemical series as stronger ligands than OH^- .

iii) According to CFT, the bond between the metal and ligands are purely ionic. It gives no account of the partly covalent nature of the metal-ligand bonds. Thus the effects directly dependent on covalence cannot be explained by CFT.

Ligand field theory (LFT) or Molecular orbital theory (MOT):-

The crystal field theory takes no account of possible covalent bonding in complexes-and regards the bonding as purely electrostatic. But the physical measurements such as electron spin resonance, NMR and nuclear quadruple resonance suggest that there is some measure of covalent bonding also in complexes. It is because of this reason that a kind of modified form of CFT has been suggested in which some parameters are empirically adjusted to allow for CFT. This modified form of CFT is often called ligand field theory LFT. However, LFT is sometimes also used as a general name for the whole gradation of theories from CFT to the molecular orbital theory, MOT.

MOT as applied to octahedral complexes:-

According to MOT the metal-ligand σ -bonding in octahedral complexes results from the overlap of suitable atomic orbitals of the central metallic cation with ligand σ -orbitals. The formation of six-metal-ligand σ -bonds (or Mo's) in an octahedral complex takes place through the following steps:

i. The central metal cation 3d-series elements contains in all nine valance-shell atomic orbitals which are: 4s, 4p_x, 4p_y, 4p_z, 3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x²-y²} and 3d_{z²}.

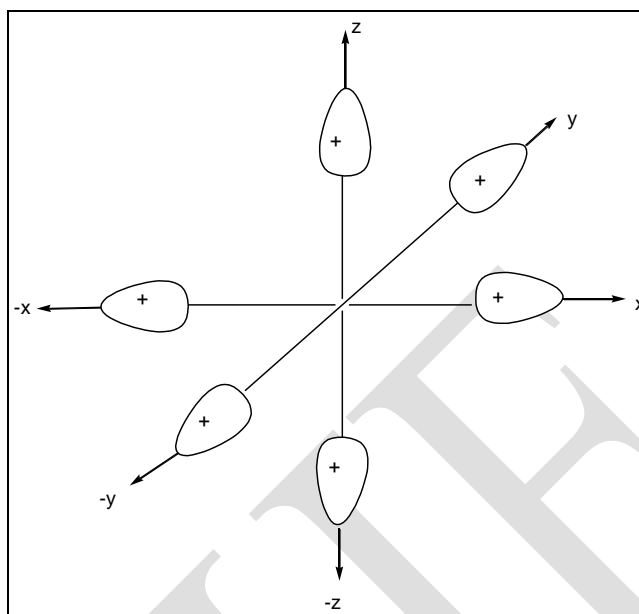
In this step we make a selection of only six suitable atomic orbitals which may overlap along the axis with group ligand σ -orbitals to form six-metal-ligand σ -bonds (or Mo's).

All the nine atomic orbitals have been grouped in to four symmetry classes which are given below.

4s \rightarrow A_{1g} or a_{1g}; 4p_x, 4p_y, 4p_z \rightarrow T_{1u} or t_{1u}; 3d_{x²-y²}, 3d_{z²} \rightarrow E_g or e_g; and 3d_{xy}, 3d_{yz}, 3d_{zx} \rightarrow T_{2g} or t_{2g}.

Now, we know that since in an octahedral complex six σ -orbitals of the six ligands are approaching along the axis fig in which ligands σ -orbitals along the +x, -x, +y, -y, +z and -z axes have been represented as σ_x , σ_{-x} , σ_{+y} , σ_{-y} , σ_z , σ_{-z} respectively these σ -orbitals in order to form six metal-ligand σ bonds or MO'S, will overlap more effectively with only these metal ion valence AO'S, that are having their lobes along axes (ie ,along the metal ligand direction).

Quite evidently, such AO'S are 4s, 4p_x, 4p_y, 4p_z, 3d_{z²} and 3d_{x²-y²}, since these orbitals have their lobes lying along the axes along which the six σ -orbitals of the six ligands are approaching towards the central metal cation to form six metal-ligands σ -bonds.



Six ligand σ -orbitals in an octahedral complex

The remaining three AO'S namely $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ do not participate in σ -bonding process, since these have their lobes oriented in space between the axes. Thus the orbitals remain non-bonding and hence are called non-bonding orbitals. These can, however, overlap sidewise with filled or unfilled π orbitals of the same six ligands to form metal-ligand π -bonds or π - MO'S. Thus these orbitals are generally referred to as π_d , $\pi(d)$ or π_{xy} , π_{yz} , π_{zx} orbitals.

In this step the σ_x , σ_{-x} ,etc orbitals of ligands combine together linearly to form such group ligand σ -orbitals that should be capable of overlapping with the central metal ion six AO'S viz $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_z^2$ and $3d_{x^2-y^2}$.

- a) Since $4s$ orbitals has the same sign in all directions, linear combination of ligand σ -orbitals which can overlap with $4s$ orbital is

$$\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z}$$

The linear combination is represented by \sum_a which in its s normalized form, is given by:

$$\sum_a = 1/ (\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z}) \dots \dots \dots A_{1g} \text{ or } a_{1g}$$

A_{1g} or a_{1g} represents group symmetry class name of

- b) Since one lobe of $4p_x$ orbital has + sign and the other has – sign, the linear combination of ligand σ -orbitals that can overlap with $4p_x$ orbital is $\sigma_x - \sigma_{-x}$.

It is represented by \sum_x which in its normalized form is given as:

$$\sum_x = 1/(\sigma_x - \sigma_x) \dots \dots \dots \text{Eg or eg}$$

Similarly $\sigma_y - \sigma_y$ and $\sigma_z - \sigma_z$ are the linear combinations of ligand σ -orbitals that overlap with $4p_y$ and $4p_z$, atomic orbitals respectively.

Thus

$$\sum_x = (\sigma_y - \sigma_y) \dots \dots \dots \text{Eg or eg}$$

$$\sum_y = (\sigma_z - \sigma_z) \dots \dots \dots \text{Eg or eg}$$

- c) Since one opposite pair of lobes of $3d_{x^2-y^2}$ orbital has a + sign and the other has - sign, the linear combination of ligand σ orbitals for this orbitals is: $\sigma_x + \sigma_x - \sigma_y - \sigma_y$ thus

$$\sum_{x^2-y^2} = 1/2 (\sigma_x + \sigma_x - \sigma_y - \sigma_y) \dots \dots \dots T_{1u} \text{ or } t_{1u}$$

- d) To find the ligand σ -orbital combination for $3d_{z^2}$ orbital poses some difficulty. The analytical function for $3d_{z^2}$ orbital is proportional to $3z^2 - r^2$.

$$\text{Thus } 3z^2 - r^2 = 3z^2 - (x^2 + y^2 + z^2) = 2z^2 - x^2 - y^2.$$

Consequently the proper combination for $3d_{z^2}$ orbital is:

$$2(\sigma_z + \sigma_z) - (\sigma_x - \sigma_x) - (\sigma_y + \sigma_y) = 2\sigma_z - 2\sigma_x - \sigma_y - \sigma_y.$$

Thus

$$\sum_{z^2} = (2\sigma_z - 2\sigma_x - \sigma_y - \sigma_y) \dots \dots \dots T_{1u} \text{ or } t_{1u}.$$

The group symmetry names given above show that there is no ligand σ -orbital with T_{2g} or t_{2g} symmetry name. Thus $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ atomic orbitals which are with T_{2g} or t_{2g} symmetry will not combine with any of the above group ligand σ -orbitals which are with $(a_{1g} + e_g + t_{1u})$ symmetry. Ie these atomic orbitals will not participate in the formation of molecular orbitals and hence remain as non-bonding orbitals.

This is the final step in which the six atomic orbitals of the central metal cation viz $4s, 4p_x, 4p_y, 4p_z, 3d_{x^2-y^2}$ and $3d_{z^2}$ overlap with six group ligand σ -orbital viz a, x, y, z, x^2-y^2 and z^2 respectively to form six sigma bonding (abbreviated as σ^6) and 6 sigma antibonding (abbreviated as σ^*) molecular orbitals. Here it should be noted that atomic orbitals and the group ligand σ -orbitals which are overlapping together to form the molecular orbitals are of the same symmetry. Thus

- a) $4s$ and a which have the same symmetry (a_{1g} symmetry) overlap to form one σ_6 Mo and σ_s^* Mo.

- b) $4p_x$ and x (both with eg symmetry) overlap to form one σ_6 Mo and σ_x^* Mo.

- c) $4p_y$ and y (both with eg symmetry) overlap to form one σ_6 Mo and $1\sigma_y^*$ Mo.

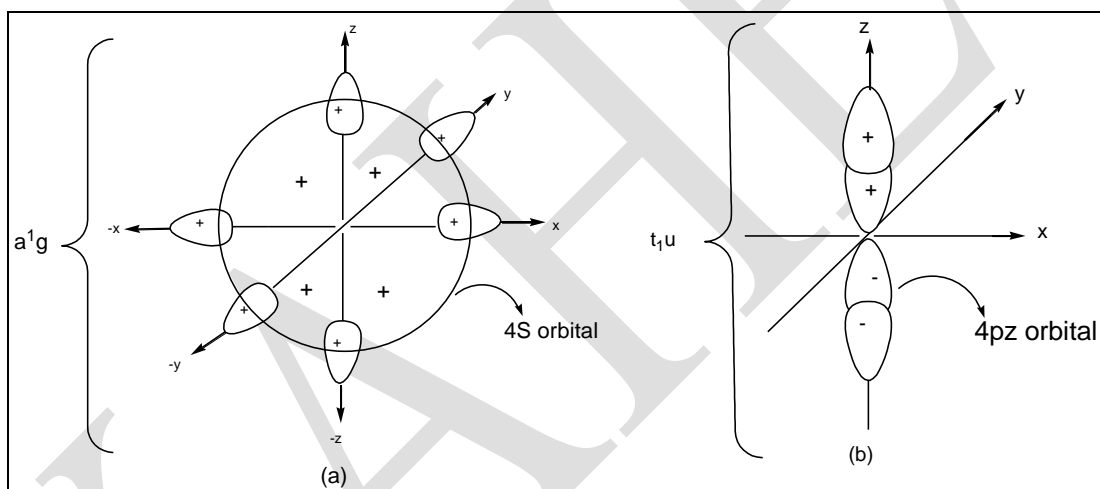
d) $4p_z$ and d_{z^2} (both with e_g symmetry) overlap to generate one σ_{g6} Mo and one σ_{g6}^* Mo.

e) $3d_{z^2}$ and d_{z^2} (both with t_{1u} symmetry) overlap to form one $\sigma_{z^{2b}}$ Mo and $\sigma_{z^{2b}}^*$ Mo.

f) $3d_{x^2-y^2}$ and $d_{x^2-y^2}$ (both with t_{1u} symmetry) overlap to give one $\sigma_{x^2-y^2}$ Mo and $1\sigma_{x^2-y^2}^*$ Mo.

Thus we see that the combination of 6 central metal atomic orbitals with 6 ligand σ -orbitals give six σ^6 and σ^* Mo in a oh -complexes. It is thus obvious that on adding 12 Mo ($6\sigma^6$ and $6\sigma^*$ Mos) to the three non-bonding A_0 's. Viz $3d_{xy}$, $3d_{yz}$, $3d_{zx}$ we get in all fifteen orbitals potentially available for electron filling.

From fig (2) the following points may be noted:



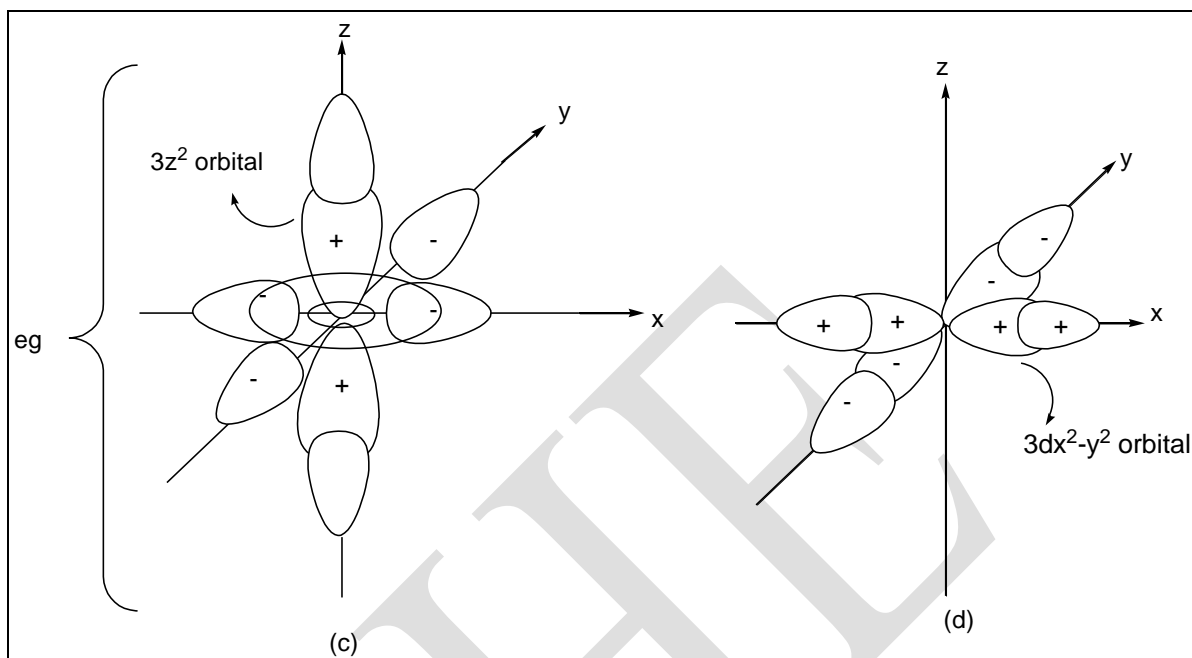


Fig (2) combination of 4s, 4p_z (similarly for 4p_x and 4p_y) 3d_{z²} and 3d_{x²-y²} A₀'s of the central metal ion or atom with group ligand σ-orbitals to form bonding σ-Mo's in an oh-complexes.

a) Overlap of metal 4s-orbital (a_{1g} symmetry orbital) with a group ligand σ-orbitals (a_{1g} symmetry).

$$\Sigma_a = (\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$$

b) Overlap of metal 4p_z orbital (t_{1u} symmetry orbital) with a group ligand σ-orbitals (t_{1u} symmetry).

$$\Sigma_z = (\sigma_z - \sigma_{-z})$$

c) Overlap of metal 3d_{z²} orbital (eg symmetry orbital) with a group ligand σ-orbitals (eg symmetry).

$$\Sigma_z^2 = (2\sigma_z - 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$$

d) Overlap of metal 3d_{x²-y²} orbital (eg symmetry orbital) with a group ligand σ-orbitals (eg symmetry).

$$\Sigma_{x^2-y^2}^2 = \frac{1}{2}(\sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y}).$$

i) The wave function of all the six ligand orbitals used for combination with 4s-orbital have the same sign (ie +sign) as the metal 4s orbital. This is a case in which the orbitals combine together with maximum positive overlap and give the bonding Mo's fig 2(a). The corresponding antibonding Mo's would involve reversal of sign of the wave function of the combining orbitals.

ii) Each of the metal p-orbitals combines with a ligand combination orbital involving two ligands as shown for the 4p_z orbital

fig (2) (b).

iii) The d_z² and d_{x²-y²} orbitals of the central metal combine with combination ligand orbitals of the same symmetry (eg –symmetry with the signs as shown in fig (2) (c) and (d).

Energy order of orbitals and their filling with electrons:

The order of energy of different orbitals formed in an octahedral complex depends on the nature of the ligands. Ie, whether the ligands are stronger or weaker. Thus the 2 cases arise:

i) When the ligands are stronger:-

Stronger ligands such as NH₃ molecule split the σ bonding Mo's namely σ_s⁶, σ_x⁶=σ_y⁶=σ_z⁶, σ_x²-y^{2b}=σ_z^{2b} more widely the energy difference, Δ₀ between the t_{2g} set of non bonding A₀'s (3d_{xy}, 3d_{yz} and 3d_{xz}) and eg set of Mo's (σ_{x²-y²}^{2*} and σ_z^{2*} Mo's) is greater than the electron pairing energy, p (ie Δ₀ > p).

In this case, the order of energy of different orbitals is shown as follows:

$$\begin{array}{l}
 \sigma_{x^*} = \sigma_{y^*} = \sigma_{z^*} (3) \dots \sigma_r^* (t_{1u}^*) \\
 \sigma_{y^*} (1) \dots (a_{1g}^*) \\
 \sigma_{x^2-y^2}^* = \sigma_{z^*}^* (2) \dots \sigma_d^* \text{ or } \sigma^* (d) (e_g^*) \\
 \Delta_0 \text{ or } 10Dq \\
 3d_{xy} = 3d_{yz} = 3d_{xz} (3) \dots \Pi_d \text{ or } \Pi(d) \text{ or } \Pi \text{ or } \Pi_{xy} = \Pi_{yz} = \Pi_{zx} (t_{2g}) \\
 \sigma_{x^2-y^2}^b - \sigma_{z^*}^b (2) \dots \sigma_d^b (e_g) \\
 \sigma_x^b = \sigma_y^b = \sigma_z^b (3) \dots \sigma_p^b (t_{1u}) \\
 \sigma_z^b (1) \dots (a_{1g})
 \end{array}$$

Numbers given in brackets indicate the degeneracy of the Mo's or A₀'s as the case may be, eg the Mo's viz σ_x^b, σ_y^b and σ_z^b are triply degenerate.

Quite evidently the σ^b -Mo's have the lowest energy, σ^* -Mo's have the highest energy while the non bonding orbitals viz $3d_{xy}, 3d_{yz}$ and $3d_{zx}$ have an energy level intermediate between the bonding and antibonding Mo's. Thus the non-bonding orbitals are more stable than the antibonding Mo's but less stable than the bonding Mo's. These orbitals remain unchanged in their energy.

Now let us see how the distribution of electrons in $[\text{Co}(\text{NH}_3)_6]^{3+}$ which contains stronger ligands viz. NH_3 molecules (ie it is a low spin complex) takes place in various orbitals according to the above order. This complex has Co as Co^{3+} (d^6 system). Thus they are in all 18 electrons in it, 12e's from six: NH_3 molecules and 6 from d-orbitals in Co^{3+} ion. The distribution of 18 electrons in various orbitals is shown in figure. Which is commonly called the MOT energy level diagram.

Fig shows that the MOT configuration of $[\text{Co}(\text{NH}_3)_6]^{3+}$ can be represented by any of the following configuration:

- i) $(\sigma_s^b)^2, (\sigma_x^b)^2 = (\sigma_y^b)^2 = (\sigma_z^b)^2, (\sigma_{(x^2-y^2)}^b)^2 = (\sigma_z^b)^2 \cdot (3d_{xy})^2 = (3d_{yz})^2 = (3d_{zx})^2$
- ii) $[6\sigma^b]^{12}, (3d_{xy})^2 = (3d_{yz})^2 = (3d_{zx})^2$
- iii) $(a_{1g})^2, (t_{1u})^6, (e_g)^1 (t_{2g})^6$
- iv) $(\sigma_s^b)^2, (\sigma_p^b)^6, (\sigma_d^b)^4 (\pi_d)^6$

The designation $[6\sigma^b]^{12}$ represents the six sigma bonding MO's $\sigma_s^b, \sigma_x^b = \sigma_y^b = \sigma_z^b, \sigma_{(x^2-y^2)}^b = \sigma_{(z^2)}^b$, all of which are completely filled. Hence the superscript 12.

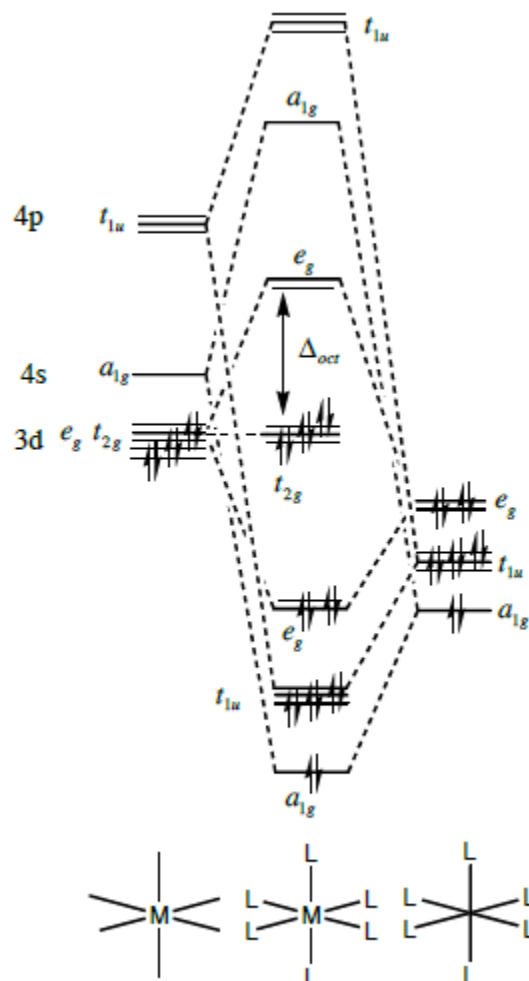


Figure ML_6 energy level diagram

MOT energy level diagram of $[Co(NH_3)_6]^{3+}$ which is a low spin oh. complex (π bonding not considered, only σ bonding considered). The e^- represented by crosses are those of six NH_3 molecule (ligand) and those represented by full arrows ($\uparrow\downarrow$) are 3d e^- s of ion (d^6 ion).

In connection with MOT energy level diagram shown in fig following points may be noted. Since the ligand orbitals are usually more electronegative than the metal AO's we have drawn the right hand energy level below any of left hand levels.

b) The crystal field splitting energy (Δ_0 or $10 Dq$) in an octahedral complex, according to MOT, is the difference in energy between the t_{2g} (d_{xy}, d_{yz}, d_{zx} orbitals) and e_g^* ($\sigma_{(x^2-y^2)}^*$ and $\sigma(z^2)^*$ MO's) energy levels.

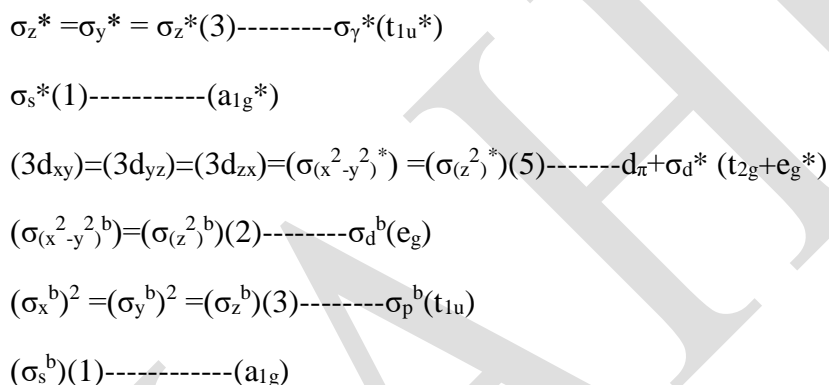
c) In general it may be assumed that, if a MO is near in energy to the energy of the ligand orbital, it would have more of the character of the ligand.

In other words the electrons in the six σ^b MO's are mainly localised on ligand orbitals, since σ orbitals of the ligands are more stable than the metal orbitals.

ii) When the ligand are weaker:-

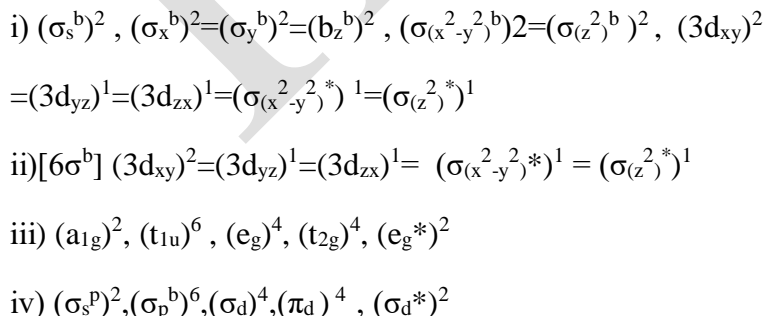
In case of weaker ligands such as F^- ion, the energy difference, Δ_0 , between the t_{2g} and e_g^* set is smaller than p (ie $\Delta_0 < p$) and hence the lowest energy antibonding MO's namely $\sigma_{(x^2-y^2)}^*$ and $\sigma_{(z^2)}^*$ have approximately the same energy as the non bonding AO's: $3d_{xy}$, $3d_{yz}$, $3d_{zx}$ (t_{2g} set).

Consequently, the order of energy becomes as shown below:



The distribution of 18 e^- s in $[CoF_6]$ which contain weaker ligand viz F^- ions (ie it is a high spin complex) takes place in various orbitals according to the above scheme as shown in MOT energy level diagram given in fig. The figure clearly shows that in case of high spin complexes, Hund's rule is obeyed.

The MO-configuration of $[CoF_6]$ can thus be represented by any of the following configurations.



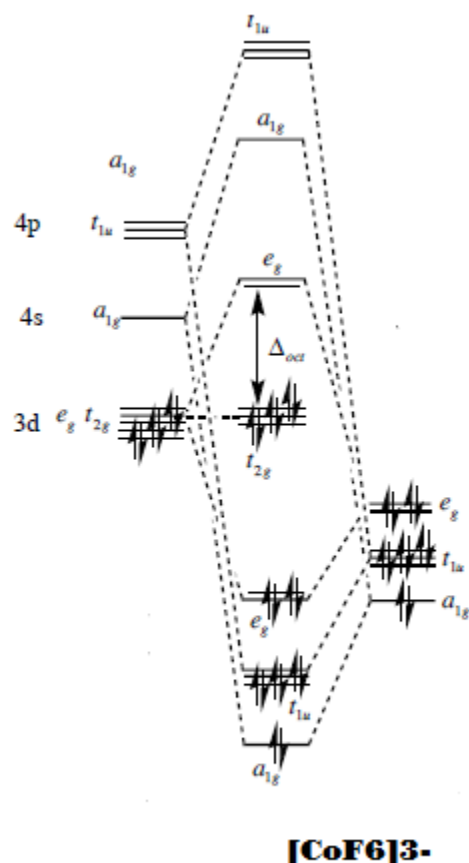


Figure ML_6 energy level diagram

Fig (2) MOT energy level diagram of $[CoF_6]^{3-}$ which is a high spin octahedral complex.

Comparison of fig (1) &(2) shows that the magnitude of Δ_0 in case of high spin complexes is smaller than that of low spin complexes.

Π -bonding in octahedral complexes:

We have so far dealt with σ -bonding between the central metal cation and the ligands having σ -orbitals in octahedral complexes. Here we shall consider the formation of Π -bond between the appropriate AO'S of the central metal cation and Π -orbitals of the ligands (usually called ligands Π -orbitals). The metal orbitals which take part in the formation of Π -bond are $P_x, P_y, P_z, d_{xy}, d_{yz}, d_{zx}$ orbitals, since these can overlap with the ligand Π orbital in sideway on fashion to form the Π -bond while the ligands Π -orbitals participating in Π -bond formation may be any of the following three types.

a) simple p-orbitals:

These may be simple p-orbitals (called p Π orbitals) which are not directed along the line joining the ligand and the metal ion, i.e p-orbitals taking part in Π -bond formation are perpendicular to one another and also to the metal ligands.

Thus there are two such p-orbitals on each of the six ligands in an octahedral complex as shown in figure in which L₁ -----L₆ are the six ligands and Π_{3x} , Π_{4x} , Π_{5x} , Π_{6x} ; Π_y , Π_{2y} , Π_{5y} , Π_{6y} and Π_{1z} , Π_{2z} , Π_{3z} , Π_{4z} are the p Π –ligands orbitals along the x-y- and z –axis respectively.

Ligands	p Π -orbitals on the ligands
L ₁	Π_{1z} , Π_{1y}
L ₂	Π_{2z} , Π_{2y}
L ₃	Π_{3z} , Π_{3x}
L ₄	Π_{4z} , Π_{4x}
L ₅	Π_{5x} , Π_{5y}
L ₆	Π_{6y} , Π_{6x}

In the first column of table are listed the ligands L₁----- L₆ and in the second column are given their p Π orbitals. The letter x in Π_{3x} ----- Π_{6x} indicates that these p Π orbitals are along the x-axis, the letter y in Π_{1y} ----- Π_{6y} indicates that these p Π orbitals lie along the y axis.similarly the letter z in Π_{1z} ----- Π_{4z} stands to indicate that these p Π - orbital are along the z-axis.The number 1,2-----5,6 are used as coefficients of x,y and z in different p Π ligand orbitals indicate that these p Π ligand orbitals are of ligands namely L₁ , L₂ ----- L₅, L₆ respectively. The arrow - heads of these p Π orbitals point in the different of the + lobe of the orbitals.Ligand p Π orbitals are always filled and are found in halide ions O²⁻,RO⁻,RS⁻ etc.Twelve ligand p Π - orbitals in an octahedral complex. Before combining with AO'S of the central metal cation these ligand p Π orbitals combine together to form group ligand Π -orbitals. It is quite easy to see that the group ligand Π -orbitals (not in the normalized form) which can overlap with, for example, d_{zx} atomic orbital is;

$$(\Pi_{1z} - \Pi_{2z} + \Pi_{5x} - \Pi_{6x})$$

Table : Proper metal and ligand Π -orbitals combination (with symmetry class name) for oh. complexes.

Group symmetry name	Central ion orbitals	Appropriate combination of ligand Π -orbitals
t_{1u} or T_{1u}	4P _x 4P _y 4P _z	$\Pi_x = 1/2 (\Pi_{3x} + \Pi_{4x} + \Pi_{5x} + \Pi_{6x})$ $\Pi_y = 1/2 (\Pi_{1y} + \Pi_{2y} + \Pi_{5y} + \Pi_{6y})$ $\Pi_z = 1/2 (\Pi_{1z} + \Pi_{2z} + \Pi_{3z} + \Pi_{4z})$
t_{2g} or T_{2g}	3d _{xy} 3d _{yz} 3d _z	$\Pi_{xy} = 1/2 (\Pi_{1y} - \Pi_{2y} + \Pi_{3y} - \Pi_{4y})$ $\Pi_{yz} = 1/2 (\Pi_{3z} - \Pi_{4z} + \Pi_{5z} - \Pi_{6y})$ $\Pi_{zx} = 1/2 (\Pi_{1z} - \Pi_{2z} + \Pi_{5x} - \Pi_{6x})$

In the last columns of table 2 is given the appropriate combination of Π - orbitals of the ligands that can overlap with P_x, p_y, P_z, d_{xy}, d_{yz}, and d_{zx} atomic orbitals. These combinations are not given in their normalized form. In fig(2) the overlap of p_x orbital of the central metal cation with group ligand Π orbitals viz. $1/2(\Pi_{1x} + \Pi_{2z} + \Pi_{3x} + \Pi_{4x})$ and of d_{zx} orbitals with group ligand Π orbitals viz. $1/2(\Pi_{1z} - \Pi_{2z} + \Pi_{5x} - \Pi_{6x})$ is shown.

Fig

- Overlap of the metal p_x atomic orbital with group ligand Π orbitals viz $(\Pi_{1z} + \Pi_{2z} + \Pi_{3z} + \Pi_{4z})$.
- Overlap of the metal d_{zx} atomic orbital ligand Π orbitals viz $(\Pi_{1z} - \Pi_{2z} + \Pi_{5x} - \Pi_{6x})$.fig(2) overlap of a metal p_z orbital and and b) metal d_{zx} orbitals with group ligand Π orbitals.

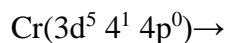
Simple d Π -orbital

These may be simple d Π -orbitals (ie d_{xy}, d_{yz}, and d_{zx} orbitals. such type of d Π -orbitals are found in phosphines ,arsines etc .these are always filled.

c) Π -Mo's

These may be Π -Mo's of poly atomic ligands such as CO, CN⁻ or pyridine. Now let us consider how the combination of the Mo's of polyatomic ligands with the metal d Π orbitals occurs. In order to illustrate such type of combination let us consider the bonding in hexa carbonyl of chromium Cr(CO)₆ in which both σ and Π bonds occur. In this compound Cr is

zero oxidation state ($\text{Cr}^0 \rightarrow 3d^5 4s^1$) Since the coordination no of Cr in $\text{Cr}(\text{CO})_6$ is six, Cr is d^2sp^3 hybridised as shown below.



We know that according to MOT the electronic configuration of CO molecule is : (z axis assumed to be the molecular axis)

—————Energy increasing—————→

Now filled sp hybrid on carbon atom overlaps with one (suitable) vacant d^2sp^3 hybrid orbital on Cr^0 to form $\text{Cr}-\text{Co}$ σ bond (fig).thus in the formation of σ –bond Co acts as a lewis base (ie as a donor).

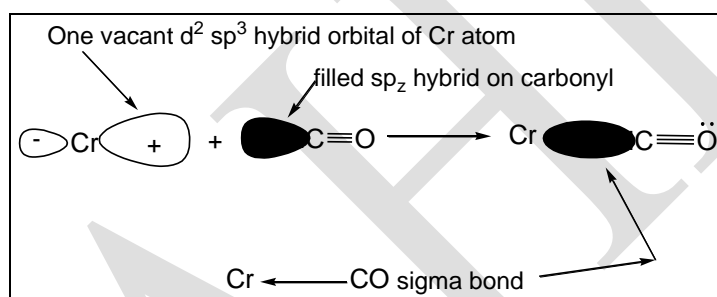


Fig : Formation of $\text{Cr}-\text{Co}$ σ bond using an unshared electron pair on carbon atom.

- One (suitable) of the filled d_{xy} , d_{yz} , and d_{zx} orbitals (t_{2g} set) on Cr overlaps with either of the empty Π^* MO's of CO (Π_x^* or Π_y^* MO) to form $\text{Cr} \rightarrow \text{Co}$ Π bond fig (2).
- Thus we see that in the information of $\text{Cr} \rightarrow \text{Co}$ Π bond, Co acts as a Lewis acid.
- $\text{Cr} \rightarrow \text{Co}$ Π bond removes electron density from the metal and thus prevents the accumulation of too much negative charge on the metal.
- This bond is called back-donation, back donation or back coordination.
- The infrared spectroscopy has shown that back coordination into the Π^* MO'S weaken the carbon to oxygen bond.
- The bond order in CO is three but in metal carbonyls it is less. The presence of both σ and Π bonds in $\text{Cr}(\text{Co})_6$.

References

Text Book:

T1.Wahid U. Malik, G. D. Tuli, R.D. Madan, 2003, selected topics in inorganic chemistry, S.Chand & company, New Delhi

T2. Huheey.J.E, E.A. Keitler, & R.L. Keitler, 2012. Inorganic chemistry, Vol-IV, Pearson Education, Singapore.

Possible Questions:

Part A:

Each question carries one mark:

1.The hybridization of Square planar symmetries is -----

- a. sp
- b. sp^2
- c. sp^3
- d. dsp^2

2. Potash Alum is an example for

- a.Simple Salt
- b. Ligand
- c. Co ordination compounds
- d. **Lattice Compounds**

3. Co ordination number for $[Ni(NH_2-CH_2-CH_2-NH_2)_3]^{2+}$ is

- a. 2
- b. 4
- c. **6**
- d. 3

4. Which is an bidentate ligand

- a. CN^-
- b. CH_3COO^-
- c. **$NH_2-CH_2-CH_2-NH_2$**
- d. NO

5. Number of Cl^- ions precipitated as AgCl by $AgNO_3$ solution in $CoCl_3 \cdot 5NH_3 \cdot H_2O$, which has the molar conductivity 430 is

- a. 0
- b. **3**
- c. 2
- d. 1

6. Primary Valency indicates

- a. Coordination number
- b. **Oxidation state**
- c. both
- d. Neutral Ligands

7. EAN for $[\text{Co}(\text{NH}_3)_6]^{3+}$ is

- a. **36**
- b. 54
- c. 18
- d. 34

8. $\Delta_{sp} =$

- a. Δ_0
- b. **$1.3 \Delta_0$**
- c. $-1.3 \Delta_0$
- d. $0.45 \Delta_0$

9. The axial Orbitals are known as

- a. d- Orbitals
- b. t_{2g} -Orbitals
- c. **e_g -Orbitals**
- d. none

10. The neutral molecules or ions which are attached with the central metal ion are called

- a. Acceptors
- b. Donars
- c. **Ligands**
- d. Coordination number

11. The geometry of the complex having coordination number 5 is -----

- a. **Trigonal bipyramidal**
- b. Hexagonal
- c. Tetrahedral
- d. Trigonal pyramidal

12. In werners theory secondary valency corresponds to

- a. Oxidation state
- b. **Coordination number**
- c. Negative ligand
- d. Positive ligand

13. Number of unpaired electrons present in $[\text{Ni}(\text{CN})_4]^{2-}$

- a. 0
- b. 2
- c. 4
- d. 5

14. The magnetic moment of $[\text{MnBr}_4]^{2-}$ is 5.9 B.M, the number of unpaired electrons is

- a. 0
- b. 1
- c. 4
- d. 5

15. The number of unpaired electrons present in $[\text{MnCl}_4]^{2-}$ complex ion is 5, the hybridisation of the complex is ----

- a. sp
- b. sp^2
- c. **sp^3**
- d. dsp^2

16. In a bidentate ligand if the two coordinating atoms are same means it is known as ----

- a. Flexidentate ligands
- b. Ambidentate ligands
- c. **Symmetrical ligands**
- d. Unsymmetrical ligands

17. The geometry of the complex which is having coordination number 3 is

- a. Tetrahedral
- b. Linear
- c. Square planar
- d. **Trigonalpyramidal**

18. Polydentate ligands in which two or more donor atoms are attached with the same metal ion and produce rings are called -----

- a. Bridged ligand
- b. **Chelating ligand**
- c. Flexidentate ligand
- d. Ambidentate ligand

19. When dissolved in water ----- dissociate into ions without loss of their identity.

- a. Simple salt
- b. **Double salt**
- c. Coordination complex
- d. Ligand

20. Ethylene diamine tetra acetic acid is an example for ----- ligand

- a. Monodentate
- b. Bidentate
- c. Tridentate
- d. **Tetradentate**

Part-B

Each question carries six marks:

1. What is crystal field stabilization energy, explain with suitable diagram?
2. Describe the Molecular orbital theory of chemical bonding
3. Construct the molecular orbital diagram of an octahedral complex involving pi bonding. Suggest two evidences for the presence of pi bonding.
4. Discuss the types of isomerism exhibited by coordination complexes, giving suitable examples.
5. Write a note on Crstal field theory?
6. Illustrate Valance bond theory with suitable example.

Part-C

Each question carries 10 marks:

1. Sketch and explain the splitting of d-orbital in tetrahedral and octahedral Complexes.
2. Describe the Molecular orbital theory of chemical bonding for $[\text{Co}(\text{NH}_3)_6]^{3+}$ Complex with diagram.
3. Explain CFT with neat diagrams?

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Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2018 onwards)
Department of Chemistry
II- semester

Inorganic Chemistry -II (Coordination Chemistry)

UNIT I- Objective Questions for online examination (Each carry 1 Marks)

Question	Option-a	Option-b	Option-c	Option-d	Answer
The hybridization of Square planar symmetries is -----	sp	sp ²	sp ³	dsp ²	dsp ²
Potash Alum is an example for	Simple Salt	Ligand	Co ordination compounds	Lattice Compounds	Lattice Compounds
Co ordination number for [Ni (NH ₂ -CH ₂ -CH ₂ -NH ₂) ₃] ²⁺ is	2	4	6	3	6
Which is an bidentate ligand	CN ⁻	CH ₃ COO ⁻	NH ₂ -CH ₂ -CH ₂ -NH ₂	NO	NH ₂ -CH ₂ -CH ₂ -NH ₂
Number of Cl ⁻ ions precipitated as AgCl by AgNO ₃ solution in CoCl ₃ . 5NH ₃ .H ₂ O , which has the molar conductivity 430 is	0	3	2	1	3
Primary Valency indicates	Coordination number	Oxidation state	both	Neutral Ligands	Oxidation state
EAN for [Co(NH ₃) ₆] ³⁺ is	36	54	18	34	36
Δ _{sp} =	Δ ₀	1.3 Δ ₀	- 1.3 Δ ₀	0.45 Δ ₀	1.3 Δ ₀
The axial Orbitals are known as	d- Orbitals	t _{2g} -Orbitals	e _g -Orbitals	none	e _g -Orbitals
The neutral molecules or ions which are attached with the central metal ion are called	Acceptors	Donars	Ligands	Coordination number	Ligands

The geometry of the complex having coordination number 5 is -----	Trigonal bipyramidal	Hexagonal	Tetrahedral	Trigonal pyramidal	Trigonal bipyramidal
In werners theory secondary valency corresponds to	Oxidation state	Coordination number	Negative ligand	Positive ligand	Coordination number
Number of unpaired electrons present in $[\text{Ni}(\text{CN})_4]^{2-}$	0	2	4	5	0
The magnetic moment of $[\text{MnBr}_4]^{2-}$ is 5.9 B.M, the number of unpaired electrons is	0	1	4	5	5
The number of unpaired electrons present in $[\text{MnCl}_4]^{2-}$ complex ion is 5, the hybridisation of the complex is -----	sp	sp ²	sp ³	dsp ²	sp ³
In a bidentate ligand if the two coordinating atoms are same means it is known as ----	Flexidentate ligands	Ambidentate ligands	Symmetrical ligands	Unsymmetrical ligands	Symmetrical ligands
The geometry of the complex which is having coordination number 3 is	Tetrahedral	Linear	Square planar	Trigonalpyramidal	Trigonalpyramidal
Polydentate ligands in which two are more donor atoms are attached with the same metal ion and produce rings are called -----	Bridged ligand	Chelating ligand	Flexidentate ligand	Ambidentate ligand	Chelating ligand
The ligands which are having only one donor atom and can coordinate to the central metal ion at one site only are called -----	Unidentate	Bidentate	Tridentate	Flexidentate	Unidentate
If the oxidation state of the complex increase then the Δ_0 value	Decreases	Increases	As such	Moderate	Increases
In the formation of σ - bonding in octahedral complexes, the nonbonding are	a_{1g}	t_{1u}	e_g	t_{2g}	t_{2g}
The total number of atoms of the ligands that can coordinate to the central metal ion is known as ----	Ligancy	Acceptors	Valency	Donors	Ligancy

According ----- theory the metal-ligand σ -bonding in octahedral complexes results from the overlap of suitable atomic orbitals of the central metallic cation with ligand σ - orbitals.	Valence bond theory	Crystalfield theory	Ligand field theory	Free electron theory	Ligand field theory
In the formation of σ - bonding in octahedral complexes , the non-bonding orbitals are	a_{1g}	t_{1u}	e_g	t_{2g}	t_{2g}
When dissolved in water ----- dissociate into ions without lose of their identity.	Simple salt	Double salt	Coordination complex	Ligand	Double salt
Ethylene diamine tetra acetic acid is an example for ----- ligand	Monodentate	Bidentate	Tridentate	Tetradentate	Tetradentate
The secondary valency for $[\text{CoCl}_2(\text{NH}_3)_4] \text{Cl}$ is ---	2	4	6	1	6
EAN for $[\text{Ni}(\text{CO})_4]$ is	12	36	18	56	36
The compounds having the same molecular formula but different structures and hence different physical and chemical properties are called -----	enantiomers	diastereomers	isomers	diastereo isomers	isomers
The isomers gives different ions in solution are known as -----	ionisation	Linkage isomer	Ligand isomer	Hydrate isomer	ionisation
Crystal field theory is also called as	Weak field theory	Strong field theory	ligand field theory	None	ligand field theory
In Crystal field theory ligands are consider as	Positive point charges	negative point charges	ligand field theory	None	negative point charges
In crystal field splitting of d orbitals d_{xy} , d_{yz} , d_{yz} orbitals are known as	a_{1g}	t_{1u}	e_g	t_{2g}	t_{2g}
Triply degenerate orbitals are	a_{1g}	e_u	e_g	t_{2g}	t_{2g}
In a NO_2^- ion if the donar atom is 'O' means the ligand is named as	Nitrato	Nitro	Nitrito	Nitrosyl	Nitrito

reaction in which the coordination number of an electron acceptor increases are called	Addition reaction	Substitution reaction	Oxidation reaction	Thermal dissociation reaction	Addition reaction
In an dissociation reaction the coordination number is	Increases	Decreases	unchanged	none	Increases
When two identical ligands are placed opposite to each other in a complex , the isomer is	space isomer	cis isomer	trans isomer	optical isomer	trans isomer
the geometry of the complexes which are having coordination number 4	Linear	square pyrimidal	octahedral	Tetrahetral	Tetrahetral
Example for complexes of $[Ma_4b_2]$ type	$[Co(NH_3)_4(NO_2)_2]$	$[Co(NH_3)_2(NO_2)_2]$	$[Pt(NH_3)_4]$	$[Co(NH_3)_3(NO_2)_3]$	$[Co(NH_3)_4(NO_2)_2]$
Hydrazinium is an example for ----- ligand	Ambidentate ligand	Positive ligand	Negative ligand	Neutral ligand	Positive ligand
For bridging group --- greek letter is written before their names	μ	ν	θ	β	ν
The central atom or ion, together with all ligands forms?	Coordination atom	Coordination complex	Coordination bond	Coordination sphere	coordination sphere
The s and p orbitals of the metal can accommodate how many electrons ?	17	10	18	16	10
Metal ions may have ?	1 Coordination number	>2 Coordination numbers	<1 Coordination numbers	>1coordination number	>1coordination number
The s, p, and d orbitals of the metal can accommodate how many electrons ?	17	16	18	19	18
Which isomerism occurs in octahedral and square planar complexes?	Stereoisomerism	Cis-trans	Meridional	Optical	Cis-trans
Which theories are more complicated ?	MO and LFT	MO and CFT	CFT and LFT	CFT and Werner theory	MO and LFT
When the complex is a cation or a neutral molecule, the name of the metal atom is?	Changed	ate is added in suffix	unchanged	oxo is added in suffix	unchanged
Which one of the following is neutral complex?	$NH_4[Co(H_2O)_2(SC$	$K[Pt(NH_3)Cl_3]$	$[Co(en)_2H_2O Cl] SO_4$	$[Co(NH_3)_3NO_2(C$	$[Co(NH_3)_3NO$

	N) ₄]			N)Cl]	₂ (CN)Cl]
The metal ions having eight electrons in their d orbitals usually form ?	Octahedra complexes	Tetrahedral complexes	Square planar complexes	Trigonal complexes	Square planar complexes
CuCl is therefore a model for a <i>tetrahedral</i> complex in which a transition-metal ion is	3 ligands	4 ligands	5 ligands	6 ligands	4 ligands
Which provides an important means of adjusting the ground state properties	Bonds	Magnetism	Isomerism	Ligands	Ligands
Antiferro magnetic coupling, results in which compound?	Diamagnetic	Magnetic	Paramagnetic	Synergic effect	Diamagnetic
The combination of ligand-to-metal σ -bonding and metal-to-ligand π -bonding is ?	Magnetic effect	Synergic effect	Paramagnetic effect	Diamagnetic effect	Synergic effect
The LFT analysis is highly dependent on the geometry of the ?	Bonds	Ligands	Electrons	Complex	Complex
The d orbitals of the ligands are usually?	Too high in energy	Low energy	High energy	Too low in energy	High energy
The s orbitals of the ligands are usually ?	Too high in energy	Low energy	High energy	Too low in energy	Too low in energy
The force of attraction between paramagnetic complexes and a magnetic field is proportional to the number of?	Paired electrons	Unpaired electrons	Charged electrons	Uncharged electrons	Unpaired electrons
Each Mn ²⁺ ion in manganese (II) oxide is surrounded by ?	Six O ²⁻ ions	Four O ²⁻ ions	Three O ²⁻ ions	Five O ²⁻ ions	Six O ²⁻ ions

Lecture notes

UNIT-II

SYLLABUS

Electronic spectra of complexes;-

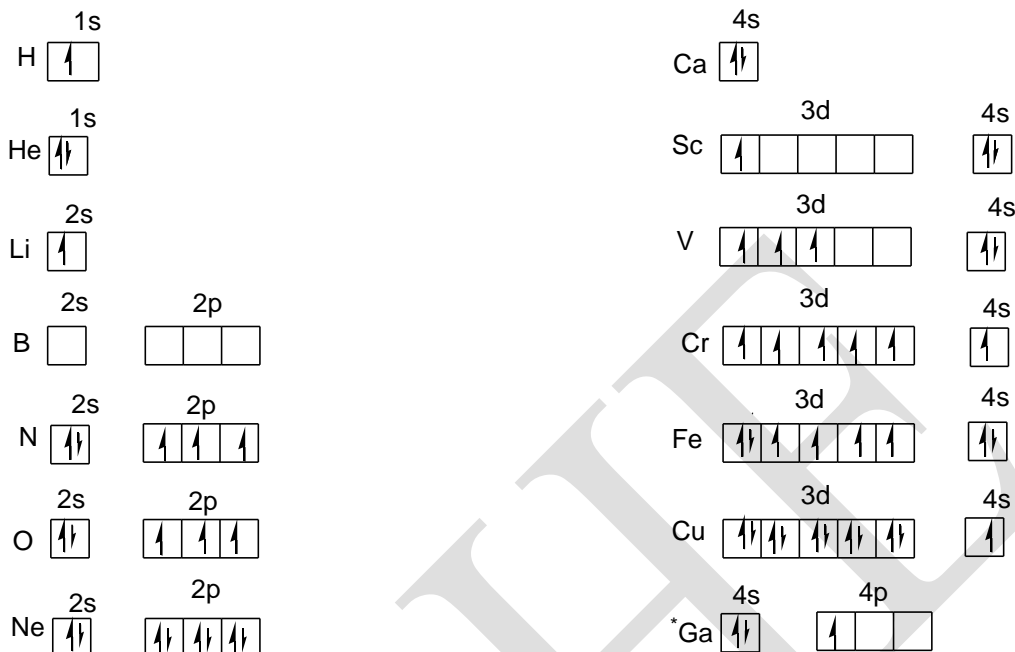
Term symbol for d-configuration. Characteristics of d-d transition and selection rules – weak and strong field limits. Orgel and Tanabe-Sugano diagrams. Jahn Teller tetrahedral distortion and spin orbit coupling. Nephelauxetic effect-charge transfer spectra.

TERM SYMBOLS;-

Relative energies of the orbits;-

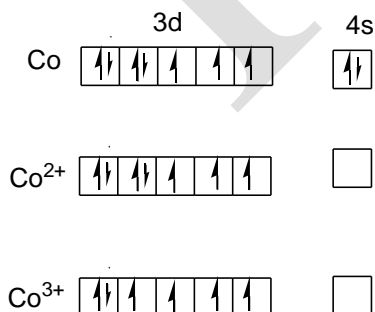
- Since inner electrons do not always effectively screen outer electrons, the relative energies of the orbitals vary with change in nuclear charge of atoms.
- The following order can be employed for writing the atomic structure of most of the atoms in the periodic table:
 $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$.
- As the main quantum number increases, the difference in energy between the orbitals decreases.
- Beyond 7s there are only very slight differences.
- In describing the atomic structure of the element by the s, p, d, and f notation, one simply adds 2 electrons to the s-orbitals, six to the p-orbitals, ten to the d-orbitals and fourteen electrons to the f-orbital.
- The lowest energy orbitals are filled first.
- Stability associated with a half filled or filled sub shells accounts for these exceptions.
- In the above description of atomic structure, 2 quantum numbers n and l have been employed.
- A more nearly complete description of the electrons in an atom can be obtained by employing all four quantum numbers; n, l, m_l and m_s .

- A box diagram representation is one method employed to indicate all four quantum numbers.
 - Usually only the valence electrons are indicated.
 - The s orbitals are indicated by a single box
 - The p orbitals are indicated by three boxes one each for the p_x , p_y , p_z orbitals.
 - The d orbitals are represented by five boxes
- One each for $d_{x^2-y^2}$, d_{xz} , d_{z^2} , d_{yz} , d_{xy} . and f orbital by seven boxes.
- A spin quantum number of $+1/2$ is indicated by the symbol \uparrow and $-1/2$ indicated by the symbol \downarrow
 - In addition to the above conventions, 2 rules are required for the application of box diagram designation to all atoms:
- 1) **PAULI EXCLUSION PRINCIPLE;-**
 - No 2 electrons in an atom have all four quantum numbers alike.
 - 2) **HUNDS RULE;-**
 - Electron will distribute themselves in degenerate orbitals so as to retain parallel spins as much as possible i.e., electrons do not pair up until they have to.



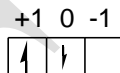
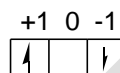
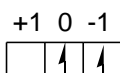
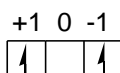
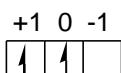
BOX DIAGRAM REPRESENTATION FOR VARIOUS ELEMENTS

- Excluding the principle quantum number, the box diagram for the outer electron of all the element is given family in the periodic table are identical (e.g p, As, Sb and Bi are like N) with the exception of some transition metals.
- In forming positive or negative ions from elements other than transition an electron is added to the next orbital to form a negative ion or the last electron added to form the element is removed to form a positive ion.
- However, for transition element the energy sequence obtained by the Aufbau order does not apply.
- The first electron removed to form the transition metal cations are the s electrons.
- The box diagrams for Co, Co^{2+} and Co^{3+} are illustrated



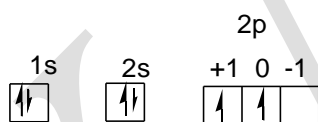
TERM SYMBOLS AND THE VECTOR METHOD:-

- An additional complication encountered in many electron system arises from the large number of ways the electron can be added to a set of orbitals
- A few possibilities for arranging 2 electrons in a set of p orbitals are



- Some of these states would be higher energy states in an atom and some combinations are degenerate.
- Inter electronic repulsion varies for the different electron arrangement, being larger for 2 electrons in same orbital than for electron in different orbitals.
- As a result of different types of inter electronic interaction/ which are absent in a single electron system, many more non degenerate states exist in a many electron system than in a single electron system.
- Furthermore, the concepts of spin and orbital angular momentum for the individual electron lose significance in a many electron system.
- These properties of the individual electron are coupled together to produce a single resultant angular momentum for the entire multi electron atom.
- This resultant momentum is described by the quantum number J.
- “ term symbol” are used to indicate both the electronic configuration and the resultant angular momentum of an atomic state.
- In order to determine J, two schemes are used to describe the coupling of all the angular momentum in the atom.
- These schemes are referred to as LS (or Russell - Saunders) coupling and jj coupling.
- The LS coupling scheme is used when spin orbital interaction are relatively small.
- The individual orbital angular momentum of the electron couple to produce a resultant angular momentum indicated by the quantum number L for the state.
- The individual electron spin moment also couple to give a resultant spin momentum described by the quantum number S.
- The L and S value determine the value of the resultant angular momentum J,
- Which can take on quantum positive values ranging from $|L-S|$ to $|L+S|$ (consecutive values are separated by 1)

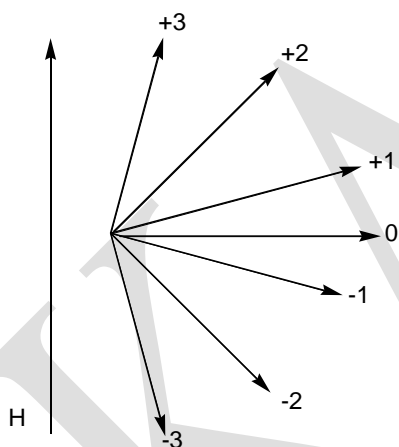
- The $| |$ indicate that the absolute value of $L-S$ is employed (ie, no regard is paid to the sign and $J \geq 0$).
 - The LS coupling scheme can be employed for all atoms except these that have high atomic numbers ($Z > 30$).
 - The jj coupling scheme is used when the spin orbital interaction are large.
 - The spin angular momentum of an individual electron couple with its orbital momentum to give an individual j for that electron.
 - The individual's j 's couple produce a resultant J for the atom.
 - The rules for determining the term symbol for the ground state according to the LS coupling scheme can be summarized.
- 1) Maximize the spin multiplicity (s); ie electron occupy degenerate orbitals so as to retain parallel spins as long as possible (Hunds rule).
 - 2) Maximize orbital angular momentum (L); ie, fill the orbitals with the highest positive m values first.
 - 3) Select the maximum J value for the ground state if the sub shell is more than half- filled, and the minimum value if the sub shell is less than half- filled.
- The rules for determining the term symbol for the ground state of an atom, assuming LS coupling, are best indicated by an example.
 - The box diagram for carbon is;



And the term symbol to be determined is 3P_0 .

- The value of the L quantum numbers is obtained by adding the m_l values for all the electron in incomplete orbitals.
- For example, in carbon $L = +1 + 0 = 1$.
- The quantum number l for an individual electron is treated as a vector with component m_l in the direction of the applied field.
- The vector sum l will have a maximum components equal to the sum of the individual components m_l
- The value for the s quantum number is the sum the spin quantum number ($m_s = \pm 1/2$) for each unpaired electron, e.g for carbon $s = 1/2 + 1/2 = 1$ (the absolute values of L and S are employed)

- Complete sub shells contribute nothing to L or S because the sum of the m_s and m_l values for a filled S, three filled P, or five filled d orbitals is zero.
- The values of L is indicated in the term symbol by the letters S,P,D,F,G,H,AND I for L values corresponding to 0,1,2,3,4,5 and 6 respectively.
- This is similar to describing l values of orbitals as s, p, d, f etc.
- Thus, the p in the term symbol of carbon indicates $L=1$.
- The number in the upper left hand corner corresponding to the spin multiplicity of the state and is given by the formula; $2\sum m_s + 1$ or $2s + 1$
- This is three for carbon and corresponding to the degeneracy resulting from all the different possible orientation of the total electron spin moment.
- Since $s=1$, the spin multiplicity is three, and there are three orientation of the spin moment in a magnetic field parallel, perpendicular, and opposed to the external field.
- This is similar to the alignment the orbital moments as indicated for the d orbitals in fig.



The m_l values included in an F term symbol.

- The values for J (as given by $|L-S|, \dots, |L+S|$) are $|L-S| = 1-1=0$,
 $|L+S| = 1+1=2$
 So, $J=0,1,2, \dots$
- Whenever the sub-shell involved is less than half-filled, the state with minimum J is lowest energy, while maximum values of J are lowest energy when the sub-shell is more than half filled.
- There will be only one J values for a half filled shell because L will be zero.

$$|L+S| = |0+S| = |L-S| = |O-S| = S.$$

- Since carbon has only 2 electrons with a capacity of six in the p-set, the value $J=0$ is lowest in energy.
- The term symbol 3p_0 results for the ground states of carbon.
- The box diagram for the ground state of v^{3+} is

+2	+1	0	-1	-2
↑	↑			

With term symbol 3F_2 ($L=3$, $S=1$, $J=4,3,2$).

- An excited state for this species represented by:

↑↓				
----	--	--	--	--

Which has the term symbol 1G_4 ($L=4$, $S=0$, $J=4$). Because of inter electronic interaction, the energies of many of the V^{3+} states are different.

- For nitrogen with a box diagram

↑	↑	↑
---	---	---

$L=0$, $S=3/2$, $J=3/2$ and the term symbol $^4S_{3/2}$ result.

- Note that there is only J value in the case with $L=0$ for $|L+S| = |L-S| = 3/2$.
- For practice, one can determine the following term symbols for the ground state of the element in parentheses:

3P_2 (S), $^2P_{3/2}$ (Cl), 3F_2 (Ti), 7S_3 (Cr), 3F_4 (Ni), 3P_0 (Si), $^4S_{3/2}$ (As), $^4I_{9/2}$ (Pr).

d-configuration:-

d^2 , d^7 , d^3 , d^8 configuration:

- The application of simple crystal field theory to a weak field d^2 complex. eg V^{111} , predict that the ground state for the gaseous ion is split into 2 sets of level by an octahedral field.
- As indicated in the section on term symbols, inter electronic repulsion would tend split the level of the gaseous ion to a greater extent than if these interaction were neglected.
- Since this is generally true for all the states in complexes formed by cations with more than one d electron, the nature of these splitting will be considered in detail for d^2 octahedral complexes.
- The 2 triplet states for a d^2 gaseous ion were found to be 3F and 3P .

- The following degenerate arrangement are possible for the ground state of octahedral d^2 complex
 $d_{xz}^1, d_{yz}^0; d_{xy}^0, d_{xz}^1, d_{yz}^1; d_{xy}^1, d_{xz}^0, d_{xy}^1$.

- The ground states is orbitally triply degenerate and the symbol $^3T_{1g}(F)$ is used to describe this state.

The following information is conveyed;-

- The symbol T indicates it is orbitally triply degenerate.
 - The superscript indicates a spin multiplicity of three ie two unpaired electron.
 - The g indicates a gerade state
 - The symbol (F) indicates this state across from the gaseous in 3F state. (orgel diagram 1)
- In addition to the $^3T_{1g}(F)$ ground state an excited state exists corresponding to the configuration in which the 2 electrons are paired in the t_{2g} level.
 - Transitions of these states are multiplicity forbidden but sometime weak adsorption band assigned to these transitions are observed.
 - The triplet exited state $t_{2g}^1 eg^1$ will be considered next.
 - If an electron is exited out of d_{xz} or d_{yz} so that the remaining electron is in d_{xy} , the exited electron will encounter less electron- electron repulsion from the electron in d_{xy} if it is placed in d_z^2 .
 - The $d_{x^2-y^2}$ orbital is less favorable because of an electron in this orbital to the electron remaining in d_{xy} .
 - This gives rise to the arrangement (a) in fig.
 - Similarly, if the electron is exited out of d_{xy} it will be most stable in $d_{x^2-y^2}$.
 - The remaining electron can be in either d_{xz} or d_{yz} giving raise to (b) and (c).
 - This sets (fig a, b, c) gives raise to the t_{2g} state which is orbitally triply degenerate and has a multiplicity of three.
 - The arrangement ($d_{xy}^1, d_{x^2-y^2}^2, d_{xz}^1, d_z^2; d_{yz}^1, d_z^2$) are higher in energy and also produce an orbitally triply degenerate state $T_{1g}(p)$.
 - Other possible arrangements corresponding to $t_{2g}^1 eg^1$ involve reversing one of the electron spins to produce state with singlet multiplicity.
 - Transition to these state from the triplet ground state are multiplicity forbidden.
 - Finally a 2 electron transition producing the excited state $(eg)^2$ or $d_z^2, d_{x^2-y^2}^2$ gives raise to singly degenerate $^3A_{2g}$ state.
 - The term symbol of V^{111} is 3F .

- The ligand field in the complex removes the 7 fold orbital degeneracy of this state (ie, $m=3,2,1,0,-1,-2,-3$) into 2 3-fold degenerate state
- $T_{1g}(F)$ and T_{2g} and one non degenerate state A_{2g} .
- This is indicated in the Orgel diagram Fig 2 for a d_2 oh complex.
- For zero Dq ie the gaseous ion, only two states, 3F and A_{2g} states.
- As Dq increases, 3F is split into the $T_{1g}(F)$, T_{2g} and A_{2g} states.
- The degeneracy of the 3p state is not removed by the ligand field and this becomes the triplet $T_1(p)$ state in octahedral complex.
- The (p) indicates this state arises from the gaseous ion 3p state.
- Dq can be calculated theoretically by evaluating the electrostatic perturbation of the ligand on the d orbitals.

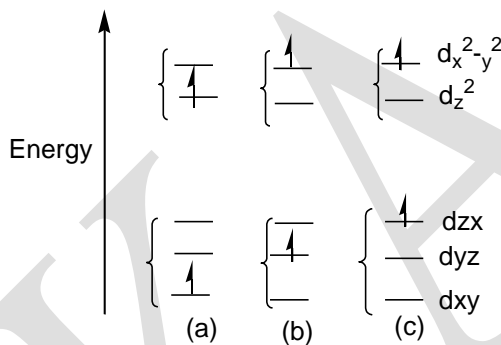


Fig 1; possible electron arrangement for $t_{2g}^1 e_g^1$

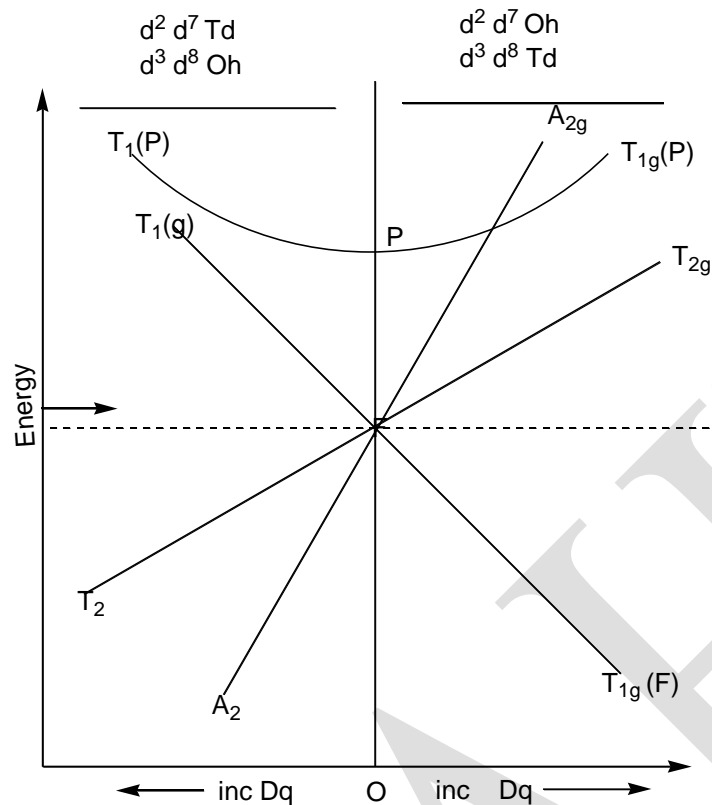


Fig 2 Orgel diagram for d^2 , d^3 , d^7 and d^8 complexes

SELECTION RULES:-

- On the basis of the symmetry and spin multiplicity of ground and excited electronic states.
 - Transition between states of the same parity are forbidden (symmetry with respect to a center of inversion) i.e., Laporte selection rule.
 -
 - Transition between states of different spin multiplicity are forbidden; i.e., spin selection rule.
 - 4A_2 and 4T_1 : spin- allowed.
 - 4A_2 and 2T_2 : spin- forbidden

Some rules for relaxation of selection rules:-

- Vibrations may temporarily change the symmetry (the center of symmetry is temporarily lost): vibronic coupling relaxes the first selection rule for d-d transition.

- 2) Tetrahedral complexes often absorb more strongly than octahedral complex metal ligand sigma bonds can be described as involving a combination of sp^3 and sd^3 hybridization of the metal orbital. ie, relax the first selection rule.
- 3) Spin orbit coupling provides a mechanism of relaxing the second selection rule.

Weak and strong field limits:-

1- When the ligand are weak (er)

- we have seen that under the influence of weak(er) ligand the energy difference, Δ_0 between t_{2g} and e_g sets is relatively small and hence all the five d- orbitals of these two sets may be supposed to be degenerate.
- ie, in presence of weak(er) ligand all the d- orbitals have the same energy and consequently the distribution of d-electron in t_{2g} and e_g sets take place according to Hund's rule which states that electron will pair with up only when each of the five d- orbitals is at least singly filled.
- Thus in weak(er) field the first three electrons numbered as 1,2,3 go to e_g - set, those numbered as 4 and 5 (2 electron) go to e_g sets those numbered as 6,7,8 (3 electron) go to t_{2g} set and the remaining 2 electron numbered as 9 and 10 will occupy e_g set.
- This can be shown as:
 $T_{2g} \ 1,2,3 \rightarrow e_g \ 4,5 \rightarrow t_{2g} \ 6,7,8 \rightarrow e_g \ 9,10.$
- As an example, if we consider the octahedral complex viz $[Co F_6]^{3-}$ which contains weaker ligand, the distribution of six d- electron of Co^{3+} ion ($Co^{3+} \rightarrow 3d^6$) in t_{2g} and e_g sets will be $t_{2g}^4 e_g^2$ (fig a).
- The complexes like $[CoF_6]^{3-}$ which contains weaker ligand are called weak field or low field complexes.
- In the formation of such complexes $\Delta_0 < P$, where p = average (or mean) pairing which is the energy required to pair 2 electron in the same orbital, and Δ_0 = octahedral crystal field splitting energy.
- Δ_0 tends to force as many electron to t_{2g} set while p tends to prevent the electron to pair in the t_{2g} level

ii) When the ligand are strong(er).

- In octahedral complexes containing stronger ligand distribution of d- electron in t_{2g} and e_g sets does not obey hunds rule.

- Thus in stronger field the first six electron numbered as 1,2,3,4,5 and 6 will go to t_{2g} set and the remaining four electrons numbered as 7,8,9,10 enter e_g sets.
- This can be shown as
 $T_{2g}^{1,2,3,4,5,6} \rightarrow e_g^{7,8,9,10}$
- Consider the distribution of six d electron of ($Co^{3+} \rightarrow 3d^6$) in the complex ion, $[Co(NH_3)_6]^{3+}$ which contain stronger ligand
- Quite obviously this distribution is $t_{2g}^6 e_g^0$ (fig b).
- Complexes like $[Co(NH_3)_6]^{3+}$ which contains stronger ligand are called strong field or high field complexes.

For these complexes $\Delta_o > p$

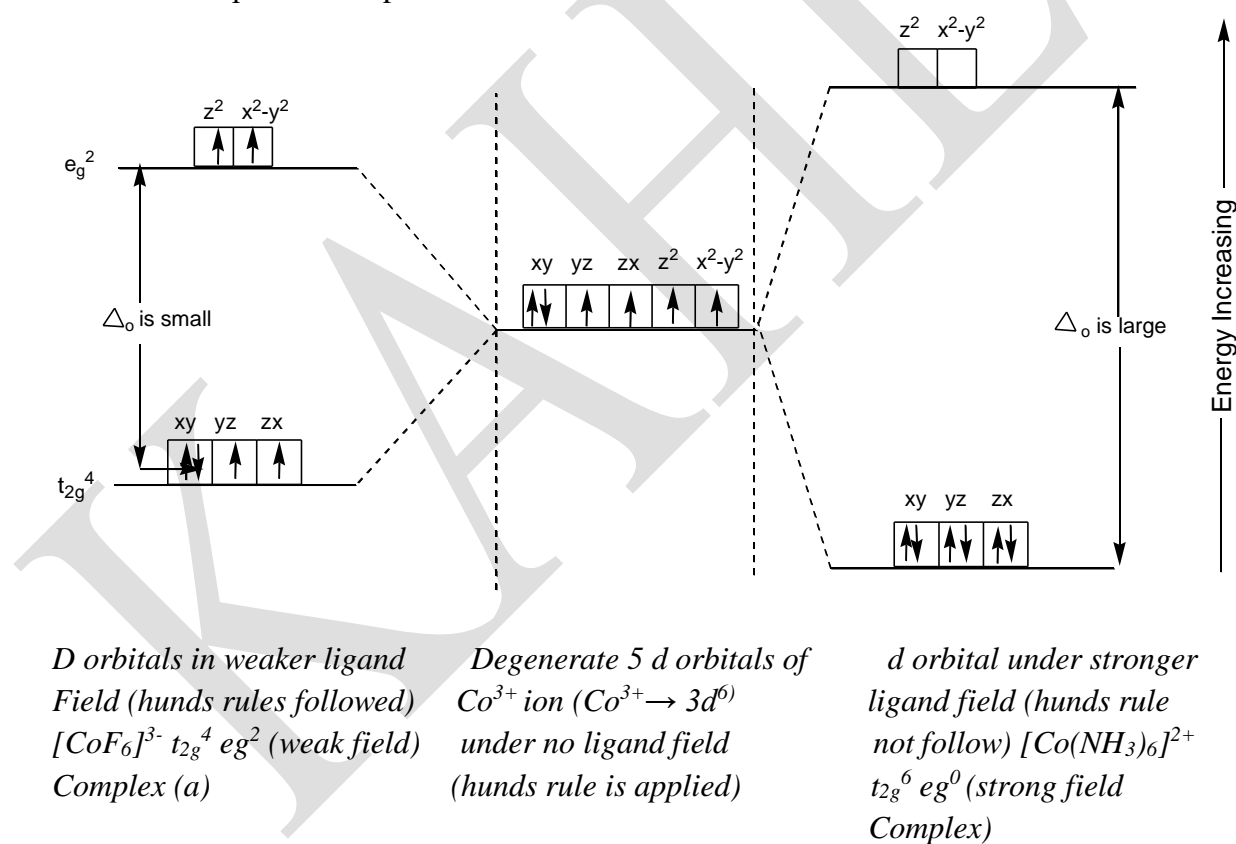


Fig:- formation of $[CoF_6]^{3-}$ which contains weaker ligand (ie, weak field complex) and $[Co(NH_3)_6]^{3+}$ which contains stronger ligand (ie, strong field complex)

Table :-

Distribution of d electron in t_{2g} and e_g sets in stronger and weaker octahedral ligand fields.

n = No. of unpaired electron

s = resultant spin- $1/2 \times n$

$p+q = x = 1, 2, 3, 4, \dots, 8, 9, \text{or } 10$.

- i) Whether the ligand field is stronger or weaker, for d^1 , d^2 and d^3 configuration, the electron go to the lower energy t_{2g} level (more stable) for d^8 , d^9 and d^{10} configuration.
 - The first six electron go to the t_{2g} level and the remaining two (in case of d^8 ion), three (in case of d^9) and four (in case of d^{10}) electron occupy the e_g level.
 - Thus, the distribution of electron of d^1 , d^2 , d^3 , d^8 , d^9 and d^{10} configuration in t_{2g} and e_g level for both stronger and weaker octahedral ligand field is the same.
- ii) For each of d^4 , d^5 , d^6 and d^7 configuration there is a different in the arrangement of electron in weaker and stronger ligand field.
- iii) **Number of unpaired electrons (n) high spin and low spin complexes:-**
 - Weak field complexes of d^4 , d^5 , d^6 and d^7 ions have greater number of unpaired electrons (n) than those of (same ion) strong field complexes and are thus with a higher value of resultant spin (s).
 - It is for the reason that the weak field and strong field complexes are also spin free or high spin (abbreviated as Hs) and spin paired or low spin (Ls) complexes respectively.
 - VBT has called these complexes as ionic (Pauling) or orbital (Huggin)) and covalent (Pauling) or inner orbital (Huggin) complexes respectively.

Dq ions	Stronger field (low spin or spin paired complexes) ($\Delta_o > p$) stronger ligand			Weaker field (high spin or free complexes)($\Delta_o < p$)		
	$t_{2g}^p e_g^q$ configu	n	s	$t_{2g}^p e_g^q$ configu	n	S
d1	$t_{2g}^1 e_g^0$	1	$1/2$	$t_{2g}^1 e_g^0$	1	$1/2$
d2	$t_{2g}^2 e_g^0$	2	1	$t_{2g}^2 e_g^0$	2	1
d3	$t_{2g}^3 e_g^0$	3	$3/2$	$t_{2g}^3 e_g^0$	3	$3/2$
d4	$t_{2g}^4 e_g^0$	2	1	$t_{2g}^3 e_g^1$	4	2
d5	$t_{2g}^5 e_g^0$	1	$1/2$	$t_{2g}^3 e_g^2$	5	$5/2$

d6	$t_{2g}^6 e_g^0$	0	0	$t_{2g}^4 e_g^2$	4	2
d7	$t_{2g}^6 e_g^1$	1	1/2	$t_{2g}^5 e_g^2$	3	3/2
d8	$t_{2g}^6 e_g^2$	2	1	$t_{2g}^6 e_g^2$	2	1
d9	$t_{2g}^6 e_g^3$	1	1/2	$t_{2g}^6 e_g^3$	1	1/2
d10	$t_{2g}^6 e_g^4$	0	0	$t_{2g}^6 e_g^4$	0	0

Table :-

In which the distribution of various d element of the central metal cation in stronger and weaker octahedral ligand field in shown discloses the following facts:

- The no, of unpaired electrons (ie, the value of the resultant spin s) in the case namely d^1 to d^3 and d^8 to d^{10} is the same in the both field, and it is due to the reason that for these configuration the questions of the formation of HS and LS complexes does not arises. The question does not arises for the system d^4 and d^7 .
- The paramagnetism of HS complex is larger than that of LS complexes, as is evident from table.
- HS complexes have more unpaired electron (ie, larger value of s) than the LS complexes (ie, smaller value of s).

Orgel diagram:-

- Orgel diagram are much simpler because excited state of multiplicity different from that of the ground state are omitted and only weak field cases are included.
- An Orgel diagram for Co^{2+} (d^7) in tetrahedral and octahedral ligand field is shown in figure 1
- Once again we see the inverse relationship between the two symmetries, which arises because a tetrahedral field is, in effect, a negative octahedral field.
- The diagram also illustrated the mixing of terms.

- As a general rule, the term having identical symmetry will mix with the extent of mixing being inversely proportional to the energy difference between them.
- for Co^{2+} the term involved are the ${}^4\text{T}_1$ (tetrahedral) and ${}^4\text{T}_{1g}$ (octahedral) levels.
- Mixing of terms exactly parallels the mixing of molecular orbitals. The upper level is raised in energy while the lower level falls.
- This is represented in the Co^{2+} diagram as diverging lines for the pairs of ${}^4\text{T}_1$ and ${}^4\text{T}_{1g}$ level
- The condition of no mixing is shown as dashed lines.
- Note that for the tetrahedral case in the absence of mixing, the two ${}^4\text{T}_1$ terms gradually approach each other in energy the field strength increases while just the opposite is true for octahedral complexes.
- As a result, the extent of mixing greater for tetrahedral complexes.
- Orgel diagram provides a convenient means of predicting the number of spin allowed absorption bands to expect in a uv/ visible spectrum for a complex.
- From fig 1, it is clear that a complex Co^{2+} (or any other d^7 ion) should produce a spectrum with three absorptions.
- A more general Orgel diagram pertaining to high spin octahedral or tetrahedral complexes of metal with to eight d electron is shown in fig 2.
- Up to this point we have considered two central issues involved in interpreting electronic spectra of transition complexes - the number and intensities of spectral lines.
- There is third important spectral feature, the widths of observed band, which we have not yet discussed.

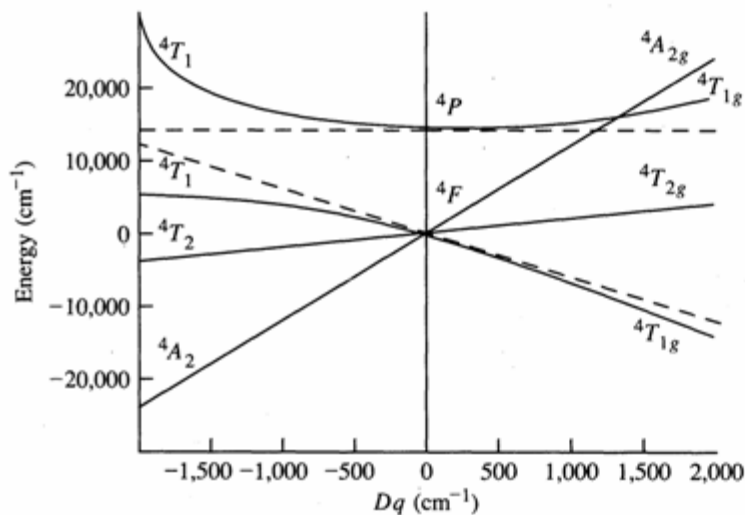


Fig. 11.39 Orgel diagram for the Co^{2+} ion in tetrahedral (left) and octahedral (right) fields. The dashed lines represent the 4T_1 terms before mixing. [From Orgel, L. E. *J. Chem. Phys.* **1955**, *23*, 1004–1014. Reproduced with permission.]

Fig 1 :- orgel diagram for the Co^{2+} ion in the tetrahedral (left) and octahedral (right) fields. The dashed lines represent the 4T_1 terms before mixing.

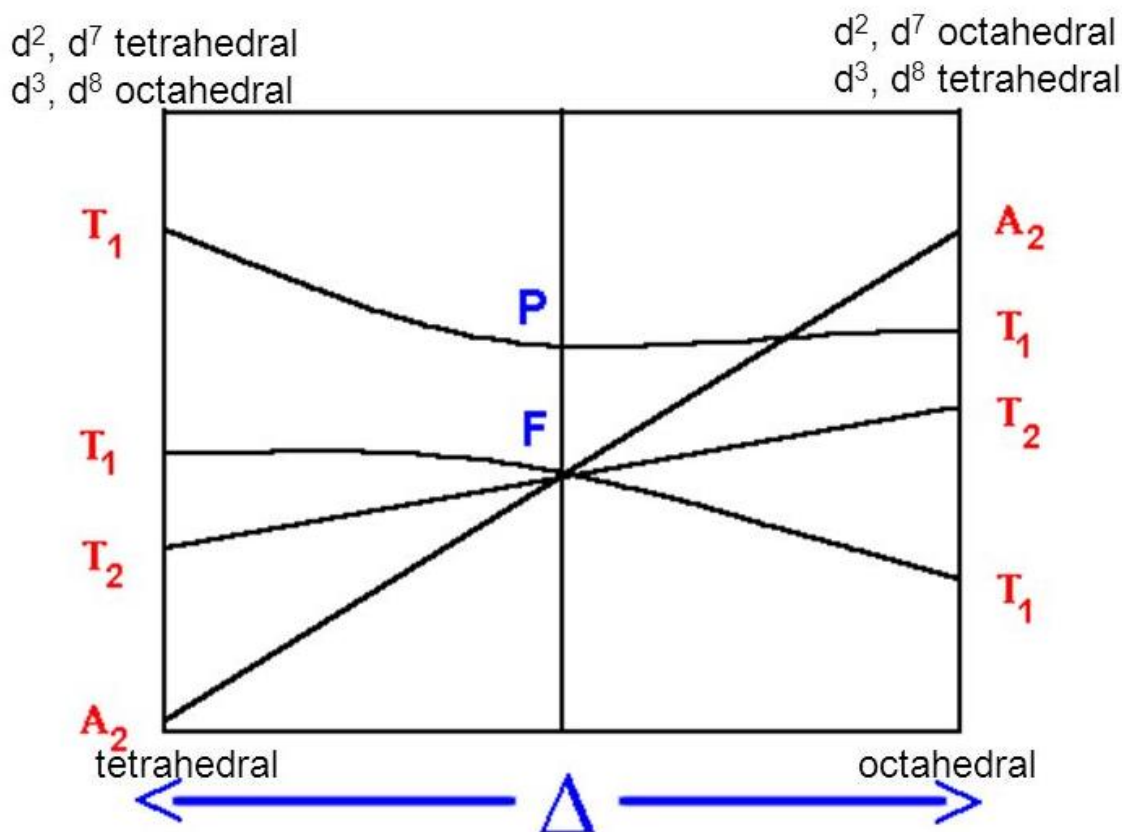


Fig 2:- orgel diagram for d², d³, d⁷ and d⁸ ions in octahedral and tetrahedral field.

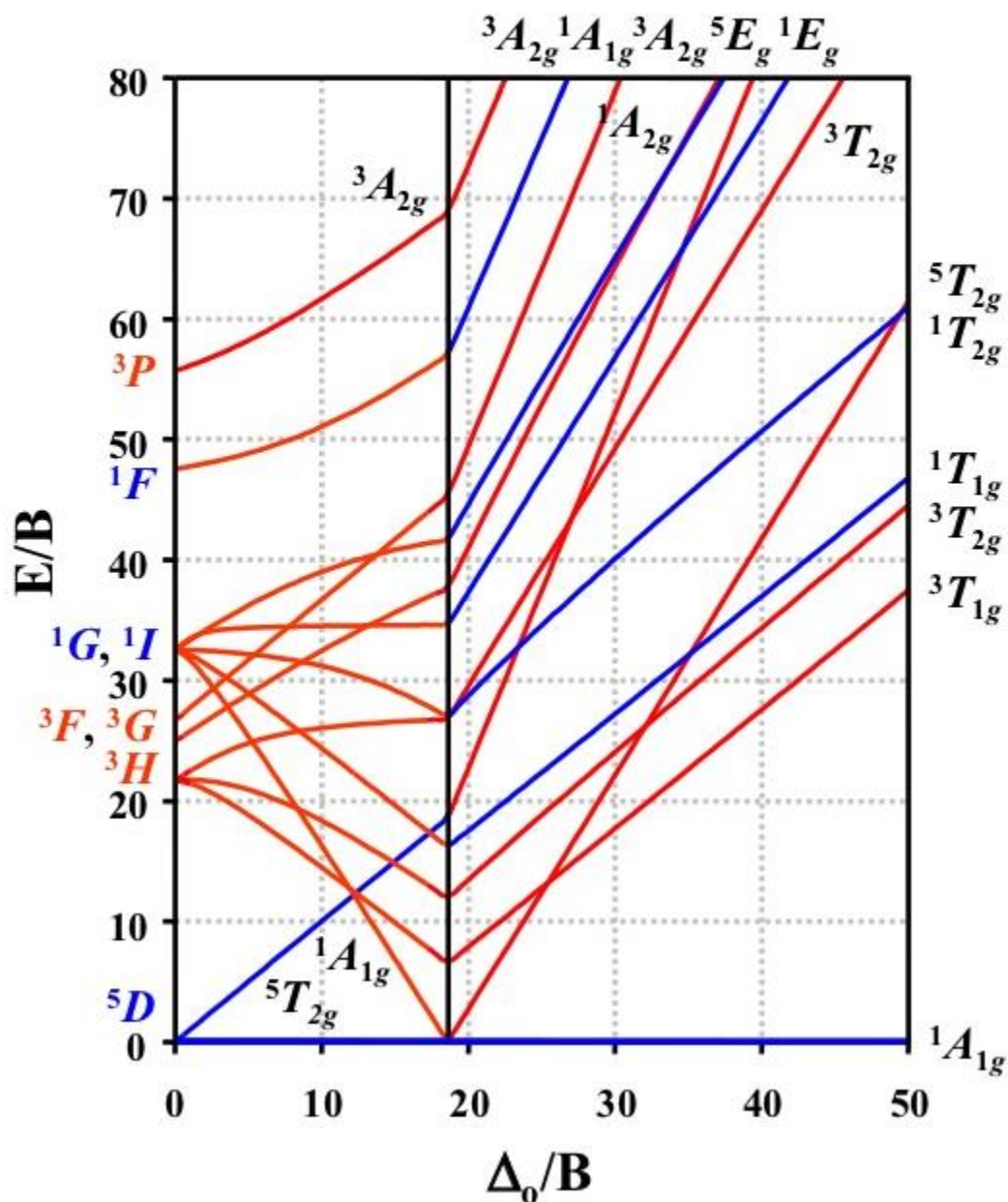
Tanabe – sugano diagram:-

- In order to treat fully the problem of interpretation of spectra, it is common to use diagrams provided by Tanabe and Sugano, which provide an alternative means of depicting the variation of term energies with field strength.
- Tanabe Sugano diagrams include both weak and strong field and hence are more comprehensive than Orgel diagrams.
- They are similar to correlation diagrams but are more useful for extracting quantitative information.
- Tanabe Sugano diagram for d⁶ octahedral complexes is shown in figure.
- The ground state is always taken as the abscissa in these diagrams with the energy of the other states plotted being relative to it.

- Inter electronic repulsion is expressed in terms of Racah parameters B and C, which are linear combination of certain Coulomb and exchange integrals pertaining to the uncomplexed ion.
- Accurate evaluation of these integrals is in general not feasible and so these factors are instead treated as empirical parameters and are obtained from the spectra of free ions.
- The parameter B is usually sufficient to evaluate the difference in energy between the states of the same spin multiplicity, however both parameters are necessary for terms of different multiplicity.
- A relationship that will prove to be quite useful in analyzing spectra is that the difference in energy between a free ion ground state F term and an excited P term of the same spin multiplicity is 15 B (as found for d^2 , d^3 , d^7 , and d^8 configuration)
- Energy (E) and field strength are expressed on a Tanabe – Sugano diagram in terms of the parameters B as E/B and Δ/B , respectively.
- In order to represent the energy level with any accuracy, it is necessary to make some assumption about the relative values of C and B.
- The ratio C/B for the diagram in fig is 4.8.
- For most transition metal ions B can be estimated as approximately 1000 cm^{-1} and $C = 4B$.
- At weak octahedral field, the ground state for a d^6 complex is $^5T_{2g}$, which originates from the free ion 5D term (fig).
- Among the excited terms at weak field limit is a $^1A_{1g}$ (from the free ion 1I), which falls precipitously in energy with increasing Δ , eventually displacing $^5T_{2g}$ as the ground term at $\Delta/B = 20$.
- The spectrum of any octahedral d^6 complex can be assigned with the help of fig.
- For high spin species such as $[\text{CoF}_6]^{3-}$, the only spin allowed transition at relatively low energies
 $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$.
- There are additional spin allowed transitions at higher energies, but they generally are masked by totally allowed transitions and hence are not observed.
- Because the slope of $^1T_{2g}$ changes more rapidly than that of $^1T_{1g}$, the two observed peaks will be further apart in energy at larger values of Δ .
- The spectra of yellow $[\text{Co}(\text{en})_3]^{3+}$ and green $[\text{Co}(\text{ox})_3]^{3-}$ (fig 2) conform to these expectations.
- Fitting an observed spectrum to its corresponding Tanabe Sugano diagram enables one to obtain the value of Δ for a complex.

- At this point spin pairing takes place, resulting in a discontinuity in the diagram, marked by the vertical line.
- From this boundary on, the low spin $^1A_{1g}$ term remains the ground state.

d^6 Tanabe-Sugano Diagram



Modified d^6 Tanabe Sugano diagram showing only the 5D , 3H , 1F , 1I terms.

Arrow represent spin allowed transition for high and low spin complexes

- In addition it is possible to evaluate the electronic repulsion parameters B
- The apparent value of B in complex is always smaller than that of free ion. This result from a phenomenon of known as Nephelauxetic effect and is attributed to delocalization of the metal electron over molecular orbital that encompass both the metal and the ligands.
- The Nephelauxetic ratio β is given by

$$\beta = B^1/B$$

- The value β is always less than one and it decreases with increases.

Jahn teller tetrahedral distortion:-

- The six coordinated complex in which all the six distances between the ligand electrons clouds and central metal ion are the same are said to be regular (ie, symmetrical) octahedral complex.
- On the other hand the six coordinated complexes in which the distance are not equal are said to be distorted octahedral complexes. Since their shape is changed (ie, distorted) the change in shape is called distortion.
- Distorted octahedral complexes may be of the following three types:
 - i) Diagonally distorted octahedral complexes which are obtained when the distortion of a regular octahedron takes place along a 2 fold axis.
 - ii) Trigonally distorted octahedral complexes which are obtained when the distortion takes place along 3 fold axis
 - iii) Tetragonally distorted octahedral complexes which are also known as tetragonal complexes.
- Tetragonal complex may be obtained by any of the following two ways:-
 - i) If the 2 trans ligand lying on the z axis in an octahedron are removed away from the central metal ion, so that their distance from the metal cation is slightly greater than it is for the other 4 ligand lying in the xy plane, we get the tetragonal structure.

- Quite obviously this structure has a two long bond along the z- axis and four short bond in xy plane.
Example;- i) it has been shown that in tetra ammine of Cu^{2+} ions aqueous solution, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_6]^{2+}$ two water molecules at larger distance from the central Cu^{2+} ion than the 4 coplanar NH_3 molecules and consequently the complex has a tetragonal shape. The two water molecules are in a plane at right angle to that containing Cu^{2+} ion and 4 NH_3 molecules are which are at equal distances from Cu^{2+} ion.
- ii) The low spin octahedral complexes of Ni^{2+} , Pd^{2+} and Pt^{2+} (all d^3 ions) undergo strong distortion and assume square planar geometry in which the 2 ligands along the z- axis are at larger distance and 4 ligand in the xy plane are at shorter distance from m^{2+} ion
- iii) In CuCl_2 crystals each Cu^{2+} ions is surrounded by six Cl ions, 4 are at a distance of 2.30 \AA and the other two are 2.95 \AA away.
- iv) In CuF_2 crystal 4 F^- ions are 1.93 \AA away from the Cu^{2+} ions while the 2 F^- ions are 2.27 \AA apart.

b) if the 2 trans ligand located as the z- axis are brought near the central metal cation so that their distances from the metal cation is smaller than, it is for the other 4 ligand in the xy plane we get a tetragonal structure.

* this structure has 2 short bonds along the z- axis and 4 long bond in xy plane.

Example:-

- i) In K_2CuF_4 the Cu^{2+} ions has two F^- at 1.95 and four at 2.08 \AA
- ii) In FeF_2 the Fe^{2+} ion has two F^- at 1.99 and four at 3.12 \AA
- In 1937 john teller put forward a theorem known as john teller theorem which can explain why certain coordinated complexes undergo distortion to assume distorted octahedral (ie tetragonal) geometry.
- This theorem states that any non linear molecular system possessing degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy and thus will remove degeneracy.
- john teller theorem only predict the occurrence of a distortion.
- Its does not predict its nature or its magnitude
- If the condistorted configuration has a center of symmetry, the distorted equilibrium configuration must have one too.

Symmetrical and unsymmetrical t_{2g} and e_g orbital;-

- t_{2g} and e_g orbitals which are empty (t_{2g}^0 and e_g^0) half filled (t_{2g}^3 and e_g^2) or completely filled (t_{2g}^6 and e_g^4) are said to be symmetrical orbitals. other than those
 - Here it should be noted that in strong field (ie, LS complex) e_g set having two electron (ie, e_g^2 set) is unsymmetrical orbital
 - Orbital other than those mentioned above are called unsymmetrical orbitals.
- Thus the symmetrical and unsymmetrical t_{2g} and e_g orbital can be written as:

t_{2g} orbital { $t_{2g}^0, t_{2g}^3, t_{2g}^6 \rightarrow$ symmetrical
 $t_{2g}^1, t_{2g}^2, t_{2g}^4, t_{2g}^5 \rightarrow$ unsymmetrical }

e_g orbital { e_g^0, e_g^4 -- symmetrical
 e_g^1, e_g^3 --- unsymmetrical
 e_g^2 —symmetrical in HS complexes [$(d(x^2-y^2)^1(dz^2)^1]$
 e_g^2 --- unsymmetrical in LS complexes [$(d(x^2-y^2)^0(dz^2)^2]$

- In table :- symmetrical [abbreviated as (sym)] and unsymmetrical [abbreviated as (unsym)] t_{2g} and e_g orbital are listed.
 - t_{2g} (sym) – e_g (sym) pair
 - t_{2g} (sym) – e_g (unsym) pair
 - t_{2g} (sym) – e_g (sym) pair

that the pair cannot exist is t_{2g} (sym) – e_g (sym) pair.

No distortion condition :-

- the d orbital which have both t_{2g} and e_g set as symmetrical orbital leads to perfectly symmetrical (ie, regular) octahedral complex
- thus it may be seen from table that the d orbital
- d^0 ($t_{2g}^0 e_g^0$), d^3 ($t_{2g}^3 e_g^0$), d^5 ($t_{2g}^3 e_g^2$), d^8 ($t_{2g}^6 e_g^2$), and d^{10} ($t_{2g}^6 e_g^4$) of HS octahedral complex and d^0 ($t_{2g}^0 e_g^0$), d^3 ($t_{2g}^3 e_g^0$), d^6 ($t_{2g}^6 e_g^0$), d^{10} ($t_{2g}^6 e_g^4$) of the octahedral complexes give perfectly regular octahedral complexes.
- Thus in these cases there is no distortion.

Condition for slight distortion :-

- When the d orbitals of the central metal ion of an octahedral complexes have t_{2g} orbital has unsymmetrical orbitals these occurs slight distortion in the complex.
- Ie, whenever the t_{2g} orbital, which do not come direct in the path of the ligand disposed octahedral around the central metal ions, but point between the ligand contain 1,2,4, and 5 electron, we shall expect only slight distortion from the regular octahedron.
- Thus as is evident from table, the HS complexes of $d^1(t_{2g}^1eg^0)$, $d^2(t_{2g}^2eg^0)$, $d^6(t_{2g}^4eg^2)$ and $d^7(t_{2g}^5eg^2)$ ions.
- The LS complexes of $d^1(t_{2g}^1eg^0)$, $d^2(t_{2g}^2eg^0)$, $d^4(t_{2g}^4eg^0)$ and $d^5(t_{2g}^5eg^0)$ ions undergo slight distortion from the octahedral shape.

Condition for strong distortion:-

- Whenever for eg orbitals which point directly towards the ligands, are unsymmetrical ie, contains 1, 3, or 2 (only is LS complexes) electron we shall be expect strong distortion. Leading to tetragonal and even to square planar complexes.
- Distortion produced in an octahedral complex due to the presence of unsymmetrical eg orbital is due to the fact that, since the directions of the eg orbitals of the central metal ion correspond with the directions of the ligand disposed octahedral around the metal ion, the octahedral arrangement of the ligand is likely to be more several distorted by the dissymmetry of the eg orbital than that of the t_{2g} orbital.
- Thus from table it can be seen that the configuration;
 $d^4(t_{2g}^3eg^1)$, $d^9(t_{2g}^6eg^3)$, of HS complex $d^7(t_{2g}^6eg^1)$, $d^8(t_{2g}^6eg^2)$, $d^9(t_{2g}^6eg^3)$ of LS complexes leads to strong distortion in octahedral complex.

conditions for various types of distortion can be summarized as;-

t_{2g} (sym) + eg (sym) \rightarrow no distortion
 t_{2g} (unsym) \rightarrow slight distortion
 eg (unsym)
 $eg^2(dx^2-y^2)^0(dz^2)^2$ in LS complexes--- strong distortion

cause of distortion with some complexes:-

- i) High spin octahedral complexes of d^4 ion have any of the following configuration;
- I $\rightarrow t_{2g}^3 (dz^2)^1 . (dx^2-y^2)^0$
 II $\rightarrow t_{2g}^3 (dz^2)^0 . (dx^2-y^2)^1$
- When the configuration has one electron in dz^2 orbital and the dx^2-y^2 orbital is empty (structure I) cation-anion interaction along the z axis is less than that the x axis and hence to a tetragonal structure .
- ii) Complex of Cu^{2+} ion (d^9 ion) such as aqueous solution of $[Cu(NH_3)_4]^{2+}$ in which the tetragonal distortion is so marked that a square planar complex result.
- This ion has a configuration $t_{2g}^6 eg^3$ in both field.
 - Evidently in this ion the 2 possible arrangement of electron in t_{2g} and eg orbital are;
 Configuration I $\rightarrow t_{2g}^6 (dz^2)^2 . (dx^2-y^2)^1$
 Configuration II $\rightarrow t_{2g}^6 (dz^2)^1 . (dx^2-y^2)^2$
 - Since the both configuration t_{2g} orbital are completely filled asymmetry (ie distortion) is caused by incomplete filling of eg orbital
 - Distorting arises mainly from the repulsion of ligand by the electron occupying eg orbital
 - If we consider configuration I namely $t_{2g}^6 (dz^2)^2 . (dx^2-y^2)^1$ the dz^2 orbital which is completely filled and point at the ligand an the z axis offers greater shielding of the Cu^{2+} nucleus than the half filled dx^2-y^2 orbital, which point towards the ligand in the xy plane.
 - Thus the ligand an the x and y axes experience a higher effective nuclear charge , while those on the z axes experience a lower effective nuclear charge.
 - Consequently the ligand on the x and y axes are drawn in closer to the Cu^{2+} nucleus and those on the z axes move further out.
 - We thus observe 4 short and 2 long bond ie, the ligand L5 and L6 existing along the z axes would be at a greater distance from the central metal ion (Cu^{2+} ion) and remaining 4 coplanar ligands L1, L2, L3 and L4 would be shorter distance from Cu^{2+} ion

$$\text{Thus } ML_5 = ML_6 > ML_1 = ML_2 = ML_3 = ML_4$$

- Where $ML_1 \dots$ Etc indicate the metal ion ligand distance fig (a)
- Ligands L5 and L6 are trans ligand while the ligands , L1, L2 L3 and L4 are equatorial ligands

If on the other hand , we consider configuration $(dz^2)^1 . (dx^2-y^2)^2 t_{2g}^6$, we shall expect on exactly opposite distortion.

- Ie, the ligand in the xy plane (ie, L1, L2, L3 and L4 ligands) would move and those (ie, L5 and L6 ligand) on the z axis would move out in from their equilibrium position in the

hypothetical regular octahedron and we would expect 2 short bond (along the z axis) and 4 long bonds (along x and y axis in the xy plane.)

Thus

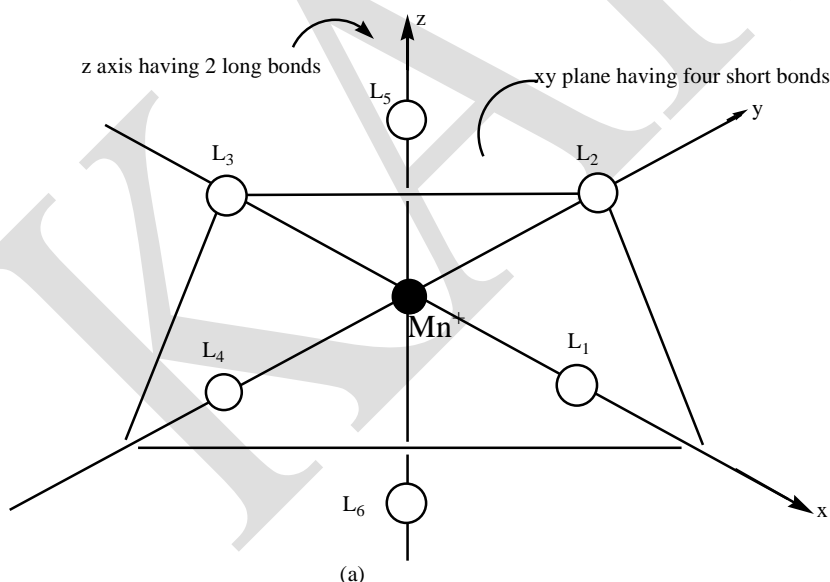
$$ML1 = ML2 = ML3 = ML4 > ML5 = ML6 \text{ (fig b)}$$

How then to decide which of the 2 possible octahedral distortion configuration

$$I \rightarrow (dz^2)^2 \cdot (dx^2-y^2)^1 t_{2g}^6 \text{ and}$$

$$II \rightarrow t_{2g}^6 (dz^2)^1 \cdot (dx^2-y^2)^2 \text{ would said the more stable complex.}$$

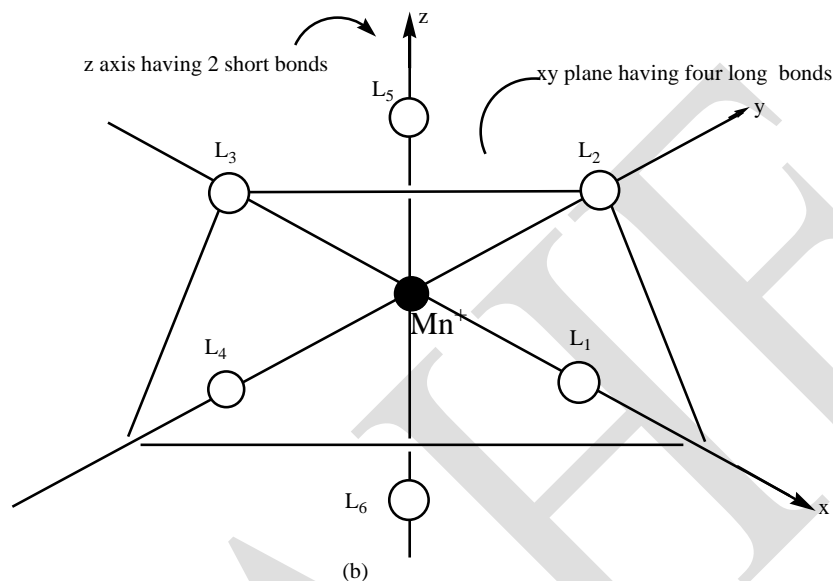
- CFT offers no way of deciding it.
- Experimental result , however , show that it is I octahedral distortion configuration namely $(dz^2)^2 \cdot (dx^2-y^2)^1 t_{2g}^6$ with 2 long and 4 short bond which is more stable. There is no theoretical explanation of the instability of structure corresponding to II configuration namely $t_{2g}^6 (dz^2)^1 \cdot (dx^2-y^2)^2$ having 4 long and 2 short bonds.



a) Configuration I $t_{2g}^6 (dz^2)^2 \cdot (dx^2-y^2)^1$ having 2 long (along a z axis) and 4 short (in the xy plane)bond ie,

$$ML5 = ML6 > ML1 = ML2 = ML3 = ML4$$

This configuration is more stable.



b) Configuration II $t_{2g}^6 (dz^2)^1 (dx^2-y^2)^2$ having 4 long (coplanar in xy plane) and 2 short (along the z axis) bond. 2 short bond are perpendicular to xy plane.

Hence,

$$ML1 = ML2 = ML3 = ML4 > ML5 = ML6$$

Table;- showing i) distribution of electron in t_{2g} and e_g orbitals in HS and LS octahedral complex

iii) Symmetrical and unsymmetrical t_{2g} and e_g orbitals.

iv) Predicted distortion in octahedral complexes

No of electrons	HS octahedral complex; weak ligand field (spin free)		LS octahedral complex strong ligand field (spin paired)	
	Distribution of electron in t_{2g} and e_g orbital and symmetrical and unsymmetrical orbitals	Predicted distribution	Distribution of electron in t_{2g} and e_g orbital and symmetrical and unsymmetrical orbitals	Predicted distribution

d0	$t_{2g}^0(\text{sym}) e_g^0(\text{sym})$	No distortion	$t_{2g}^0(\text{sym}) e_g^0(\text{sym})$	No distortion
d1	$t_{2g}^1(\text{unsym}) e_g^0(\text{sym})$	Slight distortion	$t_{2g}^1(\text{unsym}) e_g^0(\text{sym})$	Slight distortion
d2	$t_{2g}^2(\text{unsym}) e_g^0(\text{sym})$	Slight distortion	$t_{2g}^2(\text{unsym}) e_g^0(\text{sym})$	Slight distortion
d3	$t_{2g}^3(\text{sym}) e_g^0(\text{sym})$	No distortion	$t_{2g}^3(\text{sym}) e_g^0(\text{sym})$	No distortion
d4	$t_{2g}^3(\text{sym}) e_g^1(\text{unsym})$	Strong distortion	$t_{2g}^4(\text{unsym}) e_g^0(\text{sym})$	Slight distortion
d5	$t_{2g}^3(\text{sym}) e_g^2(\text{sym})$	No distortion	$t_{2g}^5(\text{unsym}) e_g^0(\text{sym})$	Slight distortion
d6	$t_{2g}^4(\text{unsym}) e_g^2(\text{sym})$	Slight distortion	$t_{2g}^6(\text{sym}) e_g^0(\text{sym})$	No distortion
d7	$t_{2g}^5(\text{unsym}) e_g^2(\text{sym})$	Slight distortion	$t_{2g}^6(\text{sym}) e_g^1(\text{unsym})$	Strong distortion
d8	$t_{2g}^6(\text{sym}) e_g^2(\text{sym})$	No distortion	$t_{2g}^6(\text{sym}) e_g^2(\text{unsym})$	Strong distortion Leading to square planar
d9	$t_{2g}^6(\text{sym}) e_g^3(\text{unsym})$	Strong distortion	$t_{2g}^6(\text{sym}) e_g^3(\text{unsym})$	Strong

d10	$t_{2g}^6(\text{sym}) e_g^4(\text{sym})$	No distortion	$t_{2g}^6(\text{sym}) e_g^4(\text{sym})$	distortion No distortion
------------	--	---------------	--	---------------------------------

Nephelauxetic effect :-

- The nephelauxetic effect is a term used in the physical chemistry of transition metals.
- It refers to a decrease in the Racah inter electronic repulsion parameter, given the symbol B , that occurs when a transition metal free ion forms a complex with ligand.
- The name comes from the Greek for cloud expanding.
- The decrease in B indicates that in the complex there is less repulsion between the 2 electrons in a given doubly occupied metal d orbital than there is in the respective M^{n+} gaseous metal ion, which in turn implies that the size of the orbital is larger in the complex.
- The electron cloud expansion effect may occur for one (or both) of two reasons:
 - 1) The effective positive charge on the metal has decreased. Because the positive charge of the metal is reduced by any negative charge on the ligands, the d orbitals can expand slightly.
 - 2) The act of overlapping with ligand orbital and forming covalent bonds increases orbital size because the resulting molecular orbital is formed from two atomic orbitals.
- Experimentally, it is observed that the size of the nephelauxetic effect always follows a certain trend with respect to the nature of the ligand present increasing thus:
 $F^- < H_2O < NH_3 < en < [NCS-N]^- < Cl^- < [CN]^- < Br^- < N_3^- < I^-$
- Although part of this series may seem quite different to the spectrochemical series of ligands – for example cyanide, ethylenediamine and fluoride seem to occupy similar positions in the two series such as chlorides, iodide and bromide, amongst others occupy very different positions.
- The ordering roughly reflects the ability of the ligand to form good covalent bonds with metal. Those that do not have a very small effect and are at the start of the series whereas those that do are at the end.
- The nephelauxetic effect does not depend upon the ligand type, but also upon the central metal ion.

- These too can be arranged in order of increasing nephelauxetic effect as follows:

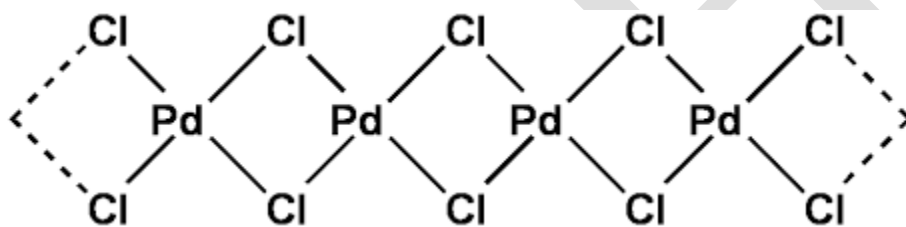


* The nephelauxetic series indicates that the spin pairing energy is greatest for fluoro complexes, and least for iodo complexes.

*The result of this is that fluoro complexes are the one most likely to be high spin.

*For Cl-Br-I-complexes, the small values of Δ_o are offset by the small values of P, so that for all second and third row d-block ions, the chloro, bromo and iodo complexes are low spin.

*Thus, Pd in PdF_2 is high-spin surrounded by six bridging fluorides, but Pd in PdCl_2 low spin, with a polymeric structure.



Charge Transfer Spectra:

*As the term implies, these transitions involve electron transfer from one part of the complexes to another.

*More specifically, an electron moves from an orbital that is mainly ligand in character to one that is mainly metal in character (ligand to metal charge transfer, LMCT) or vice versa (metal to ligand charge transfer, MLCT).

*Unlike d-d transitions, those involving charge transfer are fully allowed and these give rise to much more intense absorption, Table

Types of transition	$\sum(L \text{ mol}^{-1} \text{ cm}^{-1})$	Typical complex
Spin forbidden laporte forbidden	$10^{-3}-1$	Many octahedral complex of d^5 ions eg $[\text{Mn}(\text{H}_2\text{O})]^{2+}$
Spin allowed laporte forbidden	1-10	Many oh complexes e.g $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
	$10-10^2$	Some square planar complex e.g $[\text{PdCl}_4]^{2-}$
	10^2-10^3	6 coordination complex of low symmetry many square planar complexes particularly with organic ligand
Spin allowed laporte allowed	10^2-10^3	Some metal to ligand charge transfer bands in molecules with unsaturated ligand
	10^2-10^4	A centric complexes with ligand such as cac or those having P,As etc as donor atoms
	10^3-10^6	Many charge transfer bands transition in organic species

*When this absorption falls within the region ,they often produce rich colors and therein lies the source of practical interest in these type of transitions.

*A charge transfer transition may be regarded as an internal redox process.

*This makes it possible to use familiar ideas, such as ionization energies and electron affinities, to predict the conditions that will favor such a transition.

*Consider a crystal of sodium chloride.

*Imagine ionizing an electron from chloride ion (Hhe sodium ion (ΔH =ELECTRON AFFINITY) and transferring it to the sodium ion (ΔH negative of ionization energy).

*It could be imagined that the overall energy be supplied by a photon.

*It could be imagined that the overall energy (including $-U_0$) required to effect this process might be supplied by a photon.

*Indeed such they belong exist, but their energy is so high that belong to the ultraviolet portion of the spectrum.

*Hence sodium chloride does not absorb light. It is colorless.

*New consider how might modify the metal-ligand combination to make the electron transfer from ligand to metal more favorable.

*We would want a with relatively high ionization energy .so that it have empty orbitals at fairly low energies.

*Good candidates would be transition or post transition metals, especially in higher oxidation states.

*An ideal ligand would be non metal with a relatively low electron affinity, with would mean that it would have filled orbitals of four of fairly high energy and would be readily oxidizable.

*Chalcogenides or heavier halides would be examples of good choices.

*The net result of metal-ligand combination would that the orbitals involved in a LMCT process would be close enough in energy that the transition could violet region.

*The permanganate ion, MnO_4^- meets the criteria set forth in the proceeding.

*Manganese is in a formal oxidation state of +7 and combined with four oxide ions.

*The molecular orbital diagram for tetrahedral complexes in fig(2) allows us to identify possible LMCT transitions.

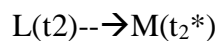
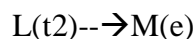
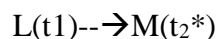
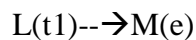
*In any tetrahedral complex ,the four lowest energy-q-bonding orbital will be filled and will be primarily ligand in character.

*Next there are 2 sets of q-non bonding Mo's one ligand centered and one metal centered.

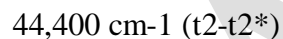
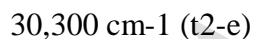
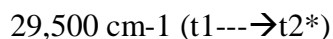
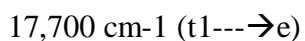
*In permanganate ,these orbital would correspond to filled oxygen 11p orbitals and empty manganese 3d orbitals ,respectively.

*All of the higher energy anti bonding molecular orbitals would be unoccupied for a manganese (v11) complex:

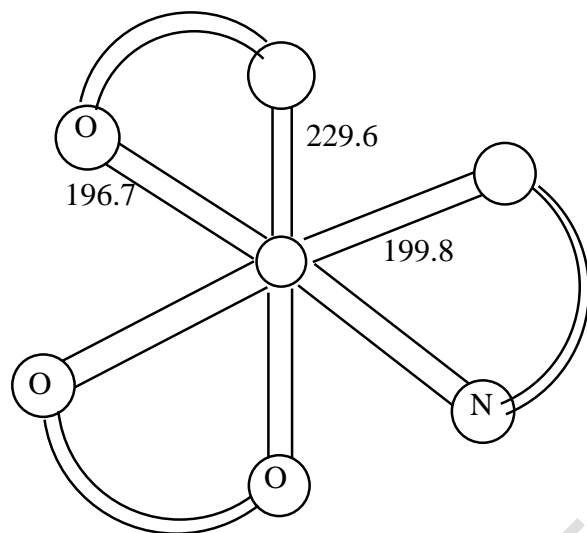
*Hence there are four possible ligand to metal transitions:



For MnO_4^- all four of these transition have been observed.



*Only the absorption at $17,700 \text{ cm}^{-1}$ falls within the visible range ($4000\text{--}28,000 \text{ cm}^{-1}$), and it is responsible for the familiar deep purple color of MnO_4^- .

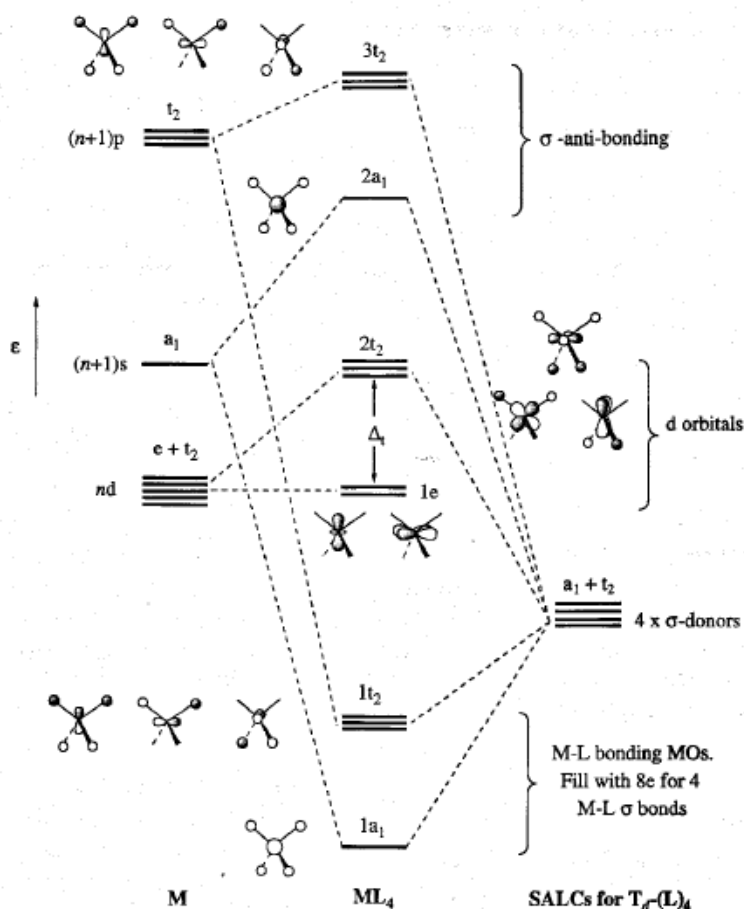


Fig(i)

Structure of [Cu(bpy)(hfa)₂]
showing Cu-O and Cu-N bond lengths (in picometers)

Tetrahedral ML_4 Complexes

The MO Diagram is thus:



REFERENCE;

1. Wahid U.Malic, G.D Tuli, R.D.Madan, 2003, selected topics in inorganic chemistry.
2. Huheey.J.E, E.A. Keitler & R.L.Keitler,2012. Inorganic chemistry,vol-IV, Pearson Education Singapore.
3. Drago.R.S. 1965, Physical methods in inorganic chemistry, Rein gold publishing corporation, Newyork.
4. Cotton. F.A& G.Wilkinson, 2003, Advanced inorganic chemistry, john wiley & sons, Newyork.

Possible Questions:

Part-A

Each question carries one mark:

1. The promotion of electrons from a lower energy orbital to higher energy orbital is termed as -

- a. Electronic transition**
- b. Energy transfer
- c. Forbidden transition
- d. None

2. Tanabe-Sugano diagrams are helpful in understanding

- a. Spectral behaviour of metal complexes**
- b. Magnetic character of complexes
- c. Identification of molecular structure
- d. The mechanism of reactions

3. The electronic transition of two energy levels of a molecule which are not having same spin multiplicity is -----

- a. Spin allowed
- b. Spin forbidden**
- c. Laporte allowed
- d. Laporte forbidden

4. The electronic transition of two energy levels having same spin multiplicity is -----

- a. Spin allowed**
- b. Spin forbidden
- c. Laporte allowed
- d. Laporte forbidden

5. A molecule with a center of symmetry, the electronic transitions gerade to gerade are

- a. Spin allowed
- b. Spin forbidden
- c. Laporte allowed
- d. Laporte forbidden**

6. A molecule with a center of symmetry, the electronic transition gerade to ungerade are

- a. Spin allowed
- b. Spin forbidden
- c. Laporte allowed**
- d. Laporte forbidden

7. The deep purple colour of MnO_4^- is due to

- a. Charge transfer from $t_1 \rightarrow e$**
- b. Charge transfer from $t_1 \rightarrow t_2^*$
- c. Charge transfer from $t_2 \rightarrow e$
- d. Charge transfer from $t_1 \rightarrow t_2^*$

8. The L value 2 indicates the term

- a. S
- b. D
- c. P
- d. F**

9. The ground state term symbol for V^{3+} ion is

- a. ^3P
- b. ^2D
- c. ^3F**
- d. ^1S

10. The excited state term symbol for d^2 configuration of arrangement of two electrons with parallel spin

- a. ^3P**
- b. ^2D
- c. ^1G
- d. ^1S

11. The excited state term symbol for d^2 configuration of arrangement of two electrons with opposite spin

- a. ^3P
- b. ^2D
- c. ^1D**
- d. ^3F

12. The ground state term symbol for d^7 configuration is

- a. ^3P

- b.² D
- c.¹ G
- d.⁴ F**

13. The spin multiplicity of d^5 configuration is

- a. 2
- b. 4
- c. 6**
- d. 5

14. The resultant orbital angular momentum quantum number for d^9 configuration is

- a. 0
- b. 2**
- c. 3
- d. 4

15. The resultant spin angular momentum quantum number for d^8 configuration is

- a. 1**
- b. 2
- c. 1 $1/2$
- d. 2 $1/2$

16. In an orbital moving from any point to the equivalent point on the same side of the center the sign of the wave function does not change, the orbitals are -----

- a. gerade**
- b. ungerade
- c. degenerate
- d. nondegenerate

17. In an orbital moving from any point to the equivalent point on the opposite side, the sign of the wave function changes, the orbital is -----

- a. gerade
- b. ungerade
- c. degenerate
- d. nondegenerate**

18. ----- is an energy level or a set of degenerate energy levels resulting from the electron-electron repulsions in an electronic arrangement.

a. Energy term

- b. Electronic spectra
- c. Degeneracy
- d. Non degeneracy

19. The ground state term symbol for Ni^{2+} is

- a. ^3P
- b. ^2D
- c. ^1D
- d. ^3F

20. Example for d^2 metal ion octahedral environment

- a. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- b. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
- c. $[\text{V}(\text{H}_2\text{O})_6]^{3+}$
- d. $[\text{Cu}(\text{H}_2\text{O})_6]^{3+}$

Part-B

Each question carries six marks

1. Write a note on d-d transitions?
2. Assign term symbol for d- ions
3. What are the rules govern in d-d transition?
4. Derive the ground term symbol for a Fe^{2+} ion. Sketch the Orgel diagram for $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ ion and mention the possible transitions.
5. Give a detailed account on Correlations diagram of d^1 to d^{10} configuration with suitable examples
6. What is Jahn-Teller effect? Illustrate with an example?
7. Explain the Tanabe-Sugano diagram of a metal complex with d^2 and d^8 configurations.

Part-C

Each question carries ten marks

1. Explain the Correlation diagram of a metal complex with d^2 and d^8 Configurations.

2. Derive the ground term symbol for a Fe^{2+} ion. Sketch the Orgel diagram for $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ ion and mention the possible transitions.
3. Discuss the different types of charge transfer spectra with typical examples

18CHP202
Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2018 onwards)
Department of Chemistry
II- semester

Inorganic Chemistry -II (Coordination Chemistry)

UNIT II- Objective Questions for online examination (Each carry 1 Marks)

Question	Option-a	Option-b	Option-c	Option-d	Answer
The promotion of electrons from an lower energy orbital to higher energy orbital is termed as -----	Electronic tranisition	Energy transfer	Forbidden transition	None	Electronic tranisition
Tanabe-Sugano diagrams are helpful in understanding	Spectral behaviour of metal complexes	Magnetic character of complexes	Identification of molecular structure	The mechanism of reactions	Spectral behaviour of metal complexes
The electronic transition of two energy levels of a molecule which are not having same spin multiplicity is -----	Spin allowed	Spin forbidden	Laporte allowed	Laporte forbidden	Spin forbidden
The electronic transition of two energy levels having same spin multiplicity is -----	Spin allowed	Spin forbidden	Laporte allowed	Laporte forbidden	Spin allowed
A molecule with a center of symmetry, the electronic transitions gerade to gerade are	Spin allowed	Spin forbidden	Laporte allowed	Laporte forbidden	Laporte forbidden
A molecule with a center of symmetry, the eletronic transition gerade to ungerade are	Spin allowed	Spin forbidden	Laporte allowed	Laporte forbidden	Laporte allowed
The deep purple colour of MnO_4^- is due to	Charge transfer from $t_1 \rightarrow e$	Charge transfer from $t_1 \rightarrow t_2^*$	Charge transfer from $t_2 \rightarrow e$	Charge transfer from $t_1 \rightarrow t_2^*$	Charge transfer from $t_1 \rightarrow e$
The L value 2 indicates the term	S	D	P	F	F
The ground state term symbol for V^{3+} ion is	^3P	^2D	^3F	^1S	^3F

The excited state term symbol for d^2 configuration of arrangement of two electrons with parallel spin	3P	2D	1G	1S	3P
The excited state term symbol for d^2 configuration of arrangement of two electrons with opposite spin	3P	2D	1D	3F	1D
The ground state term symbol for d^7 configuration is	3P	2D	1G	4F	4F
The spin multiplicity of d^5 configuration is	2	4	6	5	6
The resultant orbital angular momentum quantum number for d^9 configuration is	0	2	3	4	2
The resultant spin angular momentum quantum number for d^8 configuration is	1	2	1 1/2	2 1/2	1
In a orbital moving from any point to the equivalent point on the side of the center the sign of the wave function does not change, the orbitals is -----	gerade	ungerade	degenerate	nondegenerate	gerade
In a orbital moving from any point to the equivalent point on the opposite side, the sign of the wave function changes, the orbital is -----	gerade	ungerade	degenerate	nondegenerate	ungerade
----- is an energy level or a set of degenerate energy levels resulting from the electron-electron repulsions in an electronic arrangement.	Energy term	Electronic spectra	Degeneracy	Non degeneracy	Energy term
The ground state term symbol for Ni^{2+} is	3P	2D	1D	3F	3F
Example for d^2 metal ion octahedral environment	$[Fe(H_2O)_6]^{2+}$	$[Ti(H_2O)_6]^{3+}$	$[V(H_2O)_6]^{3+}$	$[Cu(H_2O)_6]^{3+}$	$[V(H_2O)_6]^{3+}$
which is not possible for the charge transfer transitions of d^6 configuration	$t_{1u}, t_{2u} \rightarrow t_{2g}$	$t_{1u}, t_{2u} \rightarrow t_{2g}^*$	$t_{1u}, t_{2u} \rightarrow e_g$	$t_{1u}, t_{2u} \rightarrow e_g^*$	$t_{1u}, t_{2u} \rightarrow t_{2g}^*$
The Nephelauxetic ratio β is given by,	$\beta = B'/B$	$\beta = B/B'$	$\beta = C/B'$	None	$\beta = B'/B$
Tanabe-Sugano diagrams provided the electronic spectra of	strong field	weakfield	Both strong & weak field	None	Both strong & weak field
Orgel diagram provided the electronic spectra of	strong field	weakfield	Both strong & weak	None	weakfield

			field		
On increasing delocalisation of metal electrons the Nephelauxetic ratio β -----	Increases	decreases	Constant	Zero	decreases
If the Value of l is 1 means , the value of m = ?	0	1	0,±1	2	0,±1
If the value of n=1 indicates the sub shell	s	p	d	f	s
The number of orientations in f shell is	2	3	5	7	7
The number of orientations in d orbital is	2	3	5	7	5
Distortion of octahedral geometry of $[\text{Cu}(\text{NH}_3)_6]^{2+}$ to tetragonal geometry is ----- if more electrons in d_{z^2} orbital	Elongation along Z axis	Compression along Z axis	Elongation along X axis	Elongation along Y axis	Elongation along Z axis
Distortion of octahedral geometry of $[\text{Cu}(\text{NH}_3)_6]^{2+}$ to tetragonal geometry is ----- if more electrons in $d_{x^2-y^2}$ orbital	Elongation along Z axis	Compression along Z axis	Elongation along X axis	Elongation along Y axis	Compression along Z axis
The ground state energy level as well as the excited state energy level further split up due to	Spin spin coupling	Spin spin splitting	Spin orbit coupling	None	Spin orbit coupling
The spin allowed electronic transitions occur between the two energy levels which have -----multiplicity	Different	same	Higher	Lower	same
The molecular orbital diagram for tetrahedral complexes allows ----- transitions	Ligand to metal charge transfer	Metal to ligand charge transfer	Both transitions	none	Ligand to metal charge transfer
In MnO_4^- ----- is responsible for the deep purple colour	Ligand to metal charge transfer transition	Metal to ligand charge transfer transition	Both transitions	none	Ligand to metal charge transfer transition
The colour of Cadmium yellow (CdS) is due to ----- - transition.	Ligand $\pi_p \rightarrow$ metal 5s	Ligand $\pi_p \rightarrow$ metal 6s	Ligand $\pi_p \rightarrow$ metal 5p	Ligand $\pi_p \rightarrow$ metal 3d	Ligand $\pi_p \rightarrow$ metal 5s

The colour of chrome yellow is due to ----- transition	Ligand $\pi_p \rightarrow$ metal 5s	Ligand $\pi_p \rightarrow$ metal 6s	Ligand $\pi_p \rightarrow$ metal 5p	Ligand $\pi_p \rightarrow$ metal 3d	Ligand $\pi_p \rightarrow$ metal 3d
In octahedral complexes when both t_{2g} & e_g^* orbitals are occupied , then the transition is -----	Ligand to metal charge transfer transition	Metal to ligand charge transfer transition	Both transitions	none	Metal to ligand charge transfer transition
The spin multiplicity for $^3T_{1g}$ is	1	0	3	2	3
In d^5 correlation diagram all the transition are not only Laporte forbidden, it is also -----	Spin allowed	Spin forbidden	Laporte forbidden	None	Spin forbidden
How many Orgel diagrams are there?	1	2	3	4	2
The ground state term symbol is predicted by ?	Selection rule	Huckle rule	$4n+2$ rule	Hund's rule	Hund's rule
Orgel diagrams are?	Quantitative Nature	Qualitative Nature	Effective Nature	Efficient Nature	Qualitative Nature
Transitions between states of different spin multiplicities are forbidden.	Electron selection rule	Laporte selection rule	Spin selection rule	Second selection rule	Spin selection rule
The term symbol for d^1 is?	1D	2D	4D	3D	2D
There are no d-d electron transitions in which metal complexes?	d^{10}	d^{11}	d^{12}	d^{13}	d^{10}
Tanabe-Sugano diagrams are utilized in determining ?	Atom placements	Element placements	Electron placements	Spin	Electron placements
In the $[Mn(H_2O)_6]^{2+}$ metal complex, manganese has an oxidation state of +2, thus it is a ?	d^6 ion	d^4 ion	d^3 ion	d^5 ion	d^5 ion
Which one of the following hexahydrate has no sextet spin multiplicity?	Cobalt (II)	Manganese (II)	Sodium (II)	Magnesium (II)	Manganese (II)
For, d^2 complex $[V(H_2O)_6]^{3+}$, how many bands are observed with maxima at around 17,500 and 26,000 cm^{-1} ?	1	2	3	4	2

The nephelauxetic series indicates that the spin-pairing energy is greatest for fluoro complexes, and least for?	metal complexes	Imino complexes	Iodo complexes	Coordination complexes	Iodo complexes
The nature of the attraction in a charge-transfer complex is not a stable chemical bond, and is much weaker than ?	covalent forces	Electromagnetic forces	Magnetic forces	Electrostatic forces	Covalent forces
Which one of the following is a powerful technique to characterize charge-transfer bands?	Adsorptions spectroscopy	Structural spectroscopy	Optical spectroscopy	Absorption spectroscopy	Optical spectroscopy
Blue charge-transfer band exhibited by iodine when combined with?	salt	Sugar	Starch	Fructose	Starch
In inorganic chemistry , most charge-transfer complexes involve electron transfer between ?	metal atoms and ligands	Atoms and ligands	Ligands and metals	Metals and atoms	Metal atoms and ligands
The electron donating power of a donor molecule is measured by ?	electron negativity	Atoms	Electron affinity	Ionization potential	Ionization potential
CT absorptions bands are intense and often lie in which portion of the spectrum?	Invisible	Visible	Left	Right	Visible
What occurs often in inorganic ligand chemistry involving metals?	Transfer	Charge	Charge-transfer	Magnetism	Charge-transfer
Analysis of a compound's fragmentation pattern can be used to gain which information?	Chemical	Physical	Electron	Structural	Structural
The NMR spectra of inorganic compounds are often more complicated than organics because other nuclei also have ?	Nuclear magnetic moments	Paramagnetic moments	Nuclear moments	Magnetic moments	Nuclear magnetic moments
ligand can act as an donar and acceptor	NH ₃	H ₂ O	NH ₂ NH ₃ ⁺	CO	CO

Lecture Notes

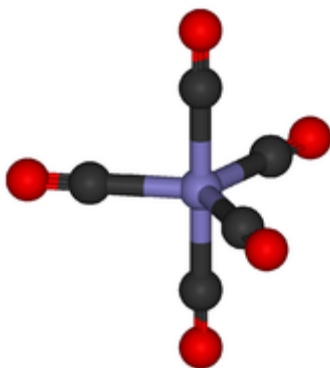
UNIT-III

SYLLABUS

METAL CARBONYLS: Methods of preparation, structure, bonding and reactions, carbonylate ions. Carbonyl halides, carbonyl hydrides-vaska's compound, complexes of molecular nitrogen and oxygen. Nitrosyl complexes, β -diketones, cyanide and isocyanide complexes. Complexes of unsaturated hydrocarbons-alkenes, allyl and dienyl complexes.

INTRODUCTION:

Metal Carbonyls



Iron pentacarbonyl
An iron atom with five CO ligands

Metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands. Metal carbonyls are useful in organic synthesis and as catalysts or catalyst precursors in homogeneous catalysis, such as hydroformylation and Reppe chemistry. In the Mond process,

nickel carbonyl is used to produce pure nickel. In organometallic chemistry, metal carbonyls serve as precursors for the preparation of other organometallic complexes.

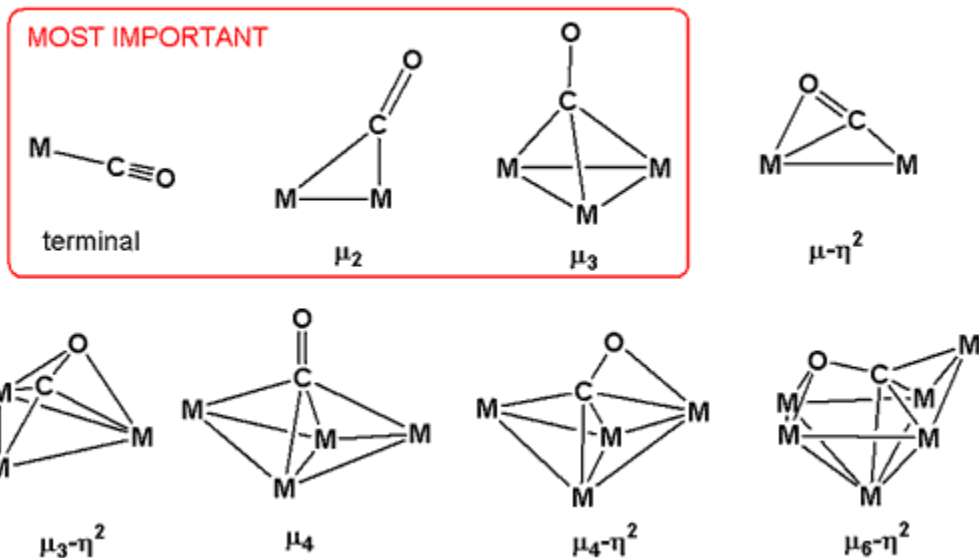
Metal carbonyls are toxic by skin contact, inhalation or ingestion, in part because of their ability to carbonylate hemoglobin to give carboxyhemoglobin, which prevents the binding of O₂.

Nomenclature and Terminology:

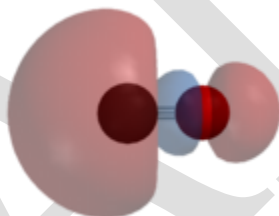
The nomenclature of the metal carbonyls depends on the charge of the complex, the number and type of central atoms, and the number and type of ligands and their binding modes. They occur as neutral complexes, as positively charged metal carbonyl cations or as negatively charged metal carbonylates. The carbon monoxide ligand may be bound terminally to a single metal atom or bridging to two or more metal atoms. These complexes may be homoleptic, that is containing only CO ligands, such as nickel carbonyl (Ni(CO)₄), but more commonly metal carbonyls are heteroleptic and contain a mixture of ligands.

Mononuclear metal carbonyls contain only one metal atom as the central atom. Except vanadium hexacarbonyl only metals with even order number such as chromium, iron, nickel and their homologs build neutral mononuclear complexes. Polynuclear metal carbonyls are formed from metals with odd order numbers and contain a metal-metal bond. Complexes with different metals, but only one type of ligand will be referred to as isoleptic. The number of carbon monoxide ligands in a metal carbonyl complex is described by a Greek numeral, followed by the word *carbonyl*. Carbon monoxide has different binding modes in metal carbonyls. They differ in the hapticity and the bridging mode. The hapticity describes the number of carbon monoxide ligands, which are directly bonded to the central atom. The denomination shall be made by the letter η^n , which is prefixed to the name of the complex. The superscript n indicates the number of bounded atoms. In monohapto coordination, such as in terminally bonded carbon monoxide, the hapticity is 1 and it is usually not separately designated. If carbon monoxide is bound via the carbon atom and via the oxygen to the metal, it will be referred to as dihapto coordinated η^2 .

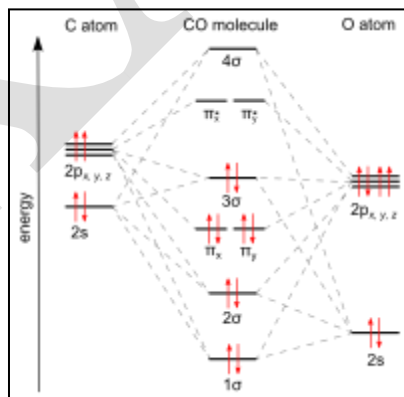
The carbonyl ligand engages in a range of bonding modes in metal carbonyl dimers and clusters. In the most common bridging mode, the CO ligand bridges a pair of metals. This bonding mode is observed in the commonly available metal carbonyls: Co₂(CO)₈, Fe₂(CO)₉, Fe₃(CO)₁₂, and Co₄(CO)₁₂. In certain higher nuclearity clusters, CO bridges between three or even four metals. These ligands are denoted μ_3 -CO and μ_4 -CO. Less common are bonding modes in which both C and O bond to the metal, e.g. μ_3 - η^2 .



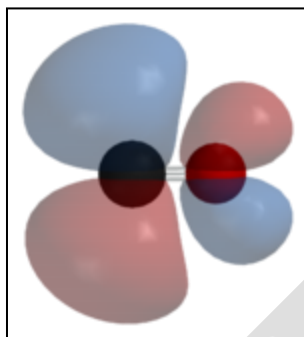
Structure and bonding



The highest occupied molecular orbital (HOMO) of CO is a σ MO



Energy level scheme of the σ and π orbitals of carbon monoxide



The lowest unoccupied molecular orbital (LUMO) of CO is a π^* antibonding MO

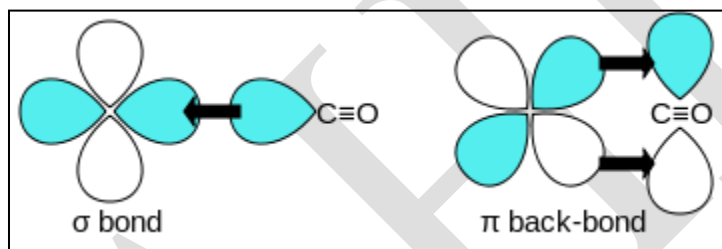


Diagram showing synergic π back-bonding in transition metal carbonyls

Carbon monoxide bonds to transition metal using "synergistic π^* back-bonding." The bonding has three components, giving rise to a partial triple bond. A sigma bond arises from overlap of the nonbonding (or weakly anti-bonding) sp-hybridized electron pair on carbon with a blend of d-, s-, and p-orbitals on the metal. A pair of π bonds arises from overlap of filled d-orbitals on the metal with a pair of π -antibonding orbitals projecting from the carbon atom of the CO. The latter kind of binding requires that the metal have d-electrons, and that the metal is in a relatively low oxidation state ($<+2$) which makes the back donation process favorable. As electrons from the metal fill the π -antibonding orbital of CO, they weaken the carbon-oxygen bond compared with free carbon monoxide, while the metal-carbon bond is strengthened. Because of the multiple bond character of the M-CO linkage, the distance between the metal and carbon atom is relatively short, often $< 1.8 \text{ \AA}$, about 0.2 \AA shorter than a metal-alkyl bond. Several canonical forms can be drawn to describe the *approximate* metal carbonyl bonding modes.

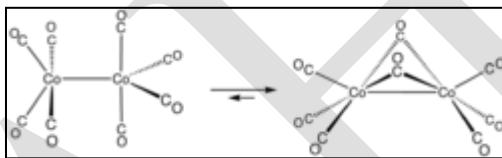
Infrared spectroscopy is a sensitive probe for the presence of bridging carbonyl ligands. For compounds with doubly bridging CO ligands, denoted μ_2 -CO or often just μ -CO, ν_{CO} , ν_{CO} is usually shifted by $100\text{--}200 \text{ cm}^{-1}$ to lower energy compared to the signatures of terminal CO, i.e. in the region 1800 cm^{-1} . Bands for face capping (μ_3) CO ligands appear at even lower energies. Typical values for rhodium cluster carbonyls are: In addition to symmetrical bridging modes, CO

can be found bridge unsymmetrically or through donation from a metal d orbital to the π^* orbital of CO. The increased π -bonding due to back-donation from multiple metal centers results in further weakening of the C-O bond.

Physical characteristics

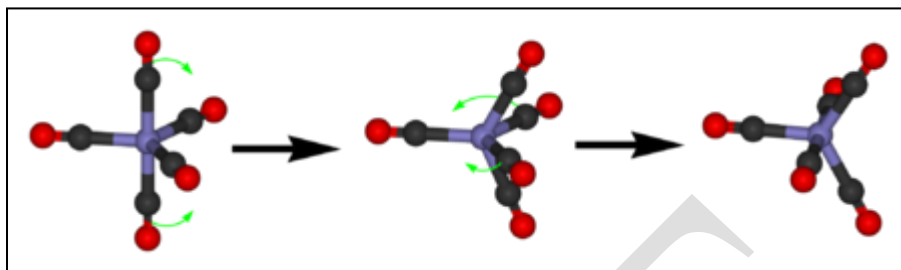
Most mononuclear carbonyl complexes are colorless or pale yellow volatile liquids or solids that are flammable and toxic. Vanadium hexacarbonyl, a uniquely stable 17-electron metal carbonyl, is a blue-black solid. Di- and polymetallic carbonyls tend to be more deeply colored. Triiron dodecacarbonyl ($\text{Fe}_3(\text{CO})_{12}$) forms deep green crystals. The crystalline metal carbonyls often are sublimable in vacuum, although this process is often accompanied by degradation. Metal carbonyls are soluble in nonpolar and polar organic solvents such as benzene, diethyl ether, acetone, glacial acetic acid and carbon tetrachloride. Some salts of cationic and anionic metal carbonyls are soluble in water or lower alcohols.

Analytical characterization



Isomers of dicobalt octacarbonyl

Apart from X-ray crystallography, important analytical techniques for the characterization of metal carbonyls are infrared spectroscopy and ^{13}C NMR spectroscopy. These two techniques provide structural information on two very different time scales. Infrared active vibrational modes, such as CO-stretching vibrations are often fast compared to intramolecular processes, whereas NMR transitions occur at lower frequencies and thus sample structures on a time scale that, it turns out, is comparable to the rate of intramolecular ligand exchange processes. NMR data provide information on "time-averaged structures," whereas IR is an instant "snapshot." Illustrative of the differing time scales, investigation of dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) by means of infrared spectroscopy provides 13 ν_{CO} bands, far more than expected for a single compound. This complexity reflects the presence of isomers with and without bridging CO-ligands. The ^{13}C -NMR spectrum of the same substance exhibits only a single signal at a chemical shift of 204 ppm. This simplicity indicates that the isomers quickly (on the NMR timescale) interconvert.



The Berry pseudorotation mechanism for iron pentacarbonyl

Iron pentacarbonyl exhibits only a single ^{13}C -NMR signal owing to rapid exchange of the axial and equatorial CO ligands by Berry pseudorotation.

Infrared spectra

Coordination number		
4	5	6
3 Carbonyl ligands		
4 Carbonyl ligands		
5 Carbonyl ligands		
6 Carbonyl ligands		

The number of IR-active vibrational modes of several prototypical metal carbonyl complexes.

An important technique for characterizing metal carbonyls is infra-red spectroscopy. The C-O vibration, typically denoted ν_{CO} , occurs at 2143 cm^{-1} for CO gas. The energies of the ν_{CO} band for the metal carbonyls correlates with the strength of the carbon-oxygen bond, and inversely correlated with the strength of the π -backbonding between the metal and the carbon. The π basicity of the metal center depends on a lot of factors; in the isoelectronic series (Ti to Fe) at the bottom of this section, the hexacarbonyls show decreasing π -backbonding as one increases

(makes more positive) the charge on the metal. π -Basic ligands increase π -electron density at the metal, and improved backbonding reduces ν_{CO} . The Tolman electronic parameter uses the $\text{Ni}(\text{CO})_3$ fragment to order ligands by their π -donating abilities.

The number of vibrational modes of a metal carbonyl complex can be determined by group theory. Only vibrational modes that transform as the electric dipole operator will have non-zero direct products and are observed. The number of observable IR transitions (but not the energies) can thus be predicted. For example, the CO ligands of octahedral complexes, e.g. $\text{Cr}(\text{CO})_6$, transform as a_{1g} , e_g , and t_{1u} , but only the t_{1u} mode (anti-symmetric stretch of the apical carbonyl ligands) is IR-allowed. Thus, only a single ν_{CO} band is observed in the IR spectra of the octahedral metal hexacarbonyls. Spectra for complexes of lower symmetry are more complex. For example, the IR spectrum of $\text{Fe}_2(\text{CO})_9$ displays CO bands at 2082, 2019, 1829 cm^{-1} . The number of IR-observable vibrational modes for some metal carbonyls are shown in the table. Exhaustive tabulations are available. These rules apply to metal carbonyls in solution or the gas phase. Low polarity solvents are ideal for high resolution. For measurements on solid samples of metal carbonyls, the number of bands can increase owing in part to site symmetry.

Compound	ν_{CO} (cm^{-1})	^{13}C NMR shift
CO	2143	181
$\text{Ti}(\text{CO})_6^{-2}$	1748	
$\text{V}(\text{CO})_6^{-1}$	1859	
$\text{Cr}(\text{CO})_6$	2000	212
$\text{Mn}(\text{CO})_5^{-}$	2100	
$\text{Fe}(\text{CO})_4^{2-}$	2204	
$\text{Fe}(\text{CO})_5$	2022, 2000	209

carbonyl	ν_{CO}, μ_1 (cm^{-1})	ν_{CO}, μ_2 (cm^{-1})	ν_{CO}, μ_3 (cm^{-1})
$\text{Rh}_2(\text{CO})_8$	2060, 2084	1846, 1862	
$\text{Rh}_4(\text{CO})_{12}$	2044, 2070, 2074	1886	
$\text{Rh}_6(\text{CO})_{16}$	2045, 2075		1819

Nuclear magnetic resonance spectroscopy

Metal carbonyls are often characterized by ^{13}C NMR spectroscopy. To improve the sensitivity of this technique, complexes are often enriched ^{13}CO . Typical chemical shift range for terminally bound ligands is 150 to 220 ppm. Bridging ligands absorb between 230 and 280 ppm. The ^{13}C signals shift toward higher fields with an increasing atomic number of the central metal.

The nuclear magnetic resonance spectroscopy can be used for experimental determination of the fluxionality. The activation energy of ligand exchanges processes can be determined by the temperature dependence of the line broadening.

Mass spectrometry

Mass spectrometry provides information about the structure and composition of the complexes. Spectra for metal polycarbonyls are often easily interpretable, because the dominant fragmentation process is the loss of carbonyl ligands ($m/z = 28$).

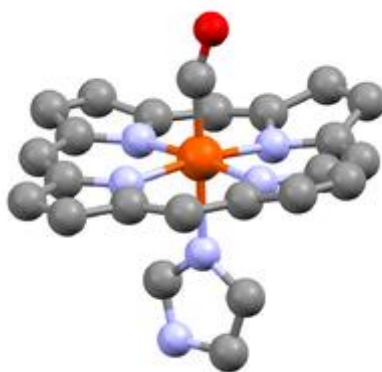


Electron impact ionization is the most common technique for characterizing the neutral metal carbonyls. Neutral metal carbonyls can be converted to charged species by derivatization, which enables the use of electrospray ionization, instrumentation for which is often widely available. For example, treatment of a metal carbonyl with alkoxide generates an anionic metallacarbonylate that is amenable to analysis by ESI-MS:



Some metal carbonyls react with azide to give isocyanato complexes with release of nitrogen. By adjusting the cone voltage and/or temperature, the degree of fragmentation can be controlled. The molar mass of the parent complex can be determined, as well as information about structural rearrangements involving loss of carbonyl ligands under ESI-MS conditions.

Occurrence in nature



A heme unit of human carboxyhemoglobin, showing the carbonyl ligand at the apical position, *trans* to the histidine residue.

In the investigation of the infrared spectrum of the Galactic Center monoxide vibrations of iron carbonyls in interstellar dust clouds were detected. Iron carbonyl clusters were also observed in Jiange H5 chondrites identified by infrared spectroscopy. Four infrared stretching frequencies were found for the terminal and bridging carbon monoxide ligands.

In the oxygen-rich atmosphere of earth metal carbonyls are subject to oxidation to the metal oxides. It is discussed whether in the reducing hydrothermal environments of the pre-biotic prehistory such complexes were formed and could have been available as catalysts for the synthesis of critical biochemical compounds such as pyruvic acid.^[26] Traces of the carbonyls of iron, nickel, and tungsten were found in the gaseous emanations from the sewage sludge of municipal treatment plants.

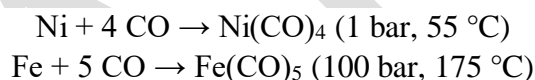
The hydrogenase enzymes contain CO bound to iron. Apparently the CO stabilizes low oxidation states, which facilitates the binding of hydrogen. The enzymes carbon monoxide dehydrogenase and acetyl coA synthase also are involved in bio-processing of CO.^[28] Carbon monoxide containing complexes are invoked for the toxicity of CO and signaling.^[29]

Synthesis

The synthesis of metal carbonyls is subject of intense organometallic research. Since the work of Mond and then Hieber, many procedures have been developed for the preparation of mononuclear metal carbonyls as well as homo-and hetero-metallic carbonyl clusters.

Direct reaction of metal with carbon monoxide

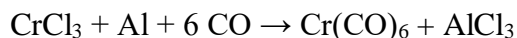
Nickel tetracarbonyl and iron pentacarbonyl can be prepared according to the following equations by reaction of finely divided metal with carbon monoxide:



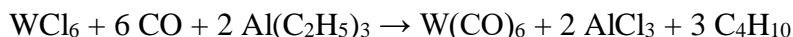
Nickel carbonyl is formed with carbon monoxide already at 80 °C and atmospheric pressure, finely divided iron reacts at temperatures between 150 and 200 °C and a carbon monoxide pressure of 50 to 200 bar. Other metal carbonyls are prepared by less direct methods.

Reduction of metal salts and oxides

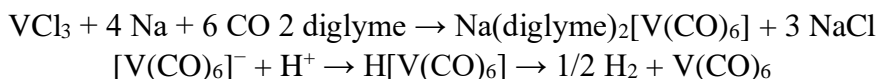
Some metal carbonyls are prepared by the reduction of metal halides in the presence of high pressure of carbon monoxide. A variety of reducing agents are employed, including copper, aluminum, hydrogen, as well as metal alkyls such as triethylaluminum. Illustrative is the formation of chromium hexacarbonyl from anhydrous chromium(III) chloride in benzene with aluminum as a reducing agent, and aluminum chloride as the catalyst:



The use of metal alkyls, e.g. triethylaluminium and diethylzinc as the reducing agent leads to the oxidative coupling of the alkyl radical to the dimer:



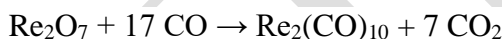
Tungsten, molybdenum, manganese, and rhodium salts may be reduced with lithium aluminum hydride. Vanadium hexacarbonyl is prepared with sodium as a reducing agent in chelating solvents such as diglyme.



In aqueous phase nickel or cobalt salts can be reduced, for example, by sodium dithionite. In the presence of carbon monoxide, cobalt salts are quantitatively converted to the tetracarbonylcobalt(-1) anion:



Some metal carbonyls are prepared using CO as the reducing agent. In this way, Hieber and Fuchs first prepared dirhenium decacarbonyl from the oxide:



If metal oxides are used carbon dioxide is formed as a reaction product. In the reduction of metal chlorides with carbon monoxide phosgene is formed, as in the preparation of osmium carbonyl chloride from the chloride salts. Carbon monoxide is also suitable for the reduction of sulfides, where carbonyl sulfide is the byproduct.

Photolysis and thermolysis

Photolysis or thermolysis of mononuclear carbonyls generates bi- and multimetallic carbonyls such as diiron nonacarbonyl ($\text{Fe}_2(\text{CO})_9$). On further heating, the products decompose eventually into the metal and carbon monoxide.

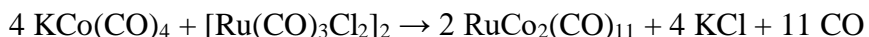


The thermal decomposition of triosmium dodecacarbonyl ($\text{Os}_3(\text{CO})_{12}$) provides higher-nuclear osmium carbonyl clusters such as $\text{Os}_4(\text{CO})_{13}$, $\text{Os}_6(\text{CO})_{18}$ up to $\text{Os}_8(\text{CO})_{23}$.

Mixed ligand carbonyls of ruthenium, osmium, rhodium, and iridium are often generated by abstraction of CO from solvents such as dimethylformamide (DMF) and 2-methoxyethanol. Typical is the synthesis of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ from the reaction of iridium(III) chloride and triphenylphosphine in boiling DMF solution.

Salt metathesis

Salt metathesis reaction of for example $\text{KCo}(\text{CO})_4$ with $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ leads selectively to mixed-metal carbonyls such as $\text{RuCo}_2(\text{CO})_{11}$.



Metal carbonyl cations and carbonylates

The synthesis of ionic carbonyl complexes is possible by oxidation or reduction of the neutral complexes. Anionic metal carbonylates can be obtained for example by reduction of dinuclear complexes with sodium. A familiar example is the sodium salt of iron tetracarbonylate ($\text{Na}_2\text{Fe}(\text{CO})_4$, *Collman's reagent*), which is used in organic synthesis.

The cationic hexacarbonyl salts of manganese, technetium and rhenium can be prepared from the carbonyl halides under carbon monoxide pressure by reaction with a Lewis acid.



The use of strong acids succeeded in preparing gold carbonyl cations such as $[\text{Au}(\text{CO})_2]^+$, which is used as a catalyst for the carbonylation of olefins. The cationic platinum carbonyl complex $[\text{Pt}(\text{CO})_4]^+$ can be prepared by working in so-called super acids such as antimony pentafluoride.

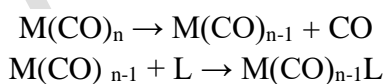
Reactions

Metal carbonyls are important precursors for the synthesis of other organometallic complexes. The main reactions are the substitution of carbon monoxide by other ligands, the oxidation or reduction reactions of the metal center and reactions of carbon monoxide ligand.

CO substitution

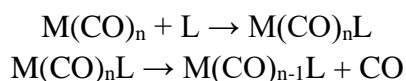
The substitution of CO ligands can be induced thermally or photochemically by donor ligands. The range of ligands is large, and includes phosphines, cyanide (CN^-), nitrogen donors, and even ethers, especially chelating ones. Olefins, especially diolefins, are effective ligands that afford synthetically useful derivatives. Substitution of 18-electron complexes generally follows a dissociative mechanism, involving 16-electron intermediates.

Substitution proceeds via a dissociative mechanism:



The dissociation energy is 105 kJ mol^{-1} for nickel carbonyl and 155 kJ mol^{-1} for chromium hexacarbonyl.

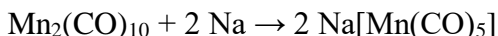
Substitution in 17-electron complexes, which are rare, proceeds via associative mechanisms with a 19-electron intermediates.



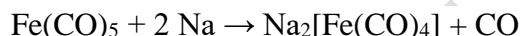
The rate of substitution in 18-electron complexes is sometimes catalysed by catalytic amounts of oxidants, via electron-transfer.

Reduction

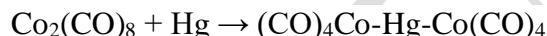
Metal carbonyls react with reducing agents such as metallic sodium or sodium amalgam to give carbonylmetalate (or carbonylate) anions:



For iron pentacarbonyl, one obtains the tetracarbonylferrate with loss of CO:

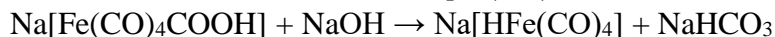
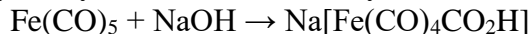


Mercury can insert into the metal-metal bonds of some polynuclear metal carbonyls:

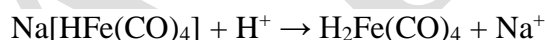


Nucleophilic attack at CO

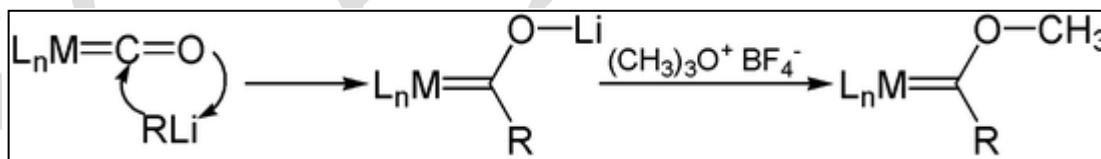
The CO ligand is often susceptible to attack by nucleophiles. For example, trimethylamine oxide and bistrimethylsilylamide convert CO ligands to CO_2 and CN^- , respectively. In the "Hieber base reaction", hydroxide ion attacks the CO ligand to give a metallacarboxylic acid, followed by the release of carbon dioxide and the formation of metal hydrides or carbonylmetalates. A well-known example of this nucleophilic addition reaction is the conversion of iron pentacarbonyl to hydridorion tetracarbonyl anion:



Protonation of the hydrido anion gives the neutral iron tetracarbonyl hydride:

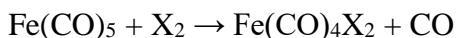


Organolithium reagents add with metal carbonyls to acylmetal carbonyl anions. O-alkylation of these anions, e.g. with Meerwein salts, affords Fischer carbenes.

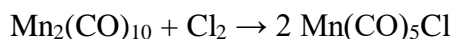


With electrophiles

Despite being in low formal oxidation states, metal carbonyls are relatively unreactive toward many electrophiles. For example, they resist attack by alkylating agents, mild acids, mild oxidizing agents. Most metal carbonyls do undergo halogenation. Iron pentacarbonyl, for example, forms ferrous carbonyl halides:



Metal-metal bonds are cleaved by halogens. Depending on the electron-counting scheme used, this can be regarded as oxidation of the metal atom:



Compounds

Most metal carbonyl complexes contain a mixture of ligands. Examples include the historically important $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and the anti-knock agent $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. The parent compounds for many of these mixed ligand complexes are the binary carbonyls, i.e. species of the formula $[\text{M}_x(\text{CO})_n]^z$, many of which are commercially available. The formula of many metal carbonyls can be inferred from the 18 electron rule.

Charge-neutral binary metal carbonyls

Group 4 elements with 4 valence electrons are rare, but substituted derivatives of $\text{Ti}(\text{CO})_7$ are known.

- Group 5 elements with 5 valence electrons, again are subject to steric effects that prevent the formation of M-M bonded species such as $\text{V}_2(\text{CO})_{12}$, which is unknown. The 17 VE $\text{V}(\text{CO})_6$ is however well known.
- Group 6 elements with 6 valence electrons form metal carbonyls $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ ($6 + 6 \times 2 = 18$ electrons). Group 6 elements (as well as group 7) are well also well known for exhibiting the cis effect (the labilization of CO in the cis position) in organometallic synthesis.
- Group 7 elements with 7 valence electrons form metal carbonyl dimers $\text{Mn}_2(\text{CO})_{10}$, $\text{Tc}_2(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$ ($7 + 1 + 5 \times 2 = 18$ electrons).
- Group 8 elements with 8 valence electrons form metal carbonyls $\text{Fe}(\text{CO})_5$, $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ ($8 + 5 \times 2 = 18$ electrons). The heavier two members are unstable, tending to decarbonylate to give $\text{Ru}_3(\text{CO})_{12}$, and $\text{Os}_3(\text{CO})_{12}$. The two other principal iron carbonyls are $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}_2(\text{CO})_9$.
- Group 9 elements with 9 valence electrons and are expected to form metal carbonyl dimers $\text{M}_2(\text{CO})_8$. In fact the cobalt derivative of this octacarbonyl is the only stable member, but all three tetramers are well known: $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and $\text{Ir}_4(\text{CO})_{12}$ ($9 + 3 + 3 \times 2 = 18$ electrons). $\text{Co}_2(\text{CO})_8$ unlike the majority of the other 18 VE transition metal carbonyls is sensitive to oxygen.
- Group 10 elements with 10 valence electrons form metal carbonyls $\text{Ni}(\text{CO})_4$ ($10 + 4 \times 2 = 18$ electrons). Curiously $\text{Pd}(\text{CO})_4$ and $\text{Pt}(\text{CO})_4$ are not stable.

Anionic binary metal carbonyls

- Group 4 elements as dianions resemble neutral group 6 derivatives: $[\text{Ti}(\text{CO})_6]^{2-}$.^[41]
- Group 5 elements as monoanions resemble again neutral group 6 derivatives: $[\text{V}(\text{CO})_6]^-$.

- Group 7 elements as monoanions resemble neutral group 8 derivatives: $[M(CO)_5]^-$ (M = Mn, Tc, Re).
- Group 8 elements as dianions resemble neutral group 10 derivatives: $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os). Condensed derivatives are also known.
- Group 9 elements as monoanions resemble neutral group 10 metal carbonyl. $[Co(CO)_4]^-$ is the best studied member.

Large anionic clusters of Ni, Pd, and Pt are also well known.

Cationic binary metal carbonyls

- Group 7 elements as monocations resemble neutral group 6 derivative $[M(CO)_6]^+$ (M = Mn, Tc, Re).
- Group 8 elements as dications also resemble neutral group 6 derivatives $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os).

Metal carbonyl hydrides

Metal Carbonyl hydride	pK _a
HCo(CO) ₄	"strong"
HCo(CO) ₃ (P(OPh) ₃)	5.0
HCo(CO) ₃ (PPh ₃)	7.0
HMn(CO) ₅	7.1
H ₂ Fe(CO) ₄	4.4, 14

Metal carbonyls are relatively distinctive in forming complexes with negative oxidation states. Examples include the anions discussed above. These anions can be protonated to give the corresponding metal carbonyl hydrides. The neutral metal carbonyl hydrides are often volatile and can be quite acidic.

Applications



Spheres of nickel manufactured by the Mond process

Metallurgical uses

Metal carbonyls are used in several industrial processes. Perhaps the earliest application was the extraction and purification of nickel via nickel tetracarbonyl by the Mond process (see also carbonyl metallurgy).

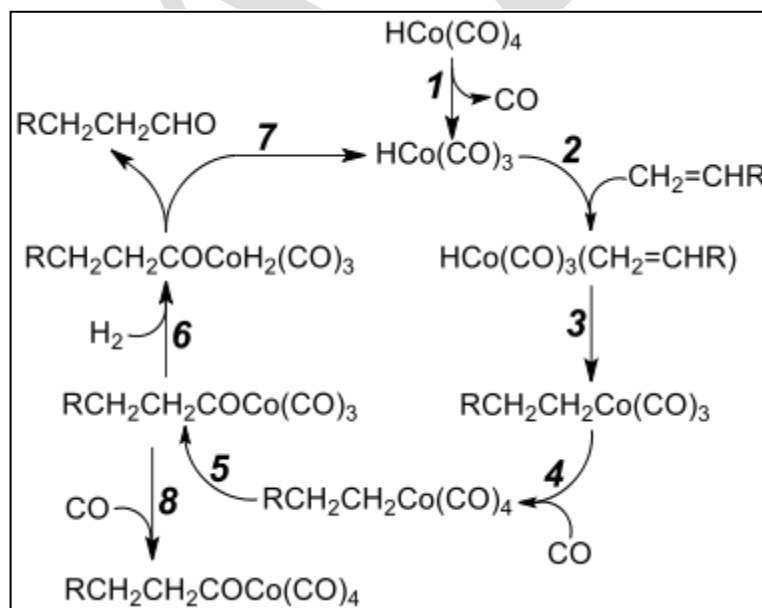
By a similar process carbonyl iron, a highly pure metal powder is prepared by thermal decomposition of iron pentacarbonyl. Carbonyl iron is used inter alia for the preparation of inductors, pigments, as dietary supplements,^[44] in the production of radar-absorbing materials in the stealth technology,^[45] and in Thermal spraying.

Catalysis

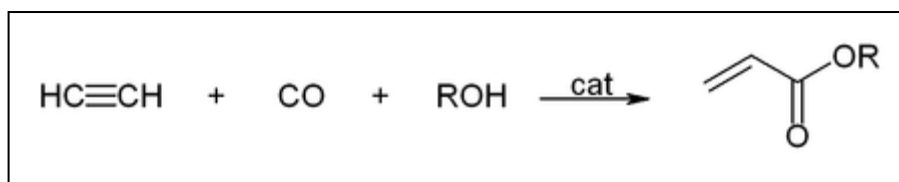
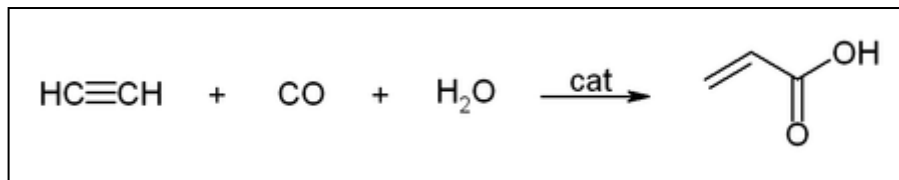
Metal carbonyls are used in a number of industrially important carbonylation reactions. In the oxo process, an olefin, dihydrogen, and carbon monoxide react together with a catalyst (e.g. dicobalt octacarbonyl) to give aldehydes. Illustrative is the production of butyraldehyde:



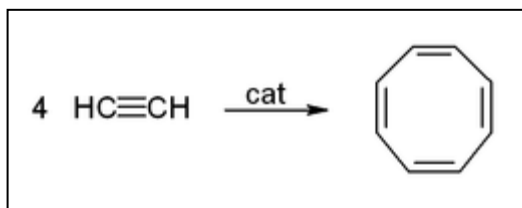
Butyraldehyde is converted on an industrial scale to 2-Ethylhexanol, a precursor to PVC plasticizers, by aldol condensation, followed by hydrogenation of the resulting hydroxyaldehyde. The "oxo aldehydes" resulting from hydroformylation are used for large-scale synthesis of fatty alcohols, which are precursors to detergents. The hydroformylation is a reaction with high atom economy, especially if the reaction proceeds with high regioselectivity.



Another important reaction catalyzed by metal carbonyls is the hydrocarboxylation. The example below is for the synthesis of acrylic acid and acrylic acid esters:



Also the cyclization of acetylene to cyclooctatetraene uses metal carbonyl catalysts:^[46]



In the Monsanto and Cativa processes, acetic acid is produced from methanol, carbon monoxide, and water using hydrogen iodide as well as rhodium and iridium carbonyl catalysts, respectively. Related carbonylation reactions afford acetic anhydride.

CO-releasing molecules (CO-RMs)

Carbon monoxide-releasing molecules are metal carbonyl complexes that are being developed as potential drugs to release CO. At low concentrations, CO functions as a vasodilatory and an anti-inflammatory agent. CO-RMs have been conceived as a pharmacological strategic approach to carry and deliver controlled amounts of CO to tissues and organs.^[47]

Related compounds

Many ligands are known to form homoleptic and mixed ligand complexes that are analogous to the metal carbonyls.

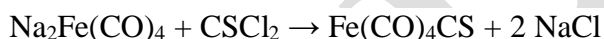
Nitrosyl complexes

Main article: metal nitrosyl complex

Metal nitrosyls, compounds featuring NO ligands, are numerous. In contrast to metal carbonyls, however, homoleptic metal nitrosyls are rare. NO is a stronger pi-acceptor than CO. Well known nitrosyl carbonyls include $\text{CoNO}(\text{CO})_3$ and $\text{Fe}(\text{NO})_2(\text{CO})_2$, which are analogues of $\text{Ni}(\text{CO})_4$.

Thiocarbonyls complexes

Complexes containing CS are known but are uncommon. The rarity of such complexes is attributable in part to the fact that the obvious source material, carbon monosulfide, is unstable. Thus, the synthesis of thiocarbonyl complexes requires more elaborate routes, such as the reaction of disodium tetracarbonylferrate with thiophosgene:



Complexes of CSe and CTe are very rare.

Phosphine complexes

All metal carbonyls undergo substitution by organophosphorus ligands. For example, the series $\text{Fe}(\text{CO})_{5-x}(\text{PR}_3)_x$ is well known for various phosphine ligands for $x = 1, 2$, and 3 . PF_3 behaves similarly but is remarkable because it readily forms homoleptic analogues of the binary metal carbonyls. For example, the volatile, stable complexes $\text{Fe}(\text{PF}_3)_5$ and $\text{Co}_2(\text{PF}_3)_8$ represent CO-free analogues of $\text{Fe}(\text{CO})_5$ and $\text{Co}_2(\text{CO})_8$ (unbridged isomer).

Isocyanide complexes

Isocyanides also form extensive families of complexes that are related to the metal carbonyls. Typical isocyanide ligands are methyl and t-butyl isocyanides (Me_3CNC). A special case is CF_3NC , an unstable molecule that forms stable complexes whose behavior closely parallels that of the metal carbonyls.

Toxicology

The toxicity of metal carbonyls is due to toxicity of carbon monoxide, the metal, and because of the volatility and instability of the complexes. Exposure occurs by inhalation, or for liquid metal carbonyls by ingestion or due to the good fat solubility by skin resorption. Most clinical experience were gained from toxicological poisoning with nickel carbonyl and iron pentacarbonyl. Nickel carbonyl is considered as one of the strongest inhalation poisons.

Inhalation of nickel carbonyl causes acute non-specific symptoms similar to a carbon monoxide poisoning as nausea, cough, headaches, fever and dizziness. After some time, severe pulmonary symptoms such as cough, tachycardia cyanosis or problems in the gastrointestinal tract occur. In addition to pathological alterations of the lung, such as by metalation of the alveoli, damages are observed in the brain, liver, kidneys, adrenal glands and the spleen. A metal carbonyl poisoning often requires a long-lasting recovery.

Chronic exposure by inhalation of low concentrations of nickel carbonyl can cause neurological symptoms such as insomnia, headaches, dizziness and memory loss. Nickel carbonyl is considered carcinogenic, but it can take 20 to 30 years from the start of exposure to the clinical manifestation of cancer.

Initial experiments on the reaction of carbon monoxide with metals were carried out by Justus von Liebig in 1834. By passing carbon monoxide over molten potassium he prepared a substance having the empirical formula KCO, which he called *Kohlenoxidkalium*. As demonstrated later, the compound was not a metal carbonyl, but the potassium salt of hexahydroxy benzene and the potassium salt of dihydroxy acetylene

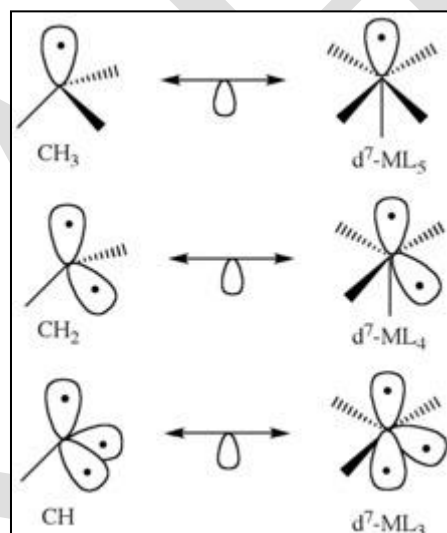
The synthesis of the first true heteroleptic metal carbonyl complex was performed by Paul Schützenberger in 1868 by passing chlorine and carbon monoxide over platinum black, where dicarbonyldichloroplatinum ($\text{Pt}(\text{CO})_2\text{Cl}_2$) was formed.

Ludwig Mond, one of the founders of Imperial Chemical Industries, investigated in the 1890s with Carl Langer and Friedrich Quincke various processes for the recovery of chlorine which was lost in the Solvay process by nickelmetals, oxides and salts. As part of their experiments the group treated nickel with carbon monoxide. They found that the resulting gas colored the gas flame of a burner in a greenish-yellowish color; when heated in a glass tube it formed a nickel mirror. The gas could be condensed to a colorless, water-clear liquid with a boiling point of 43 °C. Thus, Mond and his coworker had discovered the first pure, homoleptic metal carbonyl, nickel tetracarbonyl($\text{Ni}(\text{CO})_4$). The unusual high volatility of the metal compound nickel tetracarbonyl led Kelvin with the statement that Mond had "given wings to the heavy metals".

The following year, Mond and Marcellin Berthelot independently discovered iron pentacarbonyl, which is produced by a similar procedure as nickel tetracarbonyl. Mond recognized the economic potential of this class of compounds, which he commercially used in the Mond process and financed more research on related compounds. Heinrich Hirtz and his colleague M. Dalton Cowap synthesized metal carbonyls of cobalt, molybdenum, ruthenium, and diiron nonacarbonyl. In 1906 James Dewar and H. O. Jones were able to determine the structure of di-iron nonacarbonyl, which is produced from iron pentacarbonyl by the action of sunlight.^[60] After Mond, who died in 1909, the chemistry of metal carbonyls fell for several years in oblivion. The BASF started in 1924 the industrial production of iron pentacarbonyl by a process which was developed by Alwin Mittasch. The iron pentacarbonyl was used for the production of high-purity iron, so-called carbonyl iron, and iron oxide pigment.^[32] Not until 1927 did A. Job and A. Cassal succeed in the preparation of chromium hexacarbonyl and tungsten hexacarbonyl, the first synthesis of other homoleptic metal carbonyls.

Walter Hieber played in the years following 1928 a decisive role in the development of metal carbonyl chemistry. He systematically investigated and discovered, among other things, the Hieber base reaction, the first known route to metal carbonyl hydrides and synthetic pathways leading to metal carbonyls such as dirhenium decacarbonyl. Hieber, who was since 1934 the Director of the Institute of Inorganic Chemistry at the Technical University Munich published in four decades 249 papers on metal carbonyl chemistry.

Also in the 1930s Walter Reppe, an industrial chemist and later board member of the BASF, discovered a number of homogeneous catalytic processes, such as the hydrocarboxylation, in which olefins or alkynes react with carbon monoxide and water to form products such as unsaturated acids and their derivatives. In these reactions, for example, nickel carbonyl or cobalt carbonyls act as catalysts. Reppe also discovered the cyclotrimerization and tetramerization of acetylene and its derivatives to benzene and benzene derivatives with metal carbonyls as catalysts. BASF built in the 1960s a production facility for acrylic acid by the Reppe process, which was only superseded in 1996 by more modern methods based on the catalytic propylene oxidation.



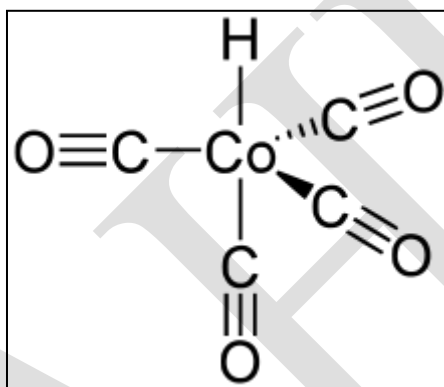
Isolobal fragments with tetrahedral or octahedral geometry

For the rational design of new complexes the concept of the isolobal analogy has been found useful. Roald Hoffmann was awarded with the Nobel Prize in chemistry for the development of the concept. The concept describes metal carbonyl fragments of $M(CO)_n$ as parts of octahedral building blocks in analogy to the tetrahedral $CH_3\cdot$, $CH_2\cdot$ or $CH\cdot$ fragments in organic chemistry. In example Dimanganese decacarbonyl is formed in terms of the isolobal analogy of two $d^7Mn(CO)_5$ fragments, that are isolobal to the methyl radical $CH_3\cdot$. In

analogy to how methyl radicals combine to form Ethane, these can combine to dimanganese decacarbonyl. The presence of isolobal analog fragments does not mean that the desired structures can be synthesized. In his Nobel Prize lecture Hoffmann emphasized that the isolobal analogy is a useful but simple model, and in some cases does not lead to success.^[63]

The economic benefits of metal-catalysed carbonylations, e.g. Reppe chemistry and hydroformylation, led to growth of the area. Metal carbonyl compounds were discovered in the active sites of three naturally occurring enzymes.

Metal carbonyl hydride

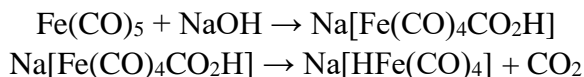


Cobalt tetracarbonyl hydride

Metal carbonyl hydrides are complexes of transition metals with carbon monoxide and hydride as ligands. These complexes are useful in organic synthesis as catalysts in homogeneous catalysis, such as hydroformylation.

Preparation

Walter Hieber prepared the first metal carbonyl hydride in 1931 by the so-called Hieber base reaction of metal carbonyls. In this reaction a hydroxide ion reacts with the carbon monoxide ligand of a metal carbonyl such as iron pentacarbonyl in a nucleophilic attack to form a metallacarboxylic acid. This intermediate releases carbon dioxide in a second step, giving the iron tetracarbonyl hydride anion. The synthesis of cobalt tetracarbonyl hydride ($\text{HCo}(\text{CO})_4$) proceeds in the same way.



A further synthetic route is the reaction of the metal carbonyl with hydrogen. The protonation of metal carbonyl anions, e.g. $[\text{Co}(\text{CO})_4]^-$, leads also to the formation of metal carbonyl hydrides.

Properties

The neutral metal carbonyl can be quite acidic. The C-H bond is bounded to the metal. The bond length for cobalt is 114 pm, the metal-ligand bond length is 176 pm and 182 pm for the

Metal Carbonyl hydride	pK _a
HCo(CO) ₄	"strong"
HCo(CO) ₃ (P(OPh) ₃)	5.0
HCo(CO) ₃ (PPh ₃)	7.0
HMn(CO) ₅	7.1
H ₂ Fe(CO) ₄	4.4, 14
[HCo(dmgh) ₂ PBu ₃]	10.5

hydrides are often volatile and the hydrogen atom is directly bonded to the metal. The metal-hydrogen bond length is 176 pm and the carbon bond length is 182 pm for axial and equatorial ligands.

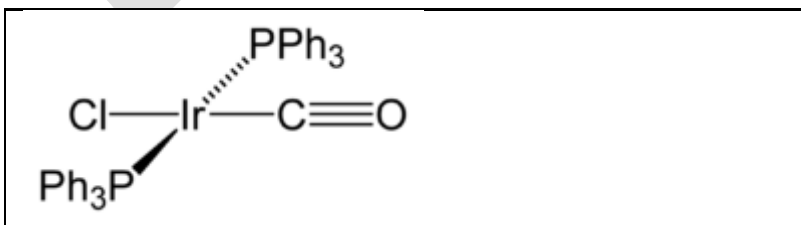
Applications

Metal carbonyl hydride are used as catalysts in the hydroformylation of olefins. Under industrial conditions the catalyst is usually formed *in situ* in a reaction of a metal salt precursor with the syngas. The hydroformylation starts with the generation of a coordinatively unsaturated 16-electron metal carbonyl hydride complex like HCo(CO)₃ or HRh(CO)(PPh₃)₂ by dissociation of a ligand. Such complexes bind olefins in a first step via π -complexation. In a second step an alkyl complex is formed by insertion of the olefin into the metal-hydrogen bond, leading once again to a 16-electron species. This complex can bind another carbon monoxide, which can insert into the metal-carbon bond of the alkyl ligand to form an acyl complex. By oxidative addition of hydrogen and elimination of the aldehyde the initial metal carbonyl hydride complex is regenerated.

Analytical characterization

It has been uncertain for a long time whether metal carbonyl hydrides contain a direct metal-hydrogen bond, although this has been suspected by Hieber for H₂Fe(CO)₄. The precise structure cannot be identified by X-ray diffraction, particularly the length of a possible metal-hydrogen bond remained uncertain. The exact structure of the metal carbonyl hydrides has been determined by using neutron diffraction and nuclear magnetic resonance spectroscopy.

Vaska's complex

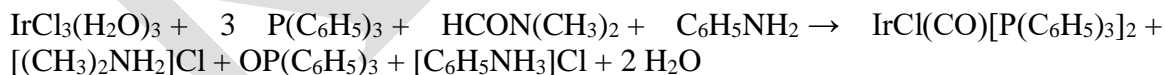


Names	
IUPAC name (<i>SP-4-1</i>)-carbonylchloridobis(triphenylphosphane)iridium(I)	
Other names Iridium(I)bis(triphenylphosphine) carbonyl chloride Vaska's complex Vaska's compound	
Other anions	$\text{IrI}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$
Other cations	$\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$
Related compounds	$\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$

Vaska's complex is the trivial name for the chemical compound *trans*-carbonylchlorobis(triphenylphosphine)iridium(I), which has the formula $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$. This square planar diamagnetic organometallic complex consists of a central iridium atom bound to two mutually *trans* triphenylphosphine ligands, carbon monoxide, and a chloride ion. The complex was first reported by J. W. DiLuzio and Lauri Vaska in 1961. Vaska's complex can undergo oxidative addition and is notable for its ability to bind to O_2 reversibly. It is a bright yellow crystalline solid.

Preparation

The synthesis involves heating virtually any iridium chloride salt with triphenylphosphine and a carbon monoxide source. The most popular method uses dimethylformamide (DMF) as a solvent, and sometimes aniline is added to accelerate the reaction. Another popular solvent is 2-methoxyethanol. The reaction is typically conducted under nitrogen. In the synthesis, triphenylphosphine serves as both a ligand and a reductant, and the carbonyl ligand is derived by decomposition of dimethylformamide, probably via a deinsertion of an intermediate $\text{Ir-C}(\text{O})\text{H}$ species. The following is a possible balanced equation for this complicated reaction.



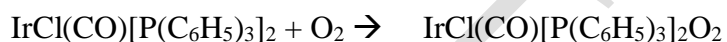
Typical sources of iridium used in this preparation are $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ and H_2IrCl_6 .

Reactions

Studies on Vaska's complex helped provide the conceptual framework for homogeneous catalysis. Vaska's complex, with 16 valence electrons, is considered "coordinatively unsaturated" and can thus bind to one two-electron or two one-electron ligands to become electronically saturated with 18 valence electrons. The addition of two one-electron ligands is called oxidative

addition. Upon oxidative addition, the oxidation state of the iridium increases from Ir(I) to Ir(III). The four-coordinated square planar arrangement in the starting complex converts to an octahedral, six-coordinate product. Vaska's complex undergoes oxidative addition with conventional oxidants such as halogens, strong acids such as HCl, and other molecules known to react as electrophiles, such as iodomethane (CH₃I).

Vaska's complex binds O₂ reversibly:



The dioxygen ligand is bonded to Ir by both oxygen atoms, so-called side-on bonding. In myoglobin and hemoglobin, by contrast, O₂ binds end-on, attaching to the metal via only one of the two oxygen atoms. The resulting dioxygen adduct reverts to the parent complex upon heating or purging the solution with an inert gas, signaled by a colour change from orange back to yellow.

Spectroscopy

Infrared spectroscopy can be used to analyse the products of oxidative addition to Vaska's complex because the reactions induce characteristic shifts of the stretching frequency of the coordinated carbon monoxide. These shifts are dependent on the amount of π -back bonding allowed by the newly associated ligands. The CO stretching frequencies for Vaska's complex and oxidatively added ligands have been documented in the literature. Vaska's complex: 1967 cm⁻¹

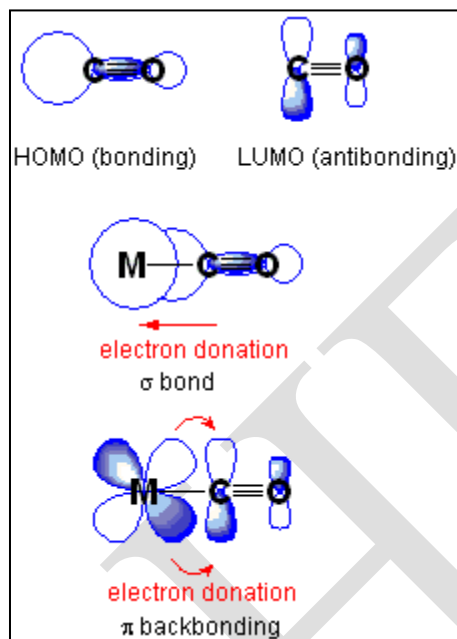
- Vaska's complex + O₂: 2015 cm⁻¹
- Vaska's complex + MeI: 2047 cm⁻¹
- Vaska's complex + I₂: 2067 cm⁻¹

Oxidative addition to give Ir(III) products reduces the π -bonding from Ir to C, which causes the increase in the frequency of the carbonyl stretching band. The stretching frequency change depends upon the ligands that have been added, but the frequency is always greater than 2000 cm⁻¹ for an Ir(III) complex.

Metal nitrosyl complex

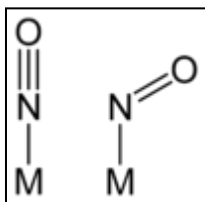
Metal nitrosyl complexes are complexes that contain nitric oxide, NO, bonded to a transition metal. Many kinds of nitrosyl complexes are known, which vary both in structure and coligand.

Bonding and structure



(Top) the HOMO and LUMO of CO. (Middle) Sigma bond. (Bottom) Back-bond.

Most complexes containing the NO ligand can be viewed as derivatives of the nitrosyl cation, NO^+ . The nitrosyl cation is isoelectronic with carbon monoxide, thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in carbonyl complexes. The nitrosyl cation serves as a two-electron donor to the metal and accepts electrons from the metal via back-bonding. The compounds $\text{Co}(\text{NO})(\text{CO})_3$ and $\text{Ni}(\text{CO})_4$ illustrate the analogy between NO^+ and CO. Similarly, two NO groups are isoelectronic with three CO groups. This trend is illustrated by the isoelectronic pair $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $[\text{Ni}(\text{CO})_4]$. These complexes are isoelectronic and, incidentally, both obey the 18-electron rule. The formal description of nitric oxide as NO^+ does not match certain measurable and calculated properties. In an alternative description, nitric oxide serves as a 3-electron donor, and the metal-nitrogen interaction is a triple bond.



Linear and bent M-NO bonds

Linear vs bent nitrosyl ligands

The M-N-O unit in nitrosyl complexes is usually linear, or no more than 15° from linear. In some complexes, however, especially when back-bonding is less important, the M-N-O angle can strongly deviate from 180° . In such cases, the NO ligand is sometimes described as the anion, NO^- . Prototypes for such compounds are the organic nitroso compounds, such as nitrosobenzene. A complex with a bent NO ligand is *trans*- $[\text{Co}(\text{en})_2(\text{NO})\text{Cl}]^+$. Trends in structure and bonding are usually analyzed using the Enemark-Feltham approach. In their framework, the factor that determines the bent vs linear NO ligands in octahedral complexes is the sum of electrons of pi-symmetry. Complexes with "pi-electrons" in excess of 6 tend to have bent NO ligands. Thus, $[\text{Co}(\text{en})_2(\text{NO})\text{Cl}]^+$, with seven electrons of pi-symmetry (six in t_{2g} orbitals and one on NO), adopts a bent NO ligand, whereas $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$, with six electrons of pi-symmetry, adopts a linear nitrosyl.

Linear and bent NO ligands can be distinguished using infrared spectroscopy. Linear M-N-O groups absorb in the range $1525\text{--}1690\text{ cm}^{-1}$, whereas bent nitrosyls absorb in the range $1650\text{--}1900\text{ cm}^{-1}$. The differing vibrational frequencies reflect the differing N-O bond orders for linear (triple bond) and bent NO (double bond).

Bridging nitrosyl ligands

Nitric oxide can also serve as a bridging ligand. In the compound $[\text{Mn}_3(\eta^5\text{C}_5\text{H}_5)_3(\mu_2\text{-NO})_3(\mu_3\text{-NO})]$, three NO groups bridge two metal centres and one NO group bridge to all three.

Enemark-Feltham notation

The Enemark-Feltham notation is used to describe the number of d-type electrons present in a complex. It is deliberately ambiguous, because the true oxidation state of a metal coordinated by non-innocent ligands is often unclear. When written with this notation, the d-electron count is always consistent no matter how the nitrosyl ligands are treated (i.e. NO^+ , NO^\cdot , or NO^-).

To illustrate its use, the {MNO} d-electron count of the $[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$ anion is shown. In this example, the cyanide ligands are "innocent", i.e., they have a charge of -1 each, -5 total. To balance the fragment's overall charge, the charge on {CrNO} is thus $+2$ ($-3 = -5 + 2$). Using the neutral electron counting scheme, Cr has 6 d electrons and NO^\cdot has one electron for a total of 7. Two electrons are subtracted to take into account that fragment's overall charge of $+2$, to give 5. Written in the Enemark-Feltham notation, the d electron count is $\{\text{CrNO}\}^5$. The results are exactly the same if the nitrosyl ligand were considered NO^+ or NO^- .

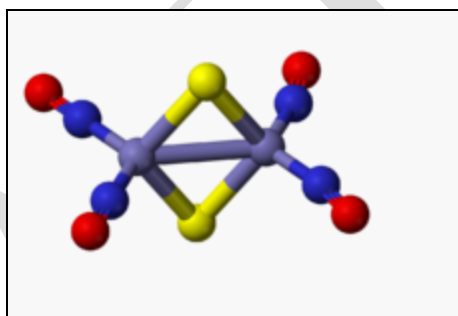
Representative classes of compounds

Homoleptic nitrosyl complexes

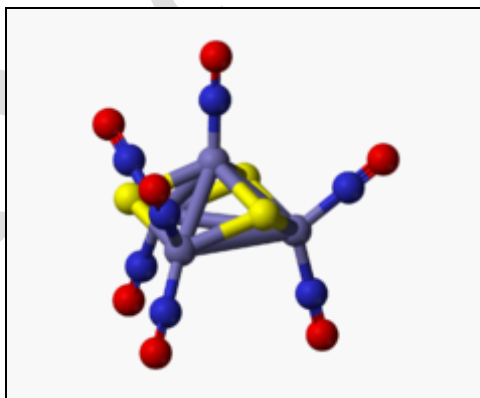
Metal complexes containing only nitrosyl ligands are called isoelectronic nitrosyls. They are rare, the premier member being $\text{Cr}(\text{NO})_4$. Even trinitrosyl complexes are uncommon, whereas polycarbonyl complexes are routine.

Roussin red and black salts

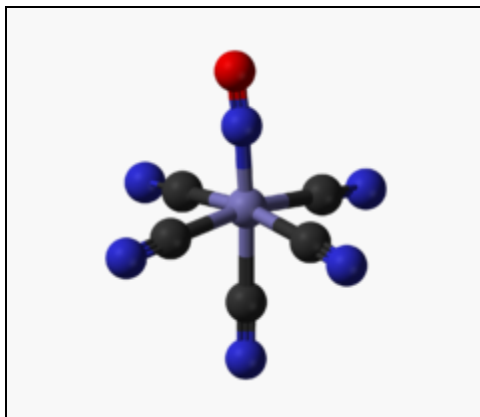
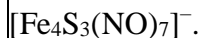
One of the earliest examples of a nitrosyl complex to be synthesized is Roussin's red salt, which is a sodium salt of the anion $[\text{Fe}_2(\text{NO})_4\text{S}_2]^{2-}$. The structure of the anion can be viewed as consisting of two tetrahedra sharing an edge. Each iron atom is bonded linearly to two NO^+ ligands and shares two bridging sulfido ligands with the other iron atom. Roussin's black salt has a more complex cluster structure. The anion in this species has the formula $[\text{Fe}_4(\text{NO})_7\text{S}_3]^-$. It has C_{3v} symmetry. It consists of a tetrahedron of iron atoms with sulfide ions on three faces of the tetrahedron. Three iron atoms are bonded to two nitrosyl groups. The iron atom on the threefold symmetry axis has a single nitrosyl group which also lies on that axis.



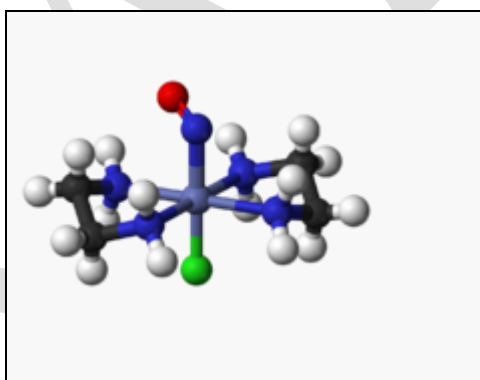
The anion in Roussin's Red Salt,
 $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$.



The anion in Roussin's black salt,



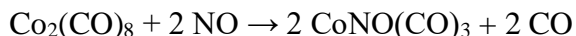
The nitroprusside anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, an octahedral complex containing a "linear NO" ligand.



trans- $[\text{Co}(\text{en})_2(\text{NO})\text{Cl}]^+$, an octahedral complex containing a "bent NO" ligand.

Preparation

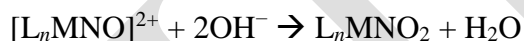
Nitrosyl complexes can be prepared by many routes. Direct formation from nitric oxide is common. The nitrosylation of cobalt carbonyl is illustrative:



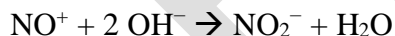
In such approaches one must guard against the tendency of nitric oxide to be oxidized by air. Replacement of ligands by the nitrosyl cation may be accomplished using nitrosyl tetrafluoroborate, $[\text{NO}][\text{BF}_4]$. Other indirect methods are indirect with the NO group deriving from some other species, often accompanied by oxidation and reduction reactions. A classic example is provided by the brown ring test in which the nitrate ion is the source of a nitric oxide ligand. Nitrosyl chloride is also useful, being applicable to $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$.

Reactions

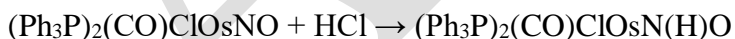
An important reaction is the acid/base equilibrium:



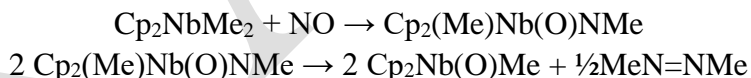
This equilibrium serves to confirm that the linear nitrosyl ligand is, formally, NO^+ , with nitrogen in the oxidation state +3



Since nitrogen is more electronegative than carbon, metal-nitrosyl complexes tend to be more electrophilic than related metal carbonyl complexes. Nucleophiles often add to the nitrogen. The nitrogen atom in bent metal nitrosyls is basic, thus can be oxidized, alkylated, and protonated, e.g.:



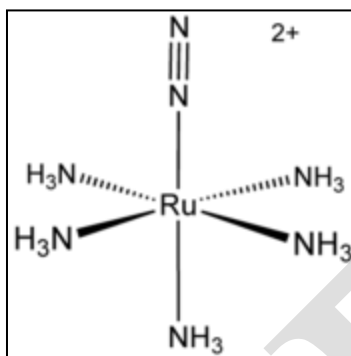
In rare cases, NO is cleaved by metal centers:



Applications

Metal-catalyzed reactions of NO are not commonly synthetically useful. Nitric oxide is however an important signalling molecule in nature and this fact is the basis of the most important applications of metal nitrosyls. The nitroprusside anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, a mixed nitrosyl cyano complex, has pharmaceutical applications as a slow release agent for NO. The signalling function of NO is effected via its complexation to haeme proteins, where it binds in the bent geometry.

Transition metal dinitrogen complex:



Structure of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$.

Metal dinitrogen complexes are coordination compounds that contain the dinitrogen molecule (N_2) as a ligand. In the area of coordination chemistry, the atomic and diatomic forms of nitrogen are distinguished, although otherwise "nitrogen" refers to N_2 .

Metal complexes of N_2 have been studied since 1965 when the first complex was reported by Allen and Senoff. This complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ was synthesised from hydrazine hydrate and ruthenium trichloride and consists of a $16e^- [\text{Ru}(\text{NH}_3)_5]^{2+}$ centre attached to one end of N_2 . Interest in such complexes arises because N_2 comprises the majority of the atmosphere and because many useful compounds contain nitrogen atoms. Biological nitrogen fixation probably occurs via the binding of N_2 to a metal center in the enzyme nitrogenase, followed by a series of steps that involve electron transfer and protonation. The hydrogenation of N_2 is only weakly exothermic, hence the industrial hydrogenation of nitrogen via the Haber-Bosch Process employs high pressures and high temperatures.

Bonding modes

In terms of its bonding to transition metals, N_2 is related to CO and acetylene as all three species have triple bonds. A variety of bonding modes have been characterized.

End-on

As a ligand, N_2 usually binds to metals as an "end-on" ligand, as illustrated by Allen and Senoff's complex. Such complexes are usually analogous to related CO derivatives. A good example of this relationship are the complexes $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$. Few complexes contain more than one N_2 ligand, and no example features three (in contrast metal hexacarbonyls are common). The dinitrogen ligand in $\text{W}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ can be reduced to produce ammonia.

An end-on complex also containing a hydride ligand is $[\text{FeH}(\text{N}_2)(\text{dmpe})_2]^+$. This cation undergoes deprotonation to form a $\text{Fe}(\text{N}_2)(\text{dmpe})_2$ which reacts with hydrogen chloride to give ammonium.

Bridging, end-on

N_2 also serves as a bridging ligand, as illustrated by $\{[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-N}_2)\}^{4+}$.

A study in 2006 of iron-dinitrogen complexes showed that the N–N bond is significantly weakened upon complexation with iron atoms with a low coordination number. The complex involved bidentate chelating ligands attached to the iron atoms in the Fe–N–N–Fe core, in which N

2 acts as a bridging ligand between the iron atoms. Increasing the coordination number of iron by modifying the chelating ligands and adding another ligand per iron atom showed an increase in the strength of the N–N bond in the resulting complex. It is thus suspected that Fe in a low-coordination environment is a key factor to the fixation of nitrogen by the nitrogenase enzyme, since its Fe–Mo cofactor also features Fe with low coordination numbers.

Side-on, bridging

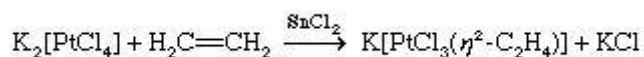
In a second mode of bridging, bimetallic complexes are known wherein the N–N vector is perpendicular to the M–M vector. One example is $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$. The dimetallic complex $\{(\text{C}_5\text{HMe}_4)_2\text{Zr}\}_2\{\mu\text{-}\eta^2\text{-N}_2\}$ reacts with H_2 . A related ditantalum tetrahydride complexes also reduce the N_2 .

Reactivity

Some metal-dinitrogen complexes catalyze the hydrogenation of N_2 to ammonia. One such catalyst is the Mo(III) triamidoaminocomplex $\text{Mo}[(\text{HIPTN})_3\text{N}]$. This system utilizes reductants such as Cp^*_2Cr and protonating reagents such as 2,6-lutidinium salts. The reducing equivalents and protons are added stepwise. The cycle begins with N_2 coordinated to Mo in an end-on fashion. The oxidation state of molybdenum remains unchanged until the last step when it is oxidized from Mo(III) to Mo(IV). For the rest of the cycle, dinitrogen is bound to Mo via a double or a triple bond accompanied by the change in oxidation state of Mo from +4 to +5 and the release of 2 equivalents of ammonia gas. Another homogeneous catalytic system based on molybdenum (Figure 9) The precatalyst is a dinitrogen-bridged dimolybdenum complex bearing PNP(2,6-bis(di-*tert*-butyl phosphinomethyl) pyridine) ligand. Adding acid to the precatalyst leads to the splitting of dinitrogen bridged dimolybdenum complex and generates an inactive molybdenum hydride cation and an active molybdenum nitrogen adduct($\text{MoPNP}(\text{N}_2)$). The latter $\text{MoPNP}(\text{N}_2)$ can then undergo a full catalytic cycle with proton and electron addition to form ammonia. However this catalytic system needs a huge excess of cobaltocene (72 equiv) and $[\text{LutH}]\text{OTf}$ (96 equiv).

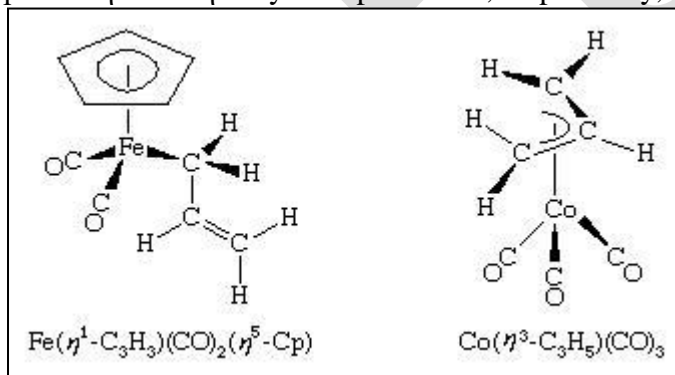
Alkene and alkyne ligands

An alkene ligand contains a π bond between carbon atoms, $C=C$, which can serve as an electron pair donor in a metal complex, as in the case of Zeise's salt (*see above* Historical developments). This complex may be prepared by bubbling ethylene, C_2H_4 , through an aqueous solution of $[PtCl_4]^{2-}$ in the presence of divalent tin, $Sn(II)$, which aids in the removal of the chloride ion (Cl^-) from the coordination sphere of the divalent platinum, $Pt(II)$.

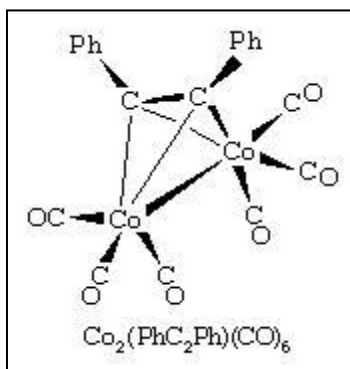


The alkene ligand bonds to the metal centre by both electron donation and acceptance, similar to the situation with carbon monoxide. Electron donor-and-acceptor character between the metal and the alkene ligand appear to be fairly evenly balanced in most ethylene complexes of the d metals.

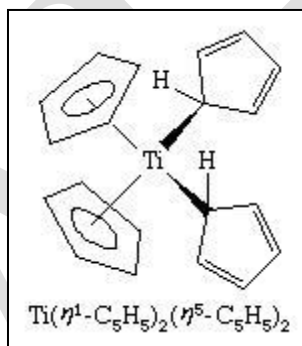
The allyl ligand, $-CH_2-CH=CH_2$, can bind to a metal atom in either of two configurations: as an η^1 -ligand or an η^3 -ligand. Because of this versatility in bonding, η^3 -allyl complexes are often highly reactive. Examples of η^1 - and η^3 -allyl complexes are, respectively, shown here.



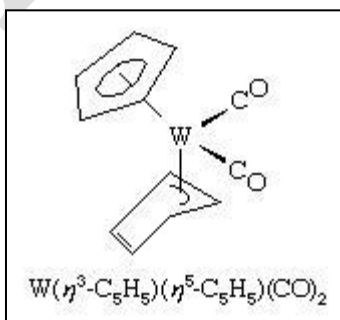
Acetylene, $H-C\equiv C-H$, has two π bonds and hence is a potential four-electron donor. Substituted acetylenes form very stable polynuclear complexes in which the acetylene can be regarded as a four-electron donor. An example is η^2 -diphenylethynehexacarbonyldicobalt, in which four of the six electrons in the triple bond of the ethyne ligand, $R-C\equiv C-R$, are shared with the two cobalt atoms (Ph represents the phenyl ligand, $-C_6H_5$). As in this example, the alkyl or aryl groups (R) on the acetylene impart stability to the metal complex—in contrast to simple acetylene ($HC\equiv CH$) complexes, where the hydrogen atoms are reactive.



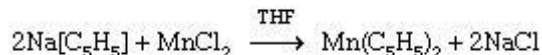
The cyclopentadienyl ligand (C_5H_5 , abbreviated Cp) has played a major role in the development of organometallic chemistry. In some metal cyclopentadienyl compounds, the metal is bonded to only one of the five carbon atoms, and in these complexes the Cp is designated as a monohapto, η^1 -, ligand, which contributes one electron to form a σ bond with the metal, as in



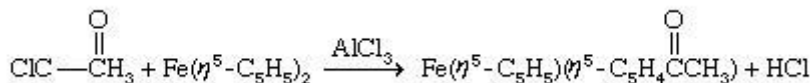
Others contain a trihapto (η^3 -) cyclopentadienyl ligand, which donates three electrons. The most common case, however, is when Cp is a pentahapto ligand contributing five electrons. Two of the bonding modes for Cp are illustrated in the following structure, which contains both η^3 - and η^5 - C_5H_5 ligands.



The bis(η^5 -cyclopentadienyl)-sandwich complexes of iron, cobalt, and nickel are readily prepared by the reaction of sodium cyclopentadienide with the corresponding *d*-metal halide.

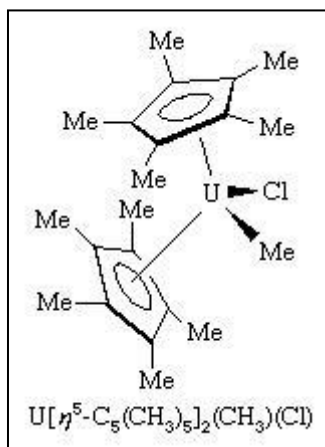


Because of their great stabilities, the 18-electron group-8 compounds ferrocene, ruthenocene, and osmocene maintain their ligand-metal bonds under rather harsh conditions, and it is possible to carry out a variety of reactions on the cyclopentadienyl ligands while they are attached to the central metal. In some cases, they undergo reactions similar to those of simple aromatic hydrocarbons, such as Friedel-Crafts substitution, which is a characteristic reaction of benzene, C_6H_6 .



It is also possible to replace the hydrogen atom on a C_5H_5 ring with a lithium atom using the highly reactive reagent butyllithium. $\text{LiC}_4\text{H}_9 + \text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2 \rightarrow \text{Fe}(\eta^5-\text{C}_5\text{H}_5)(\eta^5-\text{C}_5\text{H}_4\text{Li}) + \text{C}_4\text{H}_{10}$ This lithiated product is an excellent starting material for the synthesis of other ring-substituted products.

A closely related set of so-called bent sandwich compounds, in which the Cp rings are not parallel, are important in the organometallic chemistry of the early and middle *d*-block elements and the *f*-block elements (lanthanoids and actinoids). The Schrock carbene $\text{Ta}(\eta^5-\text{C}_5\text{H}_5)_2(\text{CH}_3)(\text{CH}_2)$, shown above, is one such example. Bent sandwich compounds are important in the organometallic chemistry of the *f*-block elements, but to achieve stability the pentamethylcyclopentadienyl ligand, $\text{C}_5(\text{CH}_3)_5$, is generally employed with these elements, as, for example, in the following uranium compound.



References:

Text Book:

T1. Huheey, J.E., E.A. Keitler, & R.L. Keitler, 2012. Inorganic chemistry, Vol-IV, Pearson Education, Singapore.

T2. Cotton, F. A., & G. Wilkinson, 2003, Advanced inorganic chemistry, John Wiley & sons, New York

Website Address:

https://en.wikipedia.org/wiki/Vaska%27s_complex

https://en.wikipedia.org/wiki/Transition_metal_dinitrogen_complex

Possible Questions:

Part-A

Each question carries one mark:

1. The Carbonyls which contain more than one metallic atoms are known as ----

a. Polydentate

b. Polynuclear

- c. Bidentate
- d. Mononuclear

2. $[\text{MnRe}(\text{CO})_9]$ is an example for

- a. Mononuclear Carbonyl
- b. Homonuclear
- c. **Heteronuclear**
- d. None

3. When Fe is directly reacted with CO at 200°C , 100 atm. pressure it gives

- a. $\text{Fe}(\text{CO})_8$
- b. $\text{Fe}(\text{CO})_3$
- c. $\text{Fe}(\text{CO})_6$
- d. **$\text{Fe}(\text{CO})_5$**

4. When Ni reacted directly with CO at 200°C , 100 atm. pressure it gives

- a. $\text{Ni}(\text{CO})_8$
- b. **$\text{Ni}(\text{CO})_4$**
- c. $\text{Ni}(\text{CO})_5$
- d. $\text{Ni}(\text{CO})_6$

5. The hybridization involved in the complex $[\text{Ni}(\text{CO})_4]$ is

- a. **sp^3**
- b. sp^2
- c. dsp^2
- d. dsp^3

6. Which one is an example for binuclear complex

- a. $\text{Mn}_2(\text{CO})_8$
- b. **$\text{Mn}_2(\text{CO})_{10}$**
- c. $\text{Mn}(\text{CO})_{10}$
- d. $\text{Mn}_2(\text{CO})_6$

7. Which one is an example for Trinuclear carbonyl

- a. **$\text{Fe}_3(\text{CO})_{12}$**
- b. $\text{Co}(\text{CO})_{12}$
- c. $\text{Fe}_2(\text{CO})_{12}$
- d. $\text{Fe}(\text{CO})_{12}$

8.The anionic carbonyl complexes are known as -----

- a. Carbonium ion
- b. carbonylate ions**
- c. Carbanion
- d. carbenium ion

9.Example for carbonylate ion is

- a. $[\text{Co}(\text{CO})_{12}]$
- b. $[\text{Co}(\text{CO})_{12}]^{+}$
- c. $[\text{Mn}(\text{CO})_5]^{-}$**
- d. $[\text{Mn}(\text{CO})_5]^{+}$

10. $\text{Mn}_2(\text{CO})_{10} + \text{H}_2 \rightarrow$

- a. $2\text{Mn}(\text{CO})_5$
- b. $\text{Mn}(\text{CO})_{10}$
- c. $2\text{HMn}(\text{CO})_5$**
- d. $\text{Mn}(\text{CO})_5$

11.The allyl group which can function as an one electron donar is known as

- a. Monohapto**
- b. Dihapto
- c. Trihapto
- d. Tetra hapto

12.Geometry of $[\text{Cr}(\text{CO})_6]$ is

- a. Octahedral**
- b. Tetrahedral
- c. Square pyramidal
- d. Triangular bipyramidal

13.the total number of electrons present in the atom of the metal forming the complex , including those gained electrons by sharing in the formation of complex is called

- a. Effective atomic number**
- b. Effective molecular number
- c. Exclusive atomic number

d. None

14. The geometry of $\text{Fe}(\text{CO})_5$ is

a. Trigonal pyramidal

b. Trigonal bipyramidal

c. Square planar

d. tetrahedral

15. The magnetic property of $\text{V}(\text{CO})_6$ is

a. Diamagnetic

b. Paramagnetic

c. Ferromagnetic

d. None

16. The physical properties of the metal alkoxides depend on the ----- and ----- of the alkyl group

a. Size & Shape

b. Valency & Size

c. Shape & Valency

d. none

17. Alkynes are more electro negative than alkenes and are therefore better

a. π acceptors

b. π donar

c. σ acceptor

d. σ donar

18. In allyl complexes it can function as a three electron donar is called

a. monohapto

b. Dihapto

c. Trihapto

d. tetra hapto

19. In allyl complexes geometrical isomers are known which arise because of the position of ---- relative to other ligands

a. Central allyl carbon atom

b. terminal allyl carbon atom

c. Central metal atom

d. Carbon- carbon bond

20. The reaction of Vaska's complex with molecular hydrogen has a characteristic of an ----

- a. Reductive elimination
- b. Oxidative addition**
- c. Oxidative elimination
- d. None

Part-B

Each question carries six marks

1. Discuss the structure of metal carbonyls.
2. Write an account on carbonylate ions?
3. Write any two preparations of carbonyl hydrides.
4. Explain the nature of bonding in dinitrogen and oxygen complexes. Write briefly on the role of dinitrogen complexes in biological nitrogen fixation.
5. Give the properties, structure & advantages of Wilkinson's catalyst
6. What is Vaska's compound? Explain
7. Discuss the preparation properties and uses of nickel carbonyl compounds?

Part-C

Each question carries ten marks

1. Explain the significance of isolobal fragments, giving suitable examples
2. How do you prepare $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$? Give their structural formulae.
3. What are metal carbonyls and write the different types with examples
4. Describe the bonding in olefin metal complexes. How do you compare it with the bonding of metal carbonyls?
5. Explain the nature of bonding in carbonyl and oxygen complexes. Write the preparation of carbonyl hydrides and carbonyl halides.

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Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2018 onwards)
Department of Chemistry
II- semester

Inorganic Chemistry -II (Coordination Chemistry)

UNIT III- Objective Questions for online examination (Each carry 1 Marks)

Question	Option-a	Option-b	Option-c	Option-d	Answer
The Carbonyls which contain more than one metallic atoms are known as ----	Polydentate	Polynuclear	Bidentate	Mononuclear	Polynuclear
[MnRe(CO) ₉] is an example for	Mononuclear Carbonyl	Homonuclear	Heteronuclear	None	Heteronuclear
When Fe is directly reacted with CO at 200 ⁰ C,100 atm.pressure it gives	Fe(CO) ₈	Fe(CO) ₃	Fe(CO) ₆	Fe(CO) ₅	Fe(CO) ₅
When Ni reacted directly with CO at 200 ⁰ C,100 atm. pressure it gives	Ni(CO) ₈	Ni(CO) ₄	Ni(CO) ₅	Ni(CO) ₆	Ni(CO) ₄
When Co reacted directly with Co at 2000C,100 atm. pressure it gives	Co ₂ (CO) ₈ Co(CO) ₈		Co ₃ (CO) ₈	Co ₂ (CO) ₆	Co ₂ (CO) ₈ Co(CO) ₈
The hybridization involved in the complex [Ni(CO) ₄] is	sp ³	sp ²	dsp ²	dsp ³	sp ³
Which one is an example for binuclear complex	Mn ₂ (CO) ₈	Mn ₂ (CO) ₁₀	Mn(CO) ₁₀	Mn ₂ (CO) ₆	Mn ₂ (CO) ₁₀
Which one is an example for Trinuclear carbonyl	Fe ₃ (CO) ₁₂	Co(CO) ₁₂	Fe ₂ (CO) ₁₂	Fe (CO) ₁₂	Fe ₃ (CO) ₁₂
The anionic carbonyl complexes are known as -- ---	Carbonium ion	carbonylate ions	Carbanion	carbenium ion	carbonylate ions
Example for carbonylate ion is	[Co(CO) ₁₂]	[Co(CO) ₁₂] ⁺	[Mn(CO) ₅] ⁻	[Mn(CO) ₅] ⁺	[Mn(CO) ₅] ⁻

$\text{Mn}_2(\text{CO})_{10} + \text{H}_2 \rightarrow$	$2\text{Mn}(\text{CO})_5$ $\text{Mn}(\text{CO})_{10}$		$2\text{HMn}(\text{CO})_5$	$\text{Mn}(\text{CO})_5$	$2\text{HMn}(\text{CO})_5$
The allyl group which can function as an one electron donar is known as	Monohapto	Dihapto	Trihapto	Tetra hapto	Monohapto
Geometry of $[\text{Cr}((\text{CO})_6)]$ is	Octahetral	Tetrahetral	Square pyramidal	Triangular bipyramidal	Octahetral
the total number of electrons present in the atom of the metal forming the complex , including those gained electrons by sharing in the formation of complex is called	Effective atomic number	Effective molecular number	Exclusive atomic number	None	Effective atomic number
The geometry of $\text{Fe}(\text{CO})_5$ is	Trigonal pyramidal	Trigonal bipyramidal	Square planar	tetrahedral	Trigonal bipyramidal
The magnetic property of $\text{V}(\text{CO})_6$ is	Diamagetic	Paramagnetic	Ferromagnetic	None	Paramagnetic
The physical properties of the metal alkoxides depend on the ----- and ----- of the alkyl group	Size & Shape	Valency & Size	Shape & Valency	none	Size & Shape
Alkynes are more electro negative than alkenes and are therefore better	π acceptors	π donar	σ acceptor	σ donar	π acceptors
In allyl complexes it can function as a three electron donar is called	monohapto	Dihapto	Trihapto	tetra hapto	Trihapto
In allyl complexes geometrical isomers are known which arise because of the position of ---- relative to other ligands	Central allyl carbon atom	terminal allyl carbon atom	Central metal atom	Carbon- carbon bond	Central allyl carbon atom
The reaction of Vaskas complex with molecular hydrogen has a characteristic of an -----	Reductive elimination	Oxidative addition	Oxidative elimination	None	Oxidative addition
An example of oxidative addition is the reaction of ----- molecular hydrogen	Vaskas complex	Octahedral complex	tetrahedral complex	None	Vaskas complex

Vaska's compound absorbs oxygen and becomes --- colour	Yellow	Orange	Red violet	Green	Orange
$[\text{Rh}(\text{Cl})(\text{PPh}_3)_3]$ is called -----	Vaska's compound	Wilkinson's catalyst	Ziegler-Natta catalyst	None	Wilkinson's catalyst
Carbonyl hydride complexes are formed by the acidification of -----	Carbonylate ions	Carbenes	carbenes	Alkynes	Carbonylate ions
Which of the following act as hydride donors	BH_4	CH_3	C_2H_5	NaHSO_4	BH_4
Complexes with coordinated hydrogen atom are	Hydro compounds	Hydroxide	hydrochloride	Hydride	Hydride
Which does not form the source of hydrogen	NaH	BH_4	LiAlH_4	H_2O	H_2O
Metal hydride complexes act as	Retarding agents	Oxidising agents	reducing agents	Dehydrogenating agents	reducing agents
Double dihydro bridge are found in	B_2H_6	BH_4	NH_3	$\text{H}_2\text{Cr}(\text{CO})_5$	B_2H_6
When dinitrogen functions as a bridging ligand, it usually exhibits ----- coordination	End-on	Side-on	Axial	None	End-on
Anionic carbonyl halides are obtained when metal carbonyls are treated with	Carbonyl hydrides	Ionic halides	Radical halides	Nitrosyls	Ionic halides
The general formula for Carbonyl halides is	$\text{M}_x(\text{CO})_y\text{X}_2$	$\text{HM}_x(\text{CO})_y\text{X}_2$	$\text{M}_x(\text{CO})_y\text{N}_2$	MX_2	$\text{M}_x(\text{CO})_y\text{X}_2$
$\text{Mn}(\text{CO})_5\text{Cl}$ heated in organic solvents at 120°C it loses	CO_2	COCl_2	CO	MnCO_3	CO
Carbonyl halides react with NH_3 to form -----	Amines	Amides	Urea	Thiourea	Urea
Phosgene is also known as -----	Carbonyl bromide	Carbonyl chloride	Carbonyl iodide	Carbonyl fluoride	Carbonyl chloride

Carbonyl chloride is produced in large quantities to make -----	Benzene	Toluene	Xylene	Toluene di isocyanate	Toluene di isocyanate
Isocyanides are better sigma donar and poorer --- -- acceptor than carbonyl group complexes.	sigma acceptors	pi donars	pi acceptors	None	pi acceptors
Which one of the following is an important building block for the synthesis of many compounds?	Carboxyhemoglobin	Carbon monoxide	Carbonylate	Carbon-di-oxide	Carbon monoxide
Cyanide will preferentially leach sulfide minerals and will react with sulfur to produce ?	Thiocyanate	Potassium cyanide	Sulfocyanate	Hydrogen cyanide	Thiocyanate
Copper cyanides are ?	High stable	Less stable	Moderately stable	Stable	Moderately stable
HCN is highly soluable in ?	Salt solution	Sugar solution	Water	Starch	Water
Which one of the following salt has a more complex cluster structure?	Sodium salt	Black-T	Potassium salt	Roussin's black	Roussin's black
Metal carbonyls generally have poor solubility with ?	Water	Alcohol	Solvent	Alcohol	Water
The most important technique for characterizing metal carbonyls is ?	UV spectroscopy	Mass Spectroscopy	Infra-red spectroscopy	NMR spectroscopy	Infra-red spectroscopy
All metal carbonyls undergo substitution by ?	Organophosphorus ligands	Phosphine ligands	Ligands	Metal	Organophosphorus ligands
Typical isocyanide ligand is ?	CO	NO	MeNC	CN	MeNC
Metal nitrosyl complexes are complexes that contain ?	Nitric oxide	Nitrosyl	Metal	MeNC	Nitric oxide
Metal nitrosyls are?	Physically important	Mechanically important	Chemically important	Biologically important	Biologically important
Which one of the following is typically adopt one of two bonding modes?	Metal nitrosyl	NO	O ₂	MeNC	NO

NO ligands can arise by oxidative degradation of other ?	Nitrogen ligands	Carbon ligands	Oxygen ligands	Hydrogen ligands	Nitrogen ligands
Nitrogen is more electronegative than ?	Hydrogen	Oxygen	Carbon	NO	Carbon
The nitroprusside anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, a mixed nitrosyl cyano complex, has pharmaceutical applications as a slow release agent for ?	CN	Fe	NO	C	NO
Which one of the following is an ambidentate ligand?	NO	NO_2	Fe	CN	NO_2
Crystal field theory, introduced by Hans Bethe in ?	1929	1932	1931	1930	1929
Ligand field theory, introduced in ?	1934	1935	1936	1936	1935
Which one of the following is used for estimation of Ca^{2+} and Mg^{2+} in hard water?	<u>EDTA</u>	Zinc	Nickel	Copper	EDTA
Which one of the following is highly paramagnetic?	$[\text{Ni}(\text{CO})_4]$	$[\text{FeF}_6]^{3-}$	$[\text{Ni}(\text{CO})_4]$	$[\text{CoF}_6]^{3-}$	$[\text{CoF}_6]^{3-}$
The most stable metallocene -----	Sodium cyclopentadienide	Ferrocene	Thallium cyclopentadiene	nickel	Ferrocene

Lecture notes

UNIT 4

SYLLABUS

CARBOCYCLIC PI COMPLEXES

Cyclopentadienyl and related complexes, synthesis bonding structure and reaction. Arene complexes –complexes of biochemical importance; Cytochromes Hemoglobin, Myoglobin, Cyanocobalamin, Chlorophyll structure and functions

Carbocyclic pi complexes

Introduction:

Cyclopentadienyl moiety acts as an important “spectator” ligand and is quite ubiquitous in organometallic chemistry. It remains inert to most nucleophiles and electrophiles and solely engages in stabilizing organometallic complexes. The cyclopentadienyl ligands form a wide array of organometallic compounds exhibiting different formulations that begin with the so-called “piano stool” CpML_n ($n = 2, 3$ or 4) type ones and extends to the most commonly observed “metallocene” Cp_2M type ones to even go beyond further to the “bent metallocene” Cp_2MX_n ($n = 1, 2$ or 3) type ones. In the “piano stool” CpML_n structure, the cyclopentadienyl (Cp) ligand is regarded as the “seat” of the piano stool while the remaining L ligands are referred to as the “legs” of the piano stool. Though the cyclopentadienyl ligand often binds to metal in a η^5 (pentahapto) fashion, *e. g.* as in ferrocene, the other form of binding to metal at lower hapticities, like that of the η^3 (trihapto) binding *e. g.* as in $(\eta^5\text{-Cp})(\eta^3\text{-Cp})\text{W}(\text{CO})_2$ and that of the η^1 (monohapto) binding *e. g.* as in $(\eta^5\text{-Cp})(\eta^1\text{-Cp})\text{Fe}(\text{CO})_2$, are also seen on certain rare occasions.

The binding modes of the cyclopentadienyl ligand in metal complexes can be ascertained to a certain degree by ^1H NMR in the diamagnetic metal complexes, in which the Cp-protons appear as a singlet between 5.5–3.5 ppm while the β and γ hydrogens come at 7–5 ppm.

Cyclopentadienyl–metal interaction

The frontier molecular orbital of the cyclopentadienyl ligand contains 5 orbitals ($\Psi_1\text{--}\Psi_5$) residing in three energy levels (Figure 1). The lowest energy orbital Ψ_1 does not contain any node and is represented by an a_1 state, followed by a doubly degenerate e_1 states that comprise of the Ψ_2 and Ψ_3 orbitals, which precede another doubly degenerate e_2 states consisting of Ψ_4

and Ψ_5 orbitals.

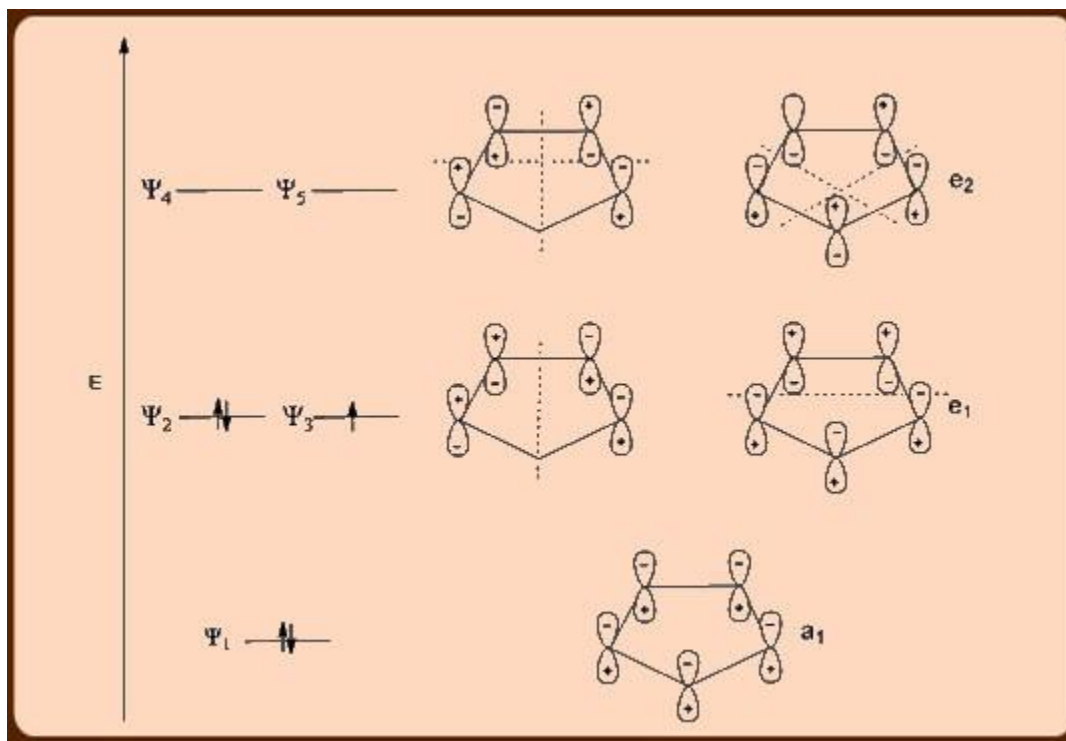
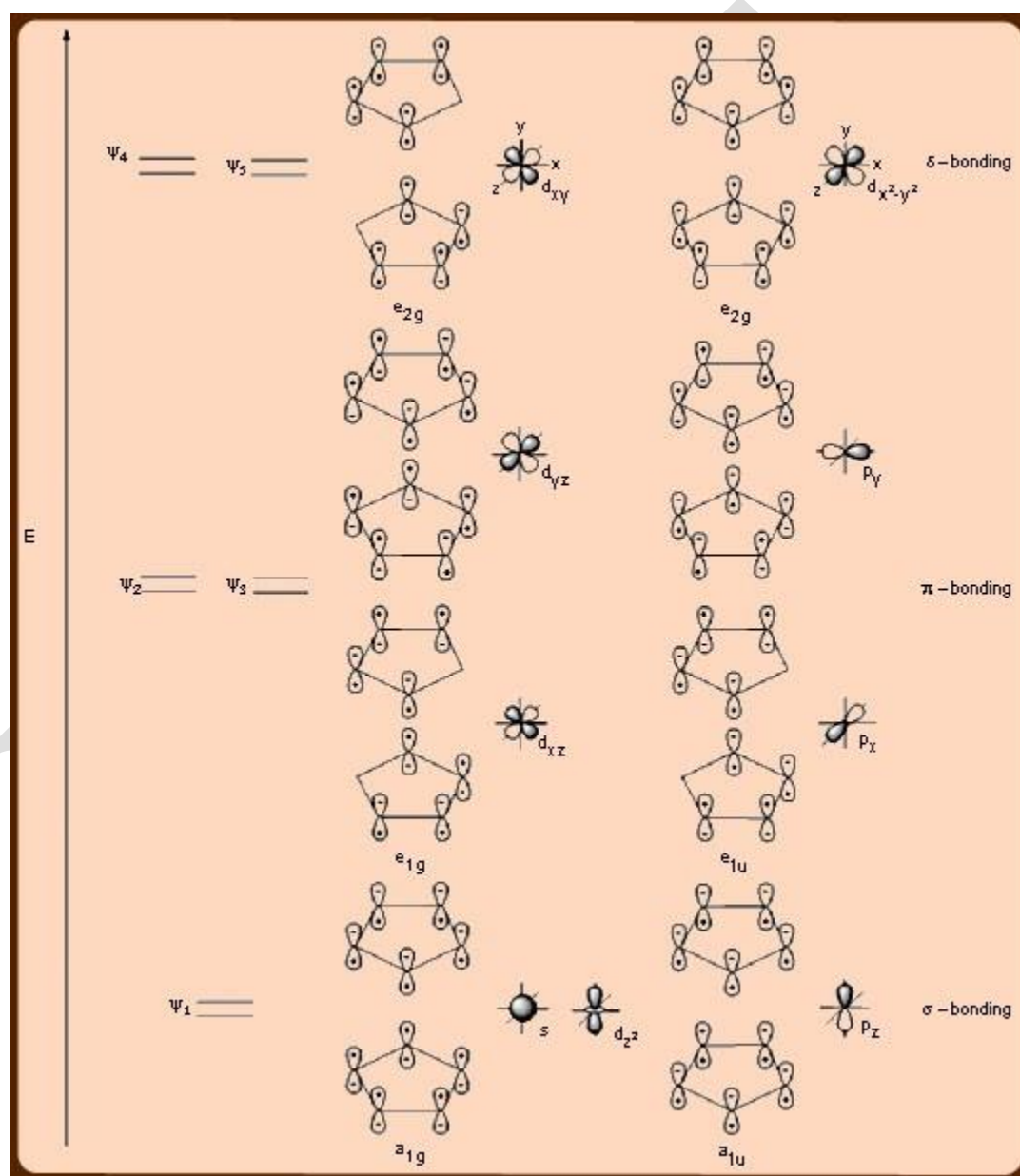


Figure 1. Molecular orbital diagram of cyclopentadienyl ligand.

The above frontier molecular orbital diagram becomes more intriguing on moving over to the metallocenes that contain two such cyclopentadienyl ligands. Specifically, in the Cp_2M system, (e. g. ferrocene) each of these above five molecular orbital of the two cyclopentadienyl ligands combines to give ten ligand molecular orbitals in three energy levels (Figure 2). Of these, the orbitals that subsequently interact with the metal orbitals to

generate the overall molecular orbital correlation diagram for the Cp_2M type of complexes are shown below (Figure 3).

Figure 2. Metal–cyclopentadienyl Bonding interactions.



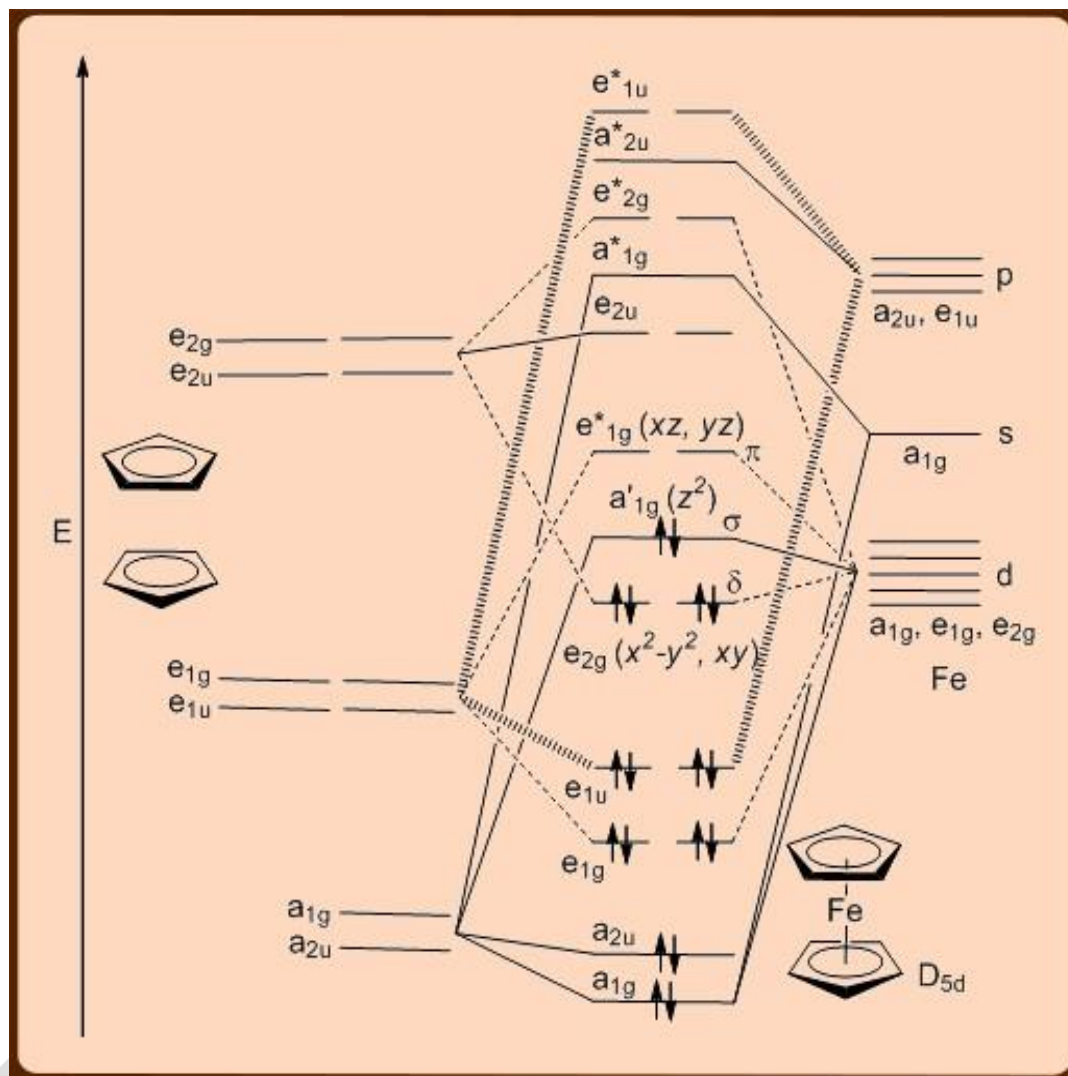


Figure 3. MO diagram of ferrocene.

Generic metallocene Cp_2M type complexes are formed for many from across the 1st row transition metal series along Sc to Zn. The number of unpaired electrons thus correlates with the number unpaired electrons present in the valence orbital of the metal (Figure 4). Of the complexes of the 1st row transition metal series, the manganocene exists in two distinct forms, one in a high-spin form with five unpaired electrons, *e.g.* as in Cp_2Mn and the other in a low-spin form with one unpaired electron, *e.g.* as in Cp^*_2Mn owing to the higher ligand field strength of the Cp^* ligand. Cobaltocene, Cp_2Co , has 19 valence electrons (VE) and thus gets easily oxidized to the diamagnetic 18 VE valence electron species, Cp_2Co^+ . Of these metallocenes, the much-renowned ferrocene, Cp_2Fe is a diamagnetic 18 VE complex,

whose molecular orbital diagram is shown above (Figure 3).

KAHE

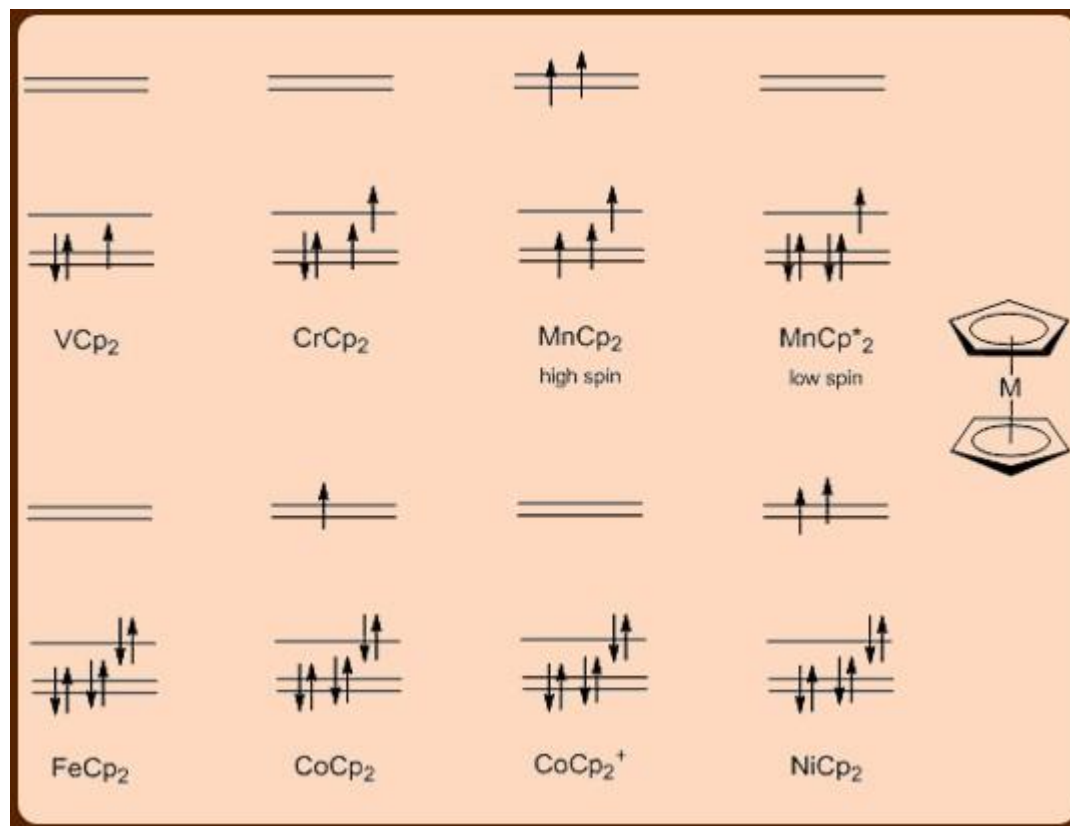
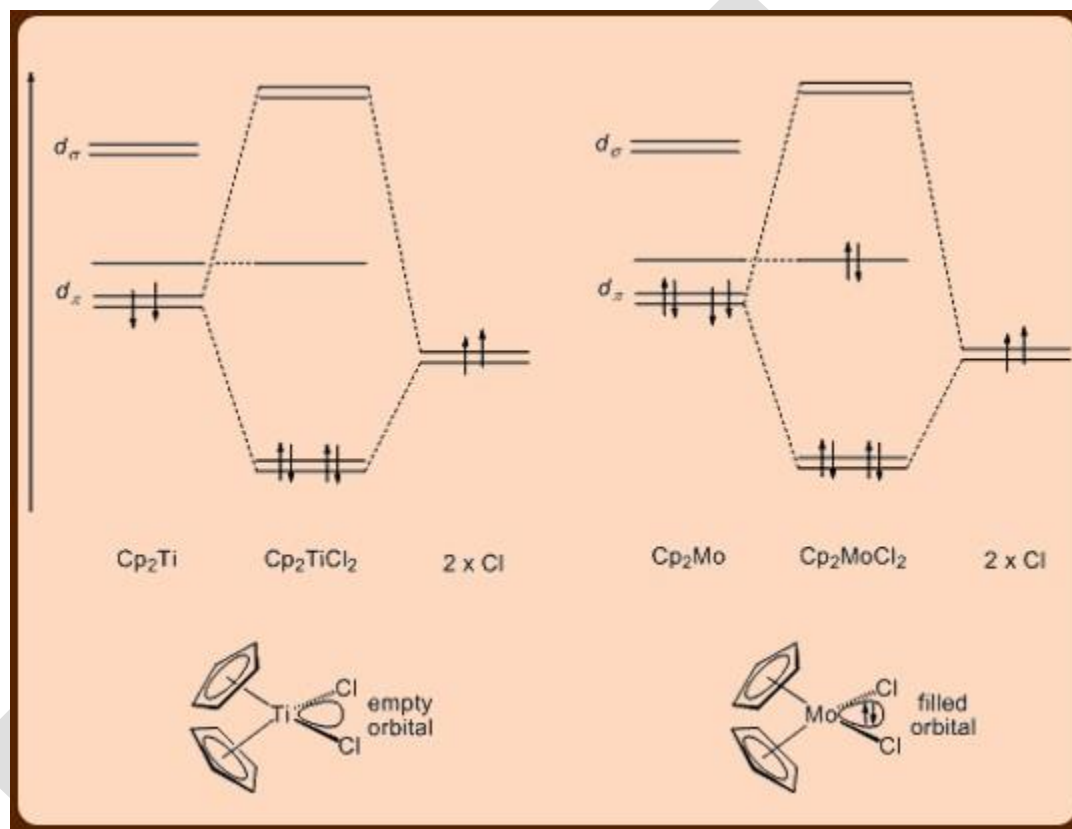


Figure 4. Metallocene

Bent metallocenes

Bent metallocenes are Cp_2MX_n type complexes formed of group 4 and the heavier



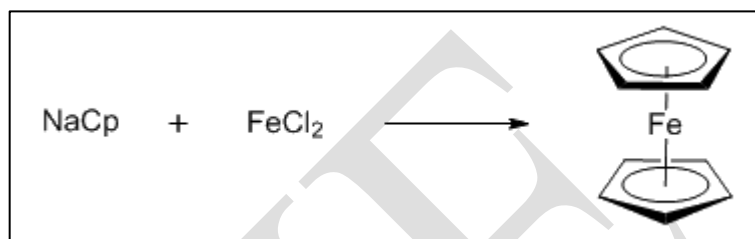
elements of groups 5–7. In these complexes the frontier doubly degenerate e_{2g} orbitals of Cp_2M fragment interacts with the filled lone pair orbitals of the ligand (Figure 5).

Figure 5. Bent metallocene.

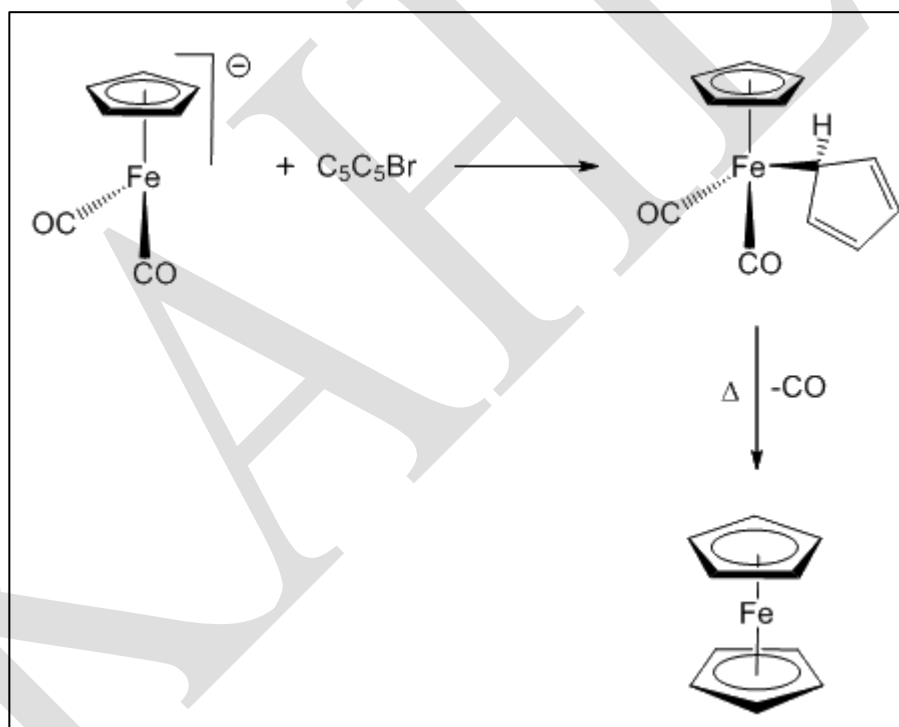
Synthesis of cyclopentadienyl-metal complexes

The metal-cyclopentadienyl complexes are synthesized by the following methods.

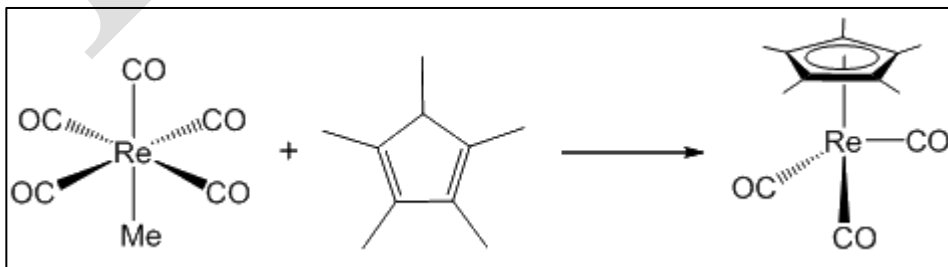
i. from Cp^-



ii. from Cp^+



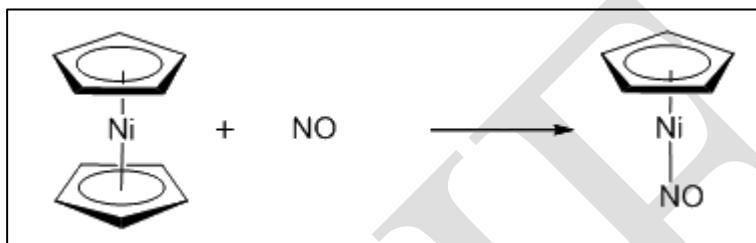
iii. from hydrocarbon



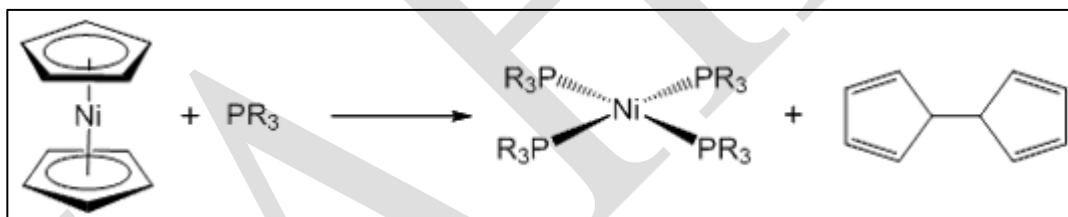
Reactivity of cyclopentadienyl-metal complexes

The reactivity of cyclopentadienyl-metal complexes of the type Cp_2M is shown for a representative nickelocene complex.

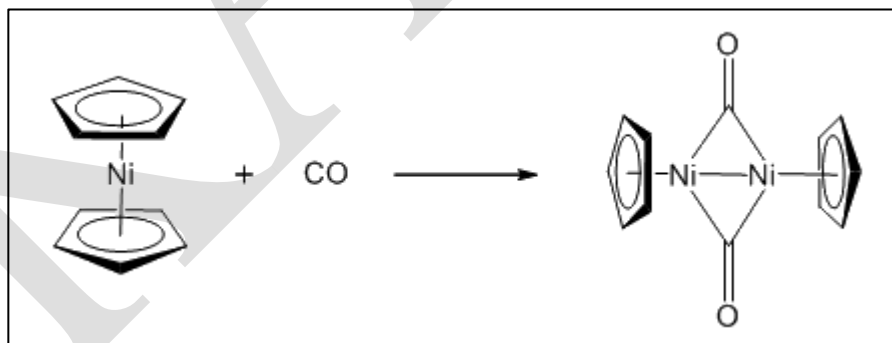
i. reaction with NO



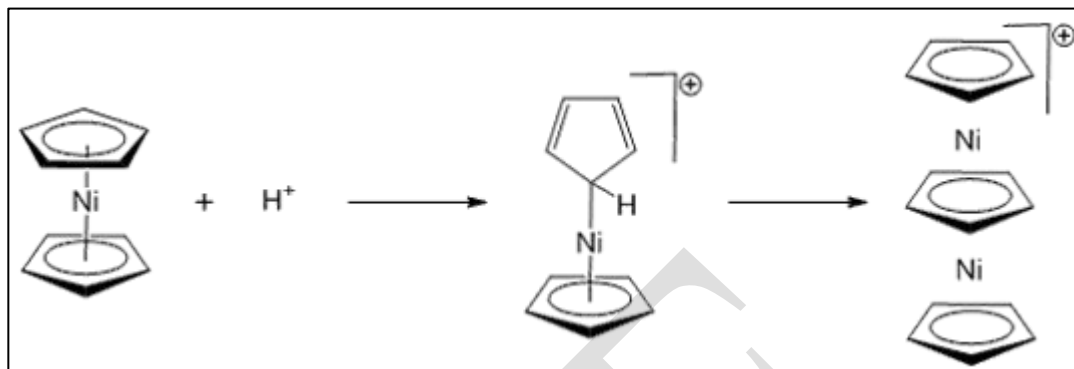
ii. reaction with PR_3



iii. reaction with CO

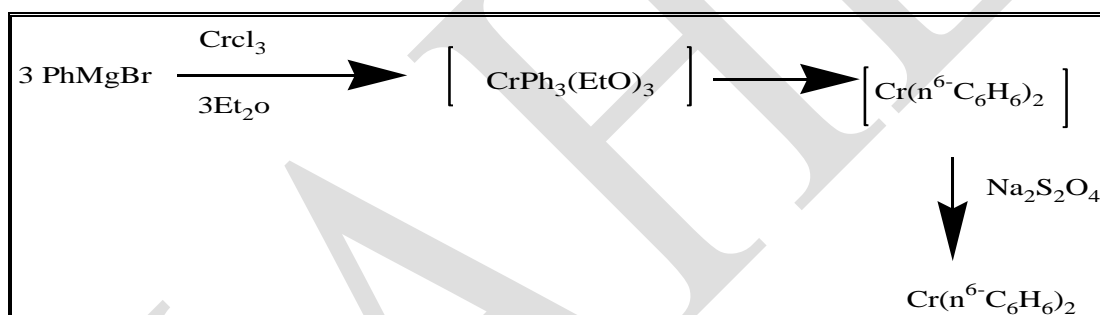


iv. reaction with H^+

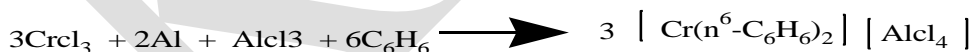


Arene Complexs:

- Although the cyclopentadienyl group is the best known aromatic ligand, there are several others of considerable importance.
- None leads to complexes as stable as the most stable metallocenes, however, and the chemistry of complexes that do form is more severely limited.
- Benzene and substituted benzenes normally act as six electron donors, although dihapto and tetrahapto complexes are also known.
- Dibenzenechromium was prepared early in this century but was not characterized until 1954.
- It was first synthesized via a Grignard synthesis.
- When PhMgBr reacts with CrCl_3 in diethyl ether solvent, a monohapto complex $[\text{Cr}(\text{Ph})_3(\text{EtO})_3]$ forms which rearranges, presumably by a free radical reaction to give, among other products, $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$
- This ion can be reduced to the neutral metallocene.

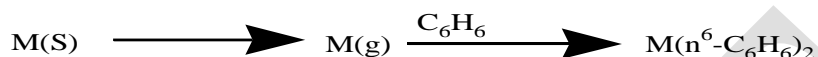


- Arene complexes are synthesized more cleanly by the Fischer-Hafner adaptation of the Friedel-Crafts reaction.
- In this reaction aluminium is used to reduce the metal salt to a lower oxidation state and with the assistance of AlCl_3 , benzene is coordinated to chromium.

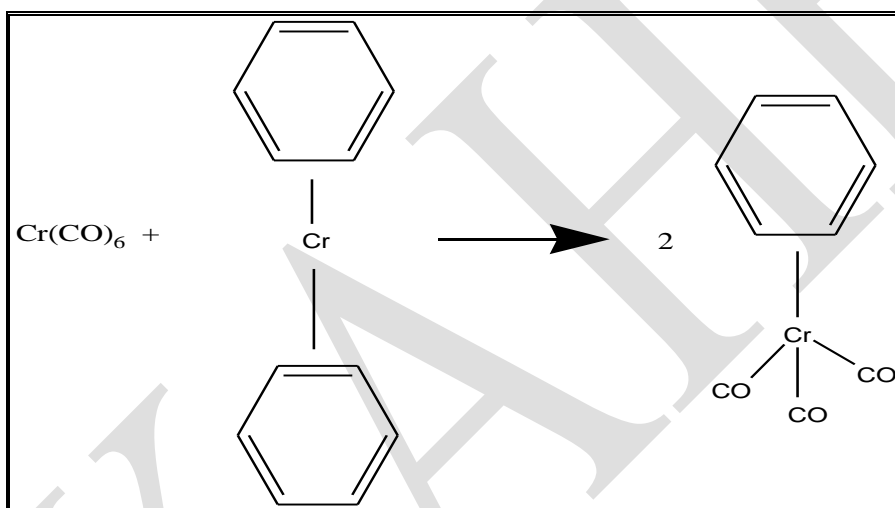


- The cation can be reduced to dibenzenechromium with sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$.
- The dibenzene complexes Cr, Mo and W are all air sensitive and those of Mo and W are especially so.
- Dibenzene chromium is a black solid that melts at 280 °C
- The success of Fischer-Hafner method depends upon the particular arene and on the skill of the experimentalist.
- Several decades ago Timms introduced a chemically innovative approach for making a variety of organometallic complexes.

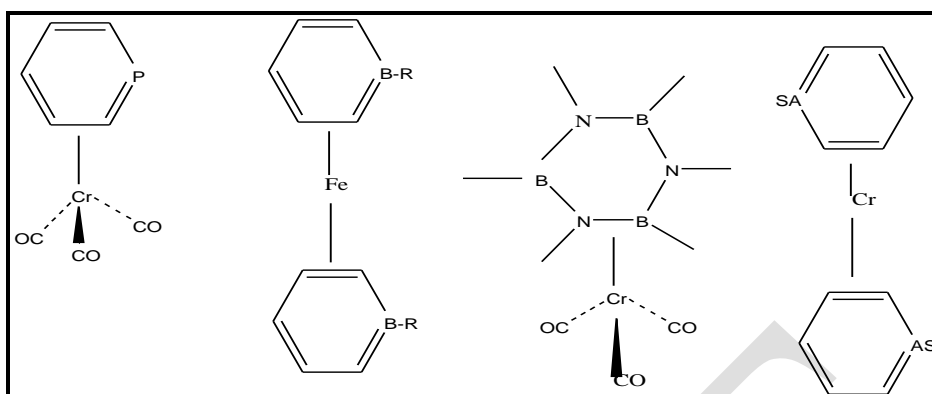
- It is based on the premise that if you wish to synthesize a zerovalent complex, it is logical to begin with a metal atom rather than with salts that must be reduced.
- Highly active metal atoms can be created by vaporizing metals under vacuum with resistive heating and then condensing the atoms on low temperature walls of a specially designed vessels (fig).
- A ligand benzene for example, can be introduced into the vessel where it will react with the metal atoms to form a complex.



- The rings of the dibenzene chromium, molybdenum, and tungsten complexes are eclipsed and have a small rotational barrier.
- Unlike ferrocene, these complexes have labile rings which can be displaced.



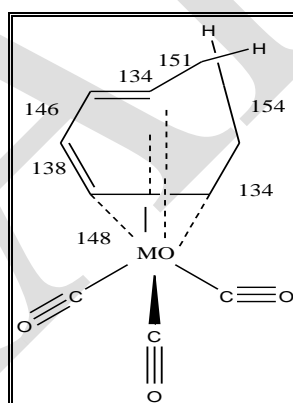
- The benzene rings can be removed completely by reaction with a more active ligand.
- $$Cr(\eta^6-C_6H_6)_2 + 6PF_3 \longrightarrow Cr(PF_3)_6 + 2C_6H_6$$
- There are a number of heteroatom six-membered aromatic rings which are analogous to benzene in that they can donate six electrons to a metal.
 - These include phosphobenzene, borabenzene anion, borazine, and arsabenzene shown in the fig(2).



- Complexes of phosphabenzene, borabenzene, borazine and arsabenzene. These six-membered rings are analogous to benzene, ie, they are six-electron donors and are aromatic.

Cycloheptatriene and tropylium complexes:

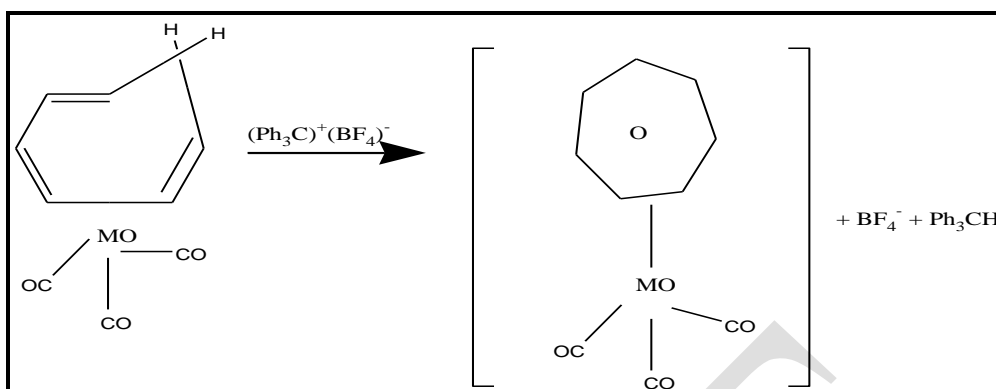
- Cycloheptatriene is a six electron donor that can form complexes similar to those of benzene but differing in the localization of the π electrons in C_7H_8 .
- The alternation in bond length in the free cycloheptatriene is obtained in the complexes



Molecular structure of tricarbonyl cycloheptatriene molybdenum(o) illustrating alternation in bond lengths and location of double bonds trans to the carbonyl ligands. bonds lengths are in picometers.

Furthermore, in $C_7H_8(Co)_3$ the double bonds are located trans to the carbonyl groups, providing an essentially octahedral environment for the metal atom.

Cycloheptatriene complexes can be oxidized (hydride ion abstraction) to form cycloheptatrienyl (sometimes called tropylium) complexes.

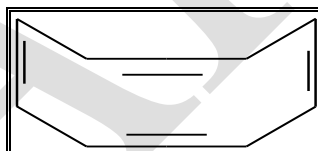


The tropylium ring is a planar with equal C-C distances. Like benzene and the cyclopentadienide anion, the tropylium cation is an aromatic, six electron species.

Cyclooctatetraene and cyclobutadiene complexes:

In accord with the Huckel rule of $4n+2$ electrons cyclobutadiene and cyclooctatetraene(cot) are nonaromatic.

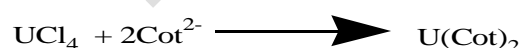
Cyclooctatetraene contains alternating bond lengths and has a tube shaped conformations.



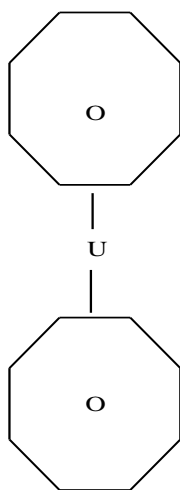
This non polar molecules becomes planar on reaction with an active metal to produce the cyclooctatetraenide anion(cot^{2-}).

The cot dianion like Cp^- , is aromatic but has ten electrons in eight π orbitals.

When it is allowed to react with tetrapositive actinides, such as U^{4+} , Np^{4+} , Th^{4+} , Pa^{4+} and Pu^{4+} a neutral metallocene results.



The uranium compounds was the first metallocene of cot^{2-} to be synthesized. A sandwich structure was proposed for it and later verified.



By analogy to ferrocene it was called uranocene. The extent of covalency and the 5f orbital contribution to the bonding in these complexes has long been debated. Recent photoelectron spectroscopy results and abinitio quantum mechanical calculations support significant covalency and f orbital involvement. A molecular orbital scheme suitable for uranocene is shown in fig.

Missing from the diagram are the low-lying nondegenerate a_g and a_{2u} orbitals, which house four of the 22 valence electrons.

These are primarily ligand orbitals and do not contribute significantly to metal-ligand bonding.

The remaining 18 electrons fill the e_{1g} , e_{1u} , e_{2g} , and e_{2u} levels and leave the e_{3u} level half filled (2 unoccupied e-s).

The e_{2u} LGO donates electron density to the e_{2u} ($5f_{xyz}$, $5f_{z(x^2-y^2)}$) orbitals and the e_{2g} LGO donates electron density to the e_{2g} ($6d_{x^2-y^2}$, $6d_{xy}$) orbitals of the uranium atom.

Neptunocene ($5f^3$) and plutonocene ($5f^4$) have one and no unpaired e-s, respectively, as predicted from fig.

The lanthanides might be expected to form similar complexes, using 4f orbitals in place of the 5f orbitals of the actinides.

They do so, generally forming $[Ln(cot)_2]^-$ complexes (D_{8d}), although $Ln(cot)Cl$ species are also known.

These complexes have been viewed as essentially ionic with minimal 4f covalent participation.

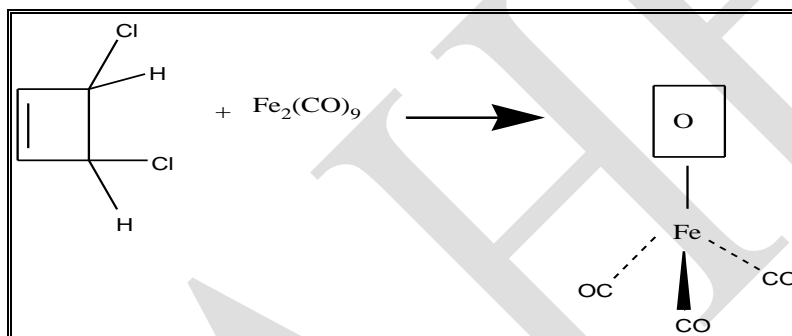
Cyclobutadiene, C_4H_4 , eluded synthesis for many years because of its reactivity.

Although simple Huckel theory predict a square molecules with two unpaired e-s, infrared studies carried out at low temperature(it dimerizes at 35k) have shown that it is rectangular with alternating single and double bonds.

In addition, all of its electrons are paired.

More sophisticated Mo treatments are in accord with results.

In 1965, a great deal of excitement was generated when a complexes containing coordination C_4H_4 was synthesized.

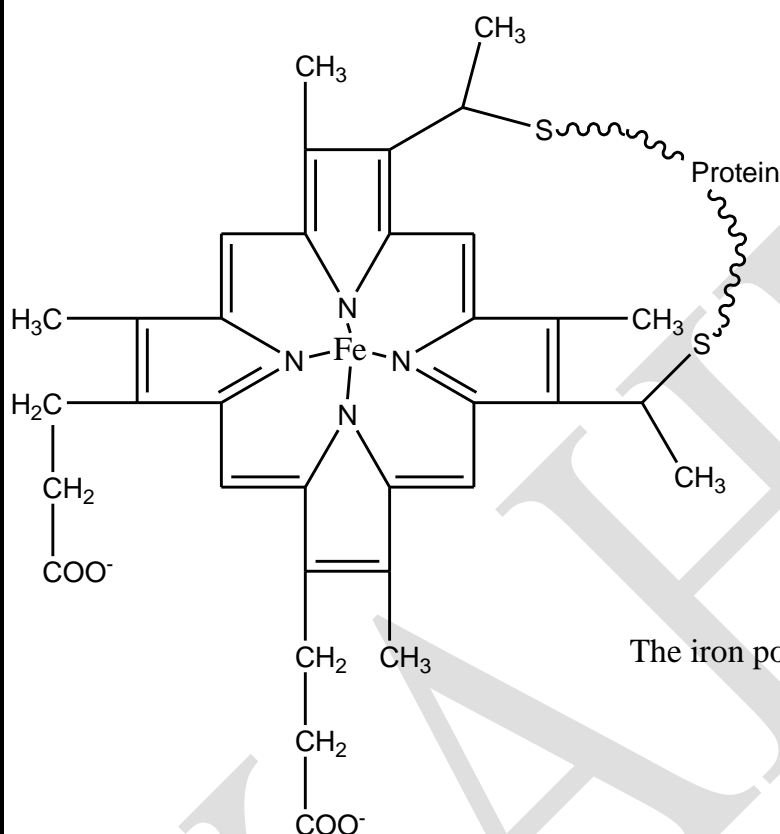


Thus cyclobutadiene, which was nonexistent at the time, was shown to be stabilized by complexation.

Oxidation of the complex liberated free cyclobutadiene which was trapped by ethyl propionate to give a cycloadduct.

The experiments established that cyclobutadiene could exist, however briefly, and led eventually to its low temperature isolation.

CYTOCHROME C:



The iron porphyrin unit in cytochrome C

- There are many cytochromes, which differ in slight detail, but these are broadly grouped together as cytochrome a, cytochrome b and cytochrome c.
- The active center of the cytochrome is the heme group
- It consists of a porphyrin ring chelated to an iron atom.
- The porphyrin ring consists of a macrocyclic pyrrole system with conjugated double bonds and various groups attached to the perimeter.
- Cytochrome C is an important biological intermediate in electron transfer.
- This metalloprotein, found in all cells, has a molecular weight of approximately 12,800 and contains 104 amino acids (in vertebrates).
- It is an electron carrier for oxidative phosphorylation, transferring electrons to O_2 .

MEAT COLOR:-

- Myoglobin contains hemes, pigments responsible for the color of red meat.
- The colour that meat takes is partly determined by the degree of oxidation of the myoglobin.
- In fresh meat the iron atom is the ferrous state bound to a dioxygen molecule (O_2).
- Meat cooked well done is brown because the iron is now in the ferric (+3) oxidation states, having lost an electron.
- If meat has been exposed to nitrites, it will remain pink because the iron atom is bound to NO, nitric oxide (true of e.g. corned beef for cured hams).
- Grilled meat can also take on a molecule of CO.
- Raw meat packed in an CO atmosphere also shows this same pink "smoke ring" due to the same principles.

Role in disease:-

- Myoglobin is released from damaged muscle tissue, which has very high concentration of myoglobin.
- The released myoglobin is filtered by the kidneys but is toxic to the renal tubular epithelium and so may cause acute renal failure.
- It is not the myoglobin itself that is toxic (it is a protoxin) but the ferriheme portion that is dissociated from myoglobin in acidic environments (e.g. acidic urine, lysosomes).
- Myoglobin is a sensitive marker for muscle injury, making it a potential marker for heart attack in patients with chest pain.
- However, elevated myoglobin has low specificity for acute myocardial (AMI) and thus CK-MB, cTnT, ECG and clinical signs should be taken into account to make the diagnosis.

Structure and bonding :-

- Myoglobin belongs to the globin super family of proteins, and as with other globins, consists of eight alpha helices connected by loops.
- Human globin contains 154 amino acids.
- Myoglobin contains a porphyrin ring with an iron at its center.
- A proximal histidine group (His-94) is attached directly to iron, and a distal histidine group (His-65) covers near the opposite face.

- The distal imidazole is not bonded to the iron but is available to interact with the substrate O_2 .
- This interaction encourages the binding of O_2 but not carbon monoxide (CO), which still binds about 240 X more strongly than O_2 .
- The binding of O_2 causes substantial structural change at the center, which strikes in radius and moves into the center of N4 pocket.
- Oxygen (ie) O_2 binding induces "spin-pairing", the five coordinate ferrous deoxy form is high spin and the six coordinate oxy form is low spin and diamagnetic.

Synthetic analogues :-

- Many models of myoglobin have been synthesized as part of a broad interaction in transition metal dioxygen complexes.
- A well known example is the picket fence porphyrin, which consists of a sterically bulky derivative of tetraphenyl porphyrin.
- In the presence of an imidazole ligand, this ferrous complex reversibly binds O_2 .
- The key property of this model is the slow formation of the μ -Oxo dimer, which is an inactive diferric state.
- In nature, such deactivation pathways are suppressed by protein matrix that prevents close approach of the Fe porphyrin assemblies.
- A picket-fence porphyrin complex of Fe, with axial coordination sites occupied by methylimidazole (green) and dioxygen.
- The R groups flank the O_2 -binding site.

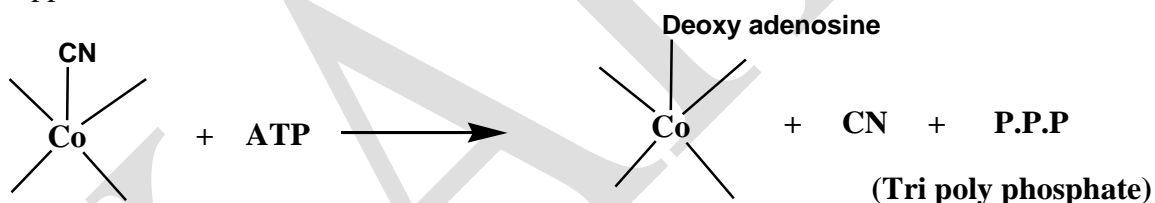
Vitamin B₁₂ -Cyanocobalamin

- Vitamin B₁₂ is an important cobalt complex. The vitamin was isolated from liver after it was found that eating large quantities of raw liver was an effective treatment for pernicious anemia.
- The term vitamin B₁₂, refers to cyanocobalamin. Vitamin B₁₂ is a coenzyme, and serves as a prosthetic group which is tightly bound to several enzymes in the body.
- It is called a biological Grignard reagent.
- Vitamin B₁₂ is unique in that it appears to be synthesized only by micro organisms especially anaerobic bacteria.
- The structure of vitamin B₁₂ complex consists of four principle components.
 - I. A cobalt (III) ion.
 - II. A macrocyclic ligand called the corrin ring which bears various substituents.
- It resembles the porphine ring, but differs in various ways, notably in the absence of one methine, $=CH-$, bridge between a pair of pyrrole rings.

I. A Complex organic portion consisting of a phosphate group, a sugar and an organic base, the latter being coordinated to the cobalt atom.

II. CN^- ligand coordinated to the cobalt ion.

- The Co atom is bonded to four ring N atoms. The fifth position is occupied by another N from a side chain (alpha-5,6-dimethyl benzimidazole) and this is also attached to corrin ring.
- The sixth group which makes up the octahedron is the active site, and is occupied by a CN^- group in cyanocobalamin.
- The CN^- is introduced in isolating the coenzyme, and is not present in the active form in living tissues.
- This position is occupied by OH^- in hydroxocobalamin by water or by an organic group such as CH_3 (methyl cobalamin) or adenosine.
- This shows that a metal to carbon sigma bond can be formed.
- The cobalamins can be reduced from Co^{III} to Co^{II} and Co^{I} in neutral or alkaline solutions both in laboratory and in Vivo (in the living body). The Co^{I} complex is strongly reducing.
- Its structure is five coordinate i.e., the site usually occupied by CN^- or OH^- is vacant.
- Vitamin B_{12} is converted to co-enzyme B_{12} by extracts from micro organisms supplemented with ATP.

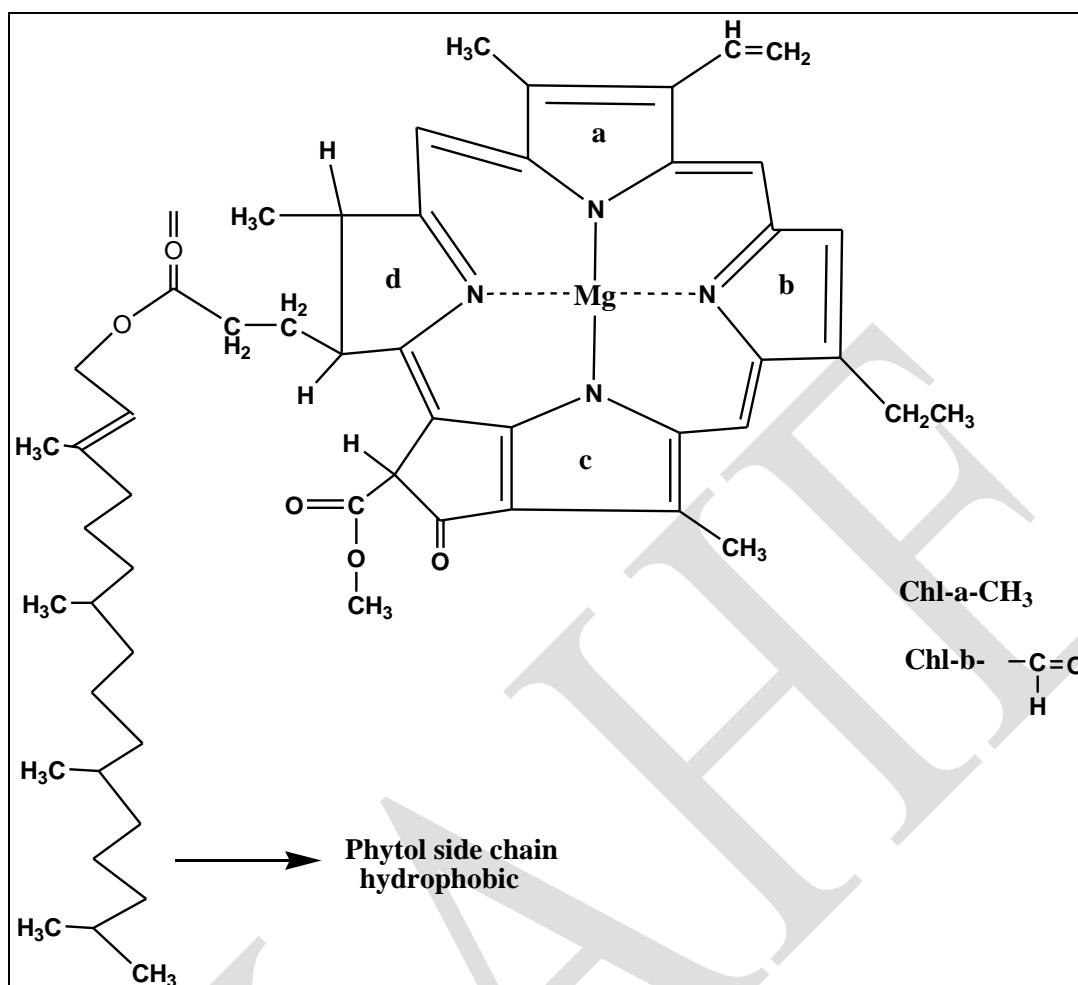


- Coenzyme B_{12} is associated with many biochemical reactions:
 - I. Conversion of methylmalonyl CoA to succinyl CoA.
 - II. Isomerisation of dicarboxylic acids e.g., glutamic acid into beta-methyl – aspartic acid.
 - III. Dismutation of vicinal diols to the corresponding aldehydes e.g., propane-1,2-diol into propionaldehyde.
 - IV. Methylation of homocysteine to form methionine.

Chlorophyll :-

- In 1905 to 1913 Zurich and Berlin carried experiment about chlorophyll.
- In 1913 Richard Willstatter discovered the structure of chlorophyll. For this he received the noble prize.

Structure of Chlorophyll :-



The basic structure is made of 4 pyrroles. A tetra pyrrole which is also called porphyrin. Mg^{2+} is present in the center of the ring as the central atom. It is covalently bounded with 2 'N' atom and coordinately bonded with 2 'N' of tetra pyrrole ring. In ring C, cyclopentanone is attached. In ring

Propionic acid + alcohol phytol \Rightarrow ester unit

Phytol consists of a long branched hydrocarbon with one C=C bond. It is derived from isoprenoid and four isoprene units. This long hydrocarbon tail renders the chlorophyll highly soluble in lipids and it also promotes when it presence in the membrane phase. Chlorophyll always occurs bound to protein. In Chl-b contains a formyl residue and Chl-a contains methyl residue. This small difference has a large influence on light absorption. Green pigment absorbed wave length below 480nm and between 550 and 700 nm. Between 480 to 550 nm the wave length light does not absorbed. In plant, the ratio of Chl-a to chl-b is about 3 to 1. Only Chl-a is a constitute of the photosynthetic reaction centre and regarded as central photosynthesis pigment.

In wide range of the visible spectrum, Chl-a does not absorb the light. So, it is non-absorbing region is named the "green window". The absorption gap is narrowed by the light absorption of Chl-b, with its minimum at a higher wave length. The energy absorbed by Chl-b can be transferred very efficiently to Chl-a. In this way, Chl-b enhances the plant efficiency for utilizing sun light energy. In a complex with protein the absorption spectrum of the bound chlorophyll may differ considerably from the absorption spectrum of free chlorophyll. In this free absorbing substance called chromophore and the chromophore-protein complex called pigments.

REFERENCE:-

1. Huheey J.E, E.A. Keiter & R.L. Keiter 2002 inorganic chemistry .vol 4 Pearson Education Singapore
2. Cotton F.A, G. Wilkinson, 2003 advanced inorganic chemistry, John Wiley & Sons, New York

Possible Questions:

Part-A

Each question carries one mark:

1. Give example for the compound which contains more than two cyclopentadienyl rings
a. Tetrakis(cyclopentadienyl) uranium
b. Ferrocene
c. Sodium cyclopentadienide
d. Thallium
2. Give an example for the compound which contains only one cyclopentadienyl ring
a. Tetrakis(cyclopentadienyl) uranium
b. Ferrocene
c. Sodium cyclopentadienide
d. Thallium
3. The compounds having only one cyclopentadienyl ring are commonly known as ----
a. Sandwich compound
b. Open-faced sandwich compound
c. Closed-faced sandwich compound
d. Triple decker
4. Ferrocene undergoes Vilsmeier reaction to yield-----
a. Amino ferrocene
b. Ferrocene carboxylaldehyde

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- c. Notro ferrocene
- d. chloro ferrocene

5. Ring substituted ferrocene reacts with acetic acid through the formation of ---- ion

- a. α Carbonium ion
- b. β carbonium ion
- c. α Carbanion
- d. β Carbanion

6. Arene complexes are mostly synthesized by ----- reaction

- a. Aldol condensation
- b. Beckmann rearrangement
- c. Reduction reaction
- d. Friedel crafts reaction

7. During the preparation of Arene complexes ---- is used to reduce the metal salt to a lower oxidation state.

- a. Aluminium
- b. Palladium
- c. Chromium
- d. Nickel

8. Benzene is coordinated to chromium in arene complexes with the assistance of ----

- a. AlCl_3
- b. LiCl_3
- c. TiCl_4
- d. H-Pd

9. The melting point of Dibenzene chromium is ----- $^{\circ}\text{C}$

- a. 270
- b. 170
- c. 280
- d. 260

10. The success of the Fischer-Hafner method depends upon the particular -----

- a. Amine
- b. Arene
- c. Aliphatic compound
- d. Aromatic compound

11. The most important naturally occurring Magnesium complex is

- a. Cytochrome
- b. Myoglobin
- c. Chlorophyll
- d. Cyanocobalamin

12.The magnesium atom in chlorophyll lies ---- the plane

- a.**Above**
- b.Below
- c.Axial
- d.Perpendicular

13.Chlorophyll absorb low energy light in

- a.Visible region
- b.**Red region**
- c.UV region
- d.ultra region

14.The exact frequency of chlorophyll depends upon

- a.**Nature of the substituent**
- b.Nature of the Functional group only
- c.Amount of the substituents
- d.None

15.The ability of chlorophyll to absorb light is due to basically to the conjugated polyene structure of the

- a.**Porphyrine ring system**
- b.Benzene ring system
- c.Naphthalene ring system
- d. Anthracene

16.The simplest bioenergetic compounds are

- a.Monochrome
- b.Phytochrome
- c.**Cytochrome**
- d.Cyanocobalamin

17.The active center of the cytochromes are

- a.Amino group
- b.**Haeme group**
- c.nitro group
- d.Sulphur group

18.Cytochrome consist of a ----- chelated to an iron atom

- a.**Porphyrin**
- b.Benzene
- c.Cyclohexene
- d.None

19.Cytochromes act as ----- intermediates in electron transfer.

- a.Free radical

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- b.oxidation
- c.Redox**
- d.none

20.The porphyrin ring consist of a macrocyclic pyrrole system with ---- double bonds

- a.Conjugated**
- b.Nonconjugated
- c.Isolated
- d.None

Part-B

Each question carries six marks

1. Write a note on cyclopentadienyl complex?
2. Explain Cytochromes
3. Write a note on Arene complexes
4. Give a comparative account of the structures and functions of hemoglobin and Myoglobin.
5. What are Cytochromes? Explain the structure of the Cytochromes. What are its functions.
6. Draw Hemoglobin structure.Explain
7. How cyclopentadienyl complexes are synthesized
8. Write a note on [\$\eta^5\$ -coordination](#) π -complexes

Part-C

Each question carries ten marks

1. Explain the structures of cyclo heptatriene and tropylium complexes.
2. Write a brief account on the structure and functions of cyanocobalamine.
3. Write a brief account on the structure and functions of Myoglobin.

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Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2018 onwards)
Department of Chemistry
II- semester

Inorganic Chemistry -II (Coordination Chemistry)

UNIT IV- Objective Questions for online examination (Each carry 1 Marks)

Question	Option-a	Option-b	Option-c	Option-d	Answer
Give example for the compound which contain more than two cyclopentadienyl rings	Tetrakis(cyclopentadienyl) uranium	Ferrocene	Sodium cyclopentadienide	thallium	Tetrakis(cyclopentadienyl) uranium
Give an example for the compound which containing only one cyclopentadienyl ring	Tetrakis(cyclopentadienyl) uranium	Ferrocene	Sodium cyclopentadienide	thallium	Sodium cyclopentadienide
the compounds having only one cyclopentadienyl ring are commonly known as ----	Sandwich compound	Openfaced sandwich compound	Closed faced sandwich compound	triple deccers	Openfaced sandwich compound
Ferrocene undergoes Vilsmeier reaction to yield-----	Amino ferrocene	Ferrocene carboxylate	Notro ferrocene	chloro ferrocene	Ferrocene carboxylate
Ring substituted ferrocene reacts with acetic acid through the formation of ---- ion	α Carbonium ion	β carbonium ion	α Carbanion	β Carbanion	α Carbonium ion
Arene complexes are mostly synthesized by ----- reaction	Aldol condensation	Beckmann rearrangement	Reduction reaction	Friedel crafts reaction	Friedel crafts reaction
During the preparation of Arene complexes ---- is used to reduce the metal salt to a lower oxidation state.	Aluminium	Paladium	Chromium	Nickel	Aluminium

Benzene is coordinated to chromium in arene complexes with the assistance of ----	AlCl ₃	LiCl ₃	TiCl ₄	H-Pd	AlCl ₃
The melting point of Dibenzene chromium is ----- °C	270	170	280	260	280
The success of the Fischer-Hafner method depends upon the particular ----	Amine	Arene	Aliphatic compound	aromatic compound	Arene
The most important naturally occurring Magnesium complex is	Cytochrome	Myoglobin	Chlorophyll	Cyanocobalamin	Chlorophyll
The magnesium atom in chlorophyll lies ---- the plane	Above	Below	Axial	Perpendicular	Above
Chlorophyll absorbs low energy light in	Visible region	Red region	UV region	ultra region	Red region
The exact frequency of chlorophyll depends upon	Nature of the substituent	Nature of the Functional group only	Amount of the substituents	None	Nature of the substituent
The ability of chlorophyll to absorb light is due basically to the conjugated polyene structure of the	Porphyrine ring system	Benzene ring system	Naphthalene ring system	Anthracene	Porphyrine
The simplest bioenergetic compounds are	Monochrome	Phytochrome	Cytochrome	Cyanocobalamin	Cytochrome
The active center of the cytochromes are	Amino group	Haeme group	nitro group	Sulphur group	Haeme group
Cytochrome consists of a ----- chelated to an iron atom	Porphyrin	Benzene	Cyclohexene	None	Porphyrin
Cytochromes act as ----- intermediates in electron transfer.	Free radical	oxidation	Redox	none	Redox

The porphyrin ring consist of a macrocyclic pyrrole system with ---- double bonds	Conjugated	Nonconjugated	Isolated	None	Conjugated
Cytochrome cannot react by simple coordination butu by an ----- mechanism	Oxidation	Reduction	Redox	Electron transfer	Electron transfer
The oxidation state of the Fe present in a porphyrin ring is	0 or +4	+2 or +3	+1 or +5	-1	+2 or +3
Cobalt os mainly ----- in its salt	positive	Negative	Dipositive	tripositive	Dipositive
Vitamin B ₁₂ consist of a highly substituted porphyrin like corrin ring in which a Co ³⁺ ion is bound to the --- nitrogen atom	3	4	1	2	4
the structure of vitamin B ₁₂ is similar to many haem iron compounds . it is called ---	Haemoglobin	Myoglobin	Albumin	Cobalamin	Cobalamin
Vitamin B ₁₂ contains a --- group in the sixth coordination position	Amino	Cyanide	Keto	none	Cyanide
Vitamin B ₁₂ contains a cyanide group in the sixth position is also called	Cyanocobalamine	Cytochrome	Hemoglobin	Myoglobin	Cyanocobal amine
The erivative of vitamin B ₁₂ concentrated in the liver is equivalent to --- ppm vitamin	1	2	3	4	1
The average human beings contain total of ---- of vitamin B ₁₂	2-5 mg	3-5 mg	2-3 mg	1-2 mg	2-5 mg

the principle role of vitamin B ₁₂ cyanocobalamin is the maturation of --- --	Hemoglobin	Myoglobin	Erythrocytes	None	Erythrocytes
the normal human diet contains between --- of vitamin B ₁₂ daily	5µg-15 µg	10µg-15 µg	2µg-5 µg	6µg-15 µg	5µg-15 µg
Alkaline solution of cyanocobalamin can be reduced to give both Co(II) and ---- species	Co(IV)	Co(III)	Co(I)	None	Co(I)
The alkaline solution of cyanocobalamin can be reduced to give both Co(II) and Co(I) species called vitamin B ₁₂ r and	Vitamin B ₁₂ S	Vitamin B ₁₂ H	Vitamin B ₁₂ t	Vitamin B ₁₂ K	Vitamin B ₁₂ S
Vitamin B ₁₂ S readily loses the --- from the sixth coordination position .	Cyanide	Amino	Keto	None	Cyanide
Vitamin B ₁₂ S is a powerful ---	Oxidising agent	Reducing agent	Protecting	Initiating agent	Reducing agent
The structure of vitamin B ₁₂ is similar to many haem iron compounds . it is called ----	Cobalamin	Haemoglobin	Albumin	Myoglobin	Cobalamin
The number of haem group present in haemoglobin -----	1	2	3	4	4
The binding power of haemoglobin with oxygen is P ^H dependent this effect is known as ----	Cooperativity effect	Bohr effect	Symmetry effect	Assymetry effect	Bohr effect
The haem group in haemoglobin consist of ---- atom	Fe	Mn	Mg	Co	Fe

which one of the following is commonly used as the starting material for the synthesis of group 4 metal cyclopentadienyl complexes?	CpSiMe ₃	NO	MeNC	Metal nitrosyl	CpSiMe ₃
Which complexes are called metallocenes?	Cyclopentadienyl	Tricyclopentadienyl	Monocyclopentadienyl	Biscyclopentadienyl	Biscyclopentadienyl
In mammals the protein makes up about how many percentage of the red blood cells?	95%	96%	97%	98%	97%
Which one of the following has an odd number of electrons?	Iron(I)	Iron(II)	Iron(III)	Iron(IV)	Iron(III)
Which have an additional light-independent enzyme and grow green in the darkness as well?	Vascular plants	Green algae	Chlamydomonas	Blue-green algae	Green algae
Chlorophyll fluorometers are used by plant researchers to assess plant ?	Chlorophyll content	Height	Length	Stress	Stress
In 2010, a near-infrared light photosynthetic pigment called Chlorophyll f may have been discovered in ?	Symbionts	Bacteria	Cyanobacteria	Acetobacter	Cyanobacteria
The general structure of chlorophyll <i>a</i> was elucidated by ?	Robert Burns	Hans Fischer	Ian Fleming	Woodward	Hans Fischer
At the center of the chlorin ring there is ?	Magnesium ion	Chlorine + Chloride	Chloride	Chlorine ion	Magnesium ion
Nitric oxide is bound to specific thiol groups in the globin protein to form an ?	N-nitrosothiol	S-nitrosothiol	M-nitrosothiol	G-nitrosothiol	S-nitrosothiol

The chlorin ring can have several different side chains, usually including a ?	Long picol chain	Long pistol chain	Long phytol chain	Small phytol chain	Long phytol chain
Chlorosis can be caused by a nutrient deficiency of?	Mg	Chlorine + Chloride	N	Fe	Fe
The vitamin B ₁₂ coenzymes are very unstable in ?	IR rays	UV light	Light	Water	Light
the use of cyanocobalamin can lead to severe ?	Hypokalemia	Hyperkalemia	Leukemia	Hyper leukemia	Hypokalemia
In humans myoglobin is encoded by which gene?	<i>MS</i>	<i>NB</i>	<i>MB</i>	<i>MG</i>	<i>MB</i>
Which is a sensitive marker for muscle injury?	Myoglobin	<i>Homoglobin</i>	<i>Metheglobin</i>	<i>Methemoglobin</i>	Myoglobin
The released myoglobin is filtered by ?	Liver	Kidney	Intestine	Pancreas	kidney
Which is a powerful way to break up and inactivate drug molecules?	Hydroxylation	Carboxylation	Dealkylation	Phosphorylation	Dealkylation
In cytochrome, which enzymes, function of heme is to facilitate the formation of reactive oxygen?	P480	P470	P460	P450	P450
Which one of the following is unable to carry oxygen?	<i>Methemoglobin</i>	<i>Metheglobin</i>	<i>Homoglobin</i>	<i>Metheglobin</i>	<i>Methemoglobin</i>

Lecture Notes

UNIT-V SYLLABUS

Reactions of coordination compounds:-

Substitution reactions in square planar and octahedral complexes – trans effect – redox reactions
Homogeneous catalysis by coordination compounds – hydroformylation carboxylation of methanol – hydrogenation of unsaturated organic compounds.

Important Types of Reactions Of Coordination Compounds

Acid-base

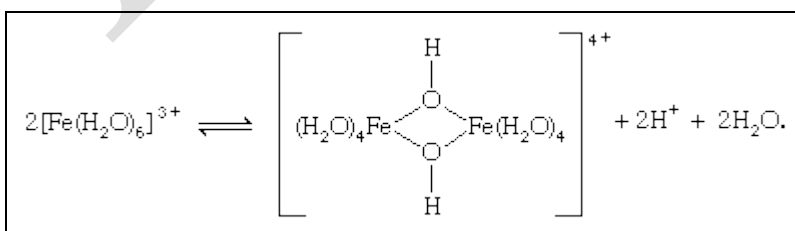
Coordination to a positive metal ion usually enhances the acidity (i.e., the tendency to lose protons) of hydrogen-containing ligands, such as water and ammonia. Thus, many metal ions in aqueous solution commonly exhibit acidic behaviour. Such behaviour is exemplified by hydrolysis reactions of the type shown in the following equilibrium:



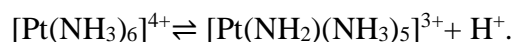
in which M represents the metal ion, n its charge, and x the number of coordinated water molecules.

The acidities of such aqua ions depend on the charge, size, and electronic configuration of the metal ion. This dependence is reflected in the values of acid dissociation constants, which range from about 10^{-14} (a value only slightly larger than for pure water, for which the dissociation constant = $10^{-15.7}$) for the hydrated lithium ion, to about 10^{-2} (a value equivalent to that of a fairly strong acid) for the hydrated uranium(4+) ion. Acid-base equilibria are rapidly established in solution, generally within a fraction of a second (*see* chemical reaction).

In some cases, hydrolysis of a metal ion may be accompanied by polymerization to form dinuclear or polynuclear hydroxo- or oxygen-bridged complexes.



Even very weakly acidic ligands, such as ammonia, can acquire appreciable acidity through coordination to a metal ion. Thus, the hexaammineplatinum(4+) ion dissociates according to the following equilibrium:



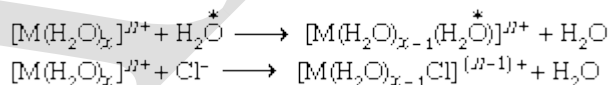
In addition to intrinsic strength, acids and bases have other properties that determine the extent of reactions. According to the hard and soft acids and bases (HSAB) theory, the metal cation and anion are considered to be acids and bases, respectively. Hard acids and bases are small and nonpolarizable, whereas soft acids and bases are larger and more polarizable. Interactions between two hard or soft acids or bases are stronger than ones between one hard and one soft acid or base. The theory can be used to explain solubilities, formation of metallic ores, and some reactions of metal cations with ligands.

Substitution

One of the most general reactions exhibited by coordination compounds is that of substitution, or replacement, of one ligand by another. This process is depicted in a generalized manner by the equation $\text{ML}_{x-1}\text{Y} + \text{Z} \rightarrow \text{ML}_{x-1}\text{Z} + \text{Y}$ for a metal complex of coordination number x . The ligands L, Y, and Z may be chemically similar or different. (Charges have been omitted here for simplicity.)

A class of substitution reactions that affords the widest possible comparison of different metal ions is the replacement of water in the coordination spheres of metal-aqua complexes in aqueous solution. The substitution may be by another water molecule (which can be labeled with the isotope oxygen-18 to permit the reaction to be followed) or by a different ligand, such as the chloride ion. Reactions of both types occur as shown below (oxygen-18 is indicated by the

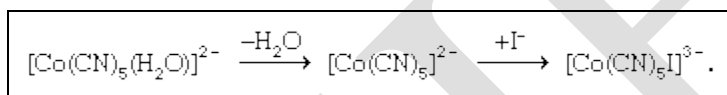
symbol $\overset{*}{\text{O}}$).



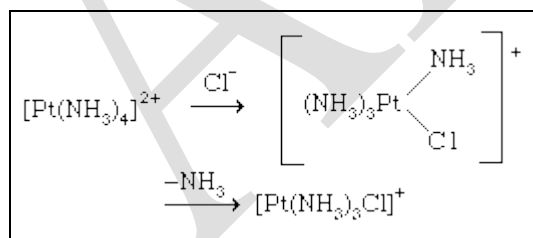
Many such reactions are extremely fast, and it has been only since 1950, following the development of appropriate experimental methods (including stopped flow, nuclear magnetic resonance, and relaxation spectrometry), that the kinetics and mechanisms of this class of reactions have been extensively investigated. Rates of substitution of metal-aqua ions have been found to span a wide range, the characteristic times required for substitution ranging from less than 10^{-9} second for monovalent ions, such as hydrated potassium ions, to several days for certain more highly charged ions, such as hexaaquachromium(3+) and hexaaquarhodium(3+).

The rate of substitution parallels the ease of loss of a water molecule from the coordination sphere of the aqua complex and thus increases with increasing size and with decreasing charge of the metal ion. For transition metal ions, electronic factors also have an important influence on rates of substitution.

There are two limiting mechanisms (or pathways) through which substitution may occur—namely, dissociative and associative mechanisms. In the dissociative mechanism, a ligand is lost from the complex to give an intermediate compound of lower coordination number. This type of reaction path is typical of octahedral complexes, many aqua complexes, and metal carbonyls such as tetracarbonylnickel. An example of a dissociative reaction pathway for an octahedral complex of cobalt is as follows:



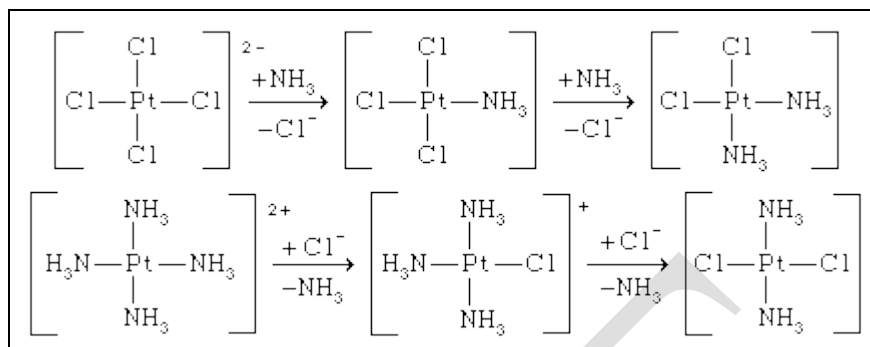
The associative mechanism for substitution reactions, on the other hand, involves association of an extra ligand with the complex to give an intermediate of higher coordination number; one of the original ligands is then lost to restore the initial coordination number. Substitution reactions of square planar complexes, such as those of the nickel(2+), palladium(2+), and platinum(2+) ions, usually proceed through associative pathways involving intermediates with coordination number five. An example of a reaction following such a pathway is



A characteristic feature of this class of reactions is the sensitivity of the rate of substitution of a given ligand to the nature of the ligand in the *trans* position. The *trans* ligand activates a ligand for replacement as follows, in decreasing order:

$\text{CO}, \text{CN}^-, \text{C}_2\text{H}_4 > \text{PR}_3, \text{H}^- > \text{NO}_2^-, \text{I}^-, \text{SCN}^- > \text{Br}^-, \text{Cl}^- > \text{NH}_3, \text{H}_2\text{O}.$

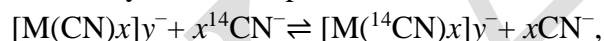
The *trans* effect may be used for synthetic purposes; thus, the reaction of the tetrachloroplatinate(2−) ion with ammonia yields *cis*-diamminedichloroplatinum, whereas the reaction of the tetraammineplatinum(2+) ion with the chloride ion gives the *trans* isomer, *trans*-diamminedichloroplatinum. The reactions are shown below.



In both reactions, the *trans* effect causes the introduction of the ligand *trans* to chloride rather than *trans* to ammonia.

Lability and inertness

In considering the mechanisms of substitution (exchange) reactions, Canadian-born American chemist Henry Taube distinguished between complexes that are *labile* (reacting completely in about one minute in 0.1 M solution at room temperature [25 °C, or 77 °F]) and those that are *inert* (under the same conditions, reacting either too slowly to measure or slowly enough to be followed by conventional techniques). These terms refer to kinetics (reaction rates) and should not be confused with the thermodynamic terms *unstable* and *stable*, which refer to equilibrium. For example, as mentioned above, most cyanide complexes are extremely stable (they possess very small dissociation constants); yet, if their rate of exchange with carbon-14-labeled cyanide, as represented in the following equation,



is measured, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Hg}(\text{CN})_4]^{2-}$ are found to be labile, whereas $[\text{Mn}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, and $[\text{Cr}(\text{CN})_6]^{3-}$ are inert. On the other hand, $[\text{Co}(\text{NH}_3)_6]^{3+}$, a kinetically inert complex, is thermodynamically stable in acidic solution. Inertness may result from the lack of a suitable low-energy pathway for the reaction. In short, stable complexes possess large positive free energies of reaction (ΔG), whereas inert complexes merely possess large positive free energies of activation (ΔG^*).

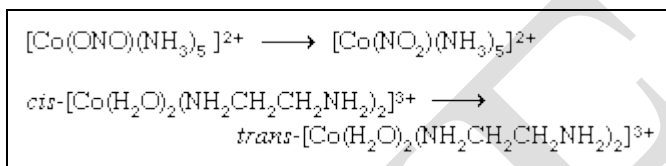
While the existence of geometric or optical isomers (*see above* Isomerism) in the solid state or in solution at nonequilibrium concentrations is evidence supporting the inertness of the complex, this does not constitute absolute proof. Conversely, the possibility of intramolecular rearrangement means that failure to isolate geometric isomers or to resolve the racemic mixture into optical isomers is not absolute proof of lability.

Taube has interpreted lability of complexes according to their electronic configuration in terms of VB theory. Labile complexes are either of the outer orbital type (outer *d* orbitals involved in bonding—e.g., sp^3d^2 as opposed to d^2sp^3 [inner orbital] for octahedral complexes) or of the inner

orbital type with at least one vacant *d* orbital (available for accommodation of a seventh group during the [associative] substitution reaction).

Isomerization

Coordination compounds that exist in two or more isomeric forms (*see above* Isomerism) may undergo reactions that convert one isomer to another. Examples are the linkage isomerization and *cis-trans* isomerization reactions depicted below.



The first of these has been shown to proceed intramolecularly (i.e., without dissociation of the nitrite ligand), whereas the second probably occurs through dissociation of one of the water-molecule ligands.

The Kinetic Trans Effect

The trans effect is an ancient but venerable observation. First noted by Chernyaev in 1926, the trans effect and its conceptual siblings (the trans influence, cis influence, and cis effect) are easy enough to comprehend. That is, it's simple enough to know what they are. To understand why they are, on the other hand, is much more difficult.

Definitions & Examples

Let's begin with definitions: what is the trans effect? There's some confusion on this point, so we need to be careful. The trans effect proper, which is often called the kinetic trans effect, refers to the observation that certain ligands increase the rate of ligand substitution when positioned trans to the departing ligand. The key word in that last sentence is "rate"—the trans effect proper is a kinetic effect. The trans influence refers to the impact of a ligand on the length of the bond trans to it in the ground state of a complex. The key phrase there is "ground state"—this is a thermodynamic effect, so it's sometimes called the thermodynamic trans effect. Adding to the insanity, cis effects and cis influences have also been observed. Evidently, ligands may also influence the kinetics or thermodynamics of their cis neighbors. All of these phenomena are independent of the metal center, but do depend profoundly on the geometry of the metal (more on that shortly).

Kinetic trans and cis effects are shown in the figure below. In both cases, we see that X^1 exhibits a stronger effect than X^2 . The geometries shown are those for which each effect is most commonly observed. The metals and oxidation states shown are prototypical.

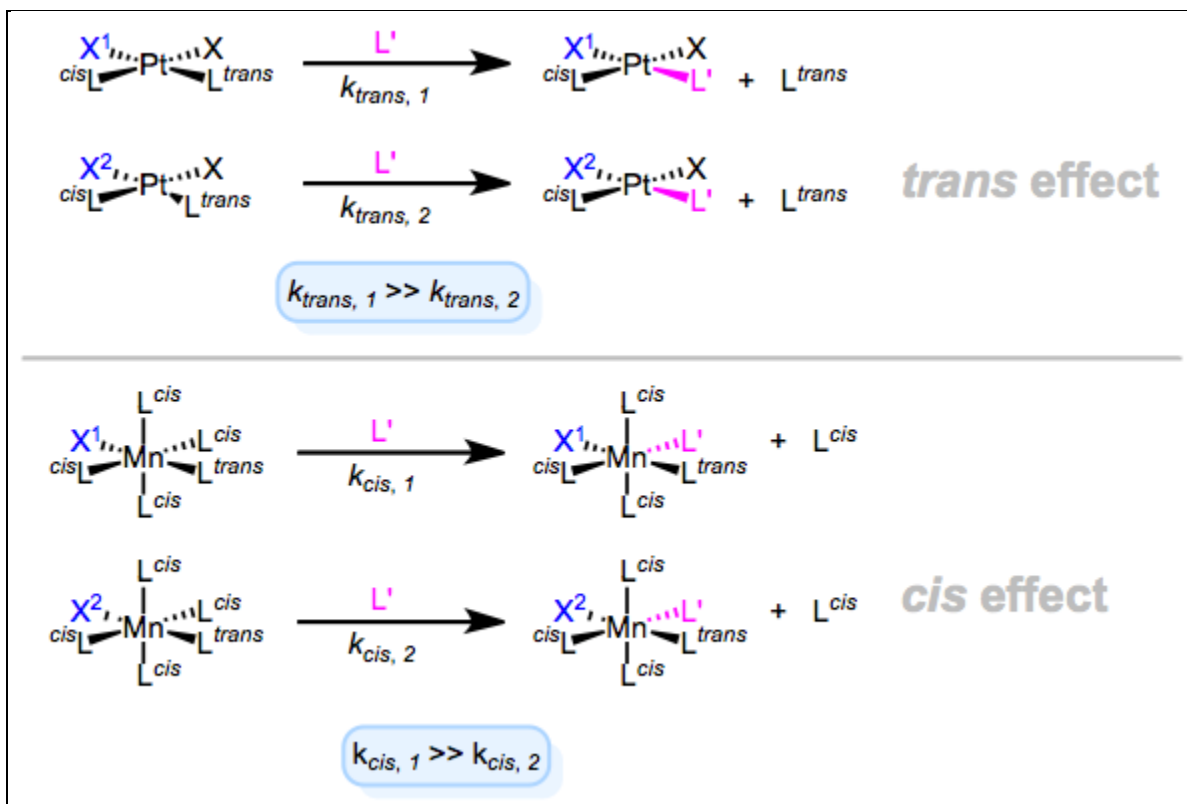


Figure 1: The kinetic trans and cis effects in action. X^1 is the stronger (trans/cis)-effect ligand in these examples.

On to the influences, which are simpler to illustrate since they're concerned with ground states, not reactions. The lengthened bonds below are exaggerated.

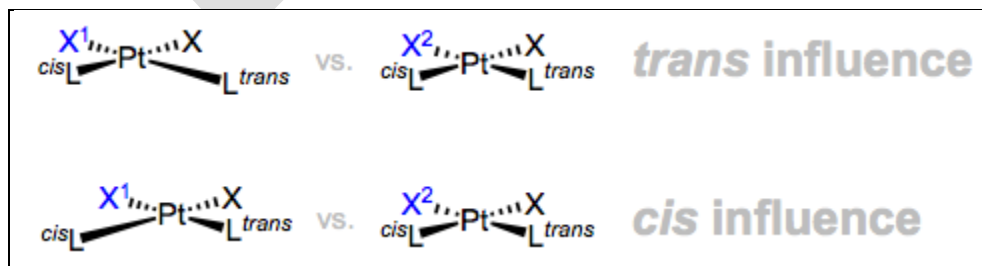


Figure 2: The trans and cis influences in action. Note the elongated bond lengths.

And there we have it folks, the thermodynamic and kinetic cis/trans effects. It's worth keeping in mind that the kinetic trans effect is most common for d8 square planar complexes, and the kinetic cis effect is most common for d6 octahedral complexes (particularly when the departing L is CO). But a lingering question remains: what makes for a strong trans effect ligand?

Origins of Effects & Influences

The trans effect and its cousins are all electronic, not steric effects. So, the electronic properties of the ligand dictate the strength of its trans effect. Let's finally dig into the trans effect series:

(weak) F^- , HO^- , H_2O < NH_3 < py < Cl^- < Br^- < I^- , SCN^- , NO_2^- , $SC(NH_2)_2$, Ph^- < SO_3^{2-} < PR_3 < AsR_3 , SR_2 , H_3C^- < H^- , NO , CO , NC^- , C_2H_4 (strong)

What's the electronic progression here? It's clear that electronegativity decreases across the series: F^- < Cl^- < Br^- < I^- < H_3C^- . From a bonding perspective, we can say that ligands with strong trans effects are strong σ -donors (or σ -bases). Yet σ -donation doesn't tell the whole story. What about ethylene and carbon monoxide, which both appear at the top of the heap? Neither of these ligands are strong σ -donors, but their π systems do interact with the metal center through backbonding. Consider the following sub-series: $S=C=N^-$ < PR_3 < CO . Backbonding increases across this series, along with the strength of the trans effect. Strong backbonders—better known as π -acceptors or π -acids—exhibit strong trans effects.

Strong trans effect = strong σ -donor + strong π -acceptor

Wonderful! Using these ideas we can identify ligands with strong trans effects. But we can dive deeper down the rabbit hole: why does this particular combination of electronic factors lead to a strong trans effect? To understand this, we need to know the mechanism of the ligand substitution reaction that's sped up by strong trans effect ligands. For 16-electron Pt(II) complexes, associative substitution is par for the course. The incoming ligand binds to the metal first, forming an 18-electron complex (yay!), which jettisons a ligand to yield a new 16-electron product. The mechanism in all its glory is shown in the figure below.

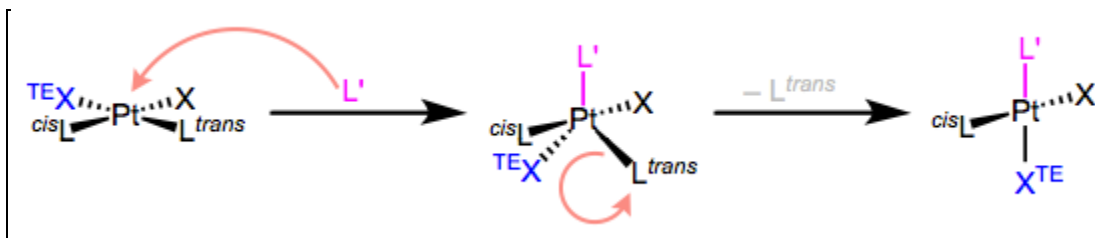


Figure 3: The mechanism of associative ligand substitution of Pt(II) complexes.

Some very important points about this mechanism:

- The incoming ligand always sits at an equatorial site in the trigonal bipyramidal intermediate. More on this another day, but I think of this result as governed by the principle of least motion. Consider the molecular gymnastics that would have to happen to place the incoming ligand in an axial position.
- Two ligands in the square plane are “pushed down” and become the other two equatorial ligands.
- Owing to microscopic reversibility, the leaving group must be one of the equatorial ligands.

The third point reveals that once L' has “pushed down” XTE and Ltrans, Ltrans has no choice but to leave (assuming XTE stays put). Thus, the trans effect has nothing to do with the second step of the mechanism, which is not rate determining anyway. The key is the first step—in particular, the “pushing down” event. Apparently, ligands with strong trans effects like to be pushed down. They like to occupy the equatorial plane of the TBP intermediate. Now here's the kicker: the equatorial sites of the TBP geometry are more π basic than the axial sites. The equatorial plane is just the xy-plane of the metal center, and the d orbitals in that plane (when occupied) are great electron sources for π -acidic ligands. Thus, π -acidic ligands want to occupy those equatorial sites, to receive the benefits of strong backbonding! Boom; strong π -acids encourage loss of the ligand trans to themselves.

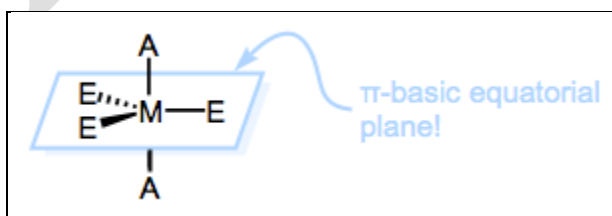


Figure 4: The equatorial sites of TBP metals are rich in electrons that can π bond.

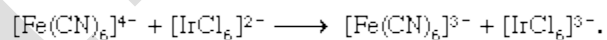
What about those pesky σ donors? Well, we can imagine that in a square planar complex, a ligand and its trans partner are competing for donation into the same d orbital. Strong σ donation from a ligand should thus weaken the bond trans to it. Although this is the thermodynamic trans effect (trans influence) in action, the resulting destabilization of the ground state relative to the transition state is a kinetic effect. On the whole, the barrier to substitution of the trans ligand goes down as σ -donating strength goes up.

This idea of “competition for the metal center” is a nice heuristic to use when thinking about the trans and cis influences. The type of metallic orbital involved in M–L bonding determines the strength of L’s trans and cis influences on neighboring ligands that also need that metallic orbital for bonding. For example: both influences are large if the metal’s s orbital is a significant contributor to M–L bonding, since it’s non-directional; the trans influence is much greater than the cis influence when metallic p orbitals are primarily involved in M–L. For a deeper explanation of these ideas, see this paper.

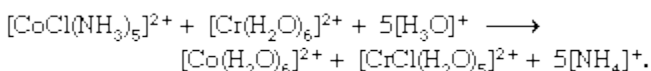
Perhaps the most valuable lesson from a study of the trans effect is that many concepts from organometallic chemistry involve more than meets the eye. Geometric effects and influences are real icebergs, in the sense that the observations and trends are easy to grasp, but difficult to explain. We had to dig all the way into the mechanism of associative ligand substitution before a satisfactory explanation emerged!

Oxidation-reduction

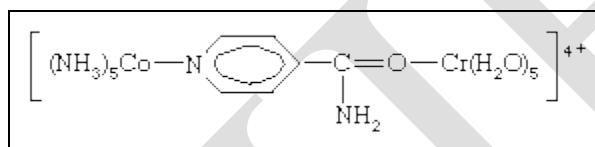
Transition metals commonly exhibit two or more stable oxidation states, and their complexes accordingly are able to undergo oxidation-reduction reactions. The simplest such reactions involve electron transfer between two complexes, with little if any accompanying rearrangement or chemical change. An example is shown below:



In other cases, oxidation-reduction is accompanied by significant chemical rearrangement. An example is



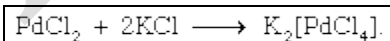
Two limiting mechanisms of electron transfer, commonly designated outer-sphere and inner-sphere mechanisms, have been recognized. Outer-sphere electron transfer occurs without dissociation or disruption of the coordination sphere of either complex—i.e., through both intact coordination spheres. The first reaction above is of this type. On the other hand, inner-sphere electron transfer—e.g., the second reaction above—proceeds by formation of a dinuclear complex in which the two metal ions are joined by a common bridging ligand (in this case the chloride ion) through which the electron is transferred. Such electron transfer also may occur through polyatomic bridging ligands to which the two metal ions are attached at different sites separated by several atoms, as in the reduction of pentaammine(isonicotinamide)cobalt(3+) by hexaaquachromium(2+) ion through a bridged intermediate:



Strikingly large differences in rates of electron transfer are observed even between closely related reactions. Thus, the rate of reduction of the pentaamminebromocobalt(3+) ion by the hexaaquachromium(2+) ion is about 10^7 times higher than that of the acetatopentaamminecobalt(2+) ion by the same chromium ion.

Synthesis of Coordination Compounds

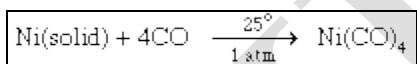
The great variety of coordination compounds is matched by the diversity of methods through which such compounds can be synthesized. Complex halides, for example, may be prepared by direct combination of two halide salts (either in the molten state or in a suitable solvent). Palladium chloride and potassium chloride, for example, react to give the complex potassium tetrachloropalladate(2-), as shown in the following equation:



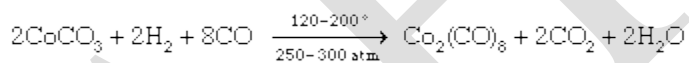
Another widely used route to coordination compounds is through the direct combination of a metal ion and appropriate ligands in solution. Thus, the addition of a sufficiently high concentration of ammonia to an aqueous solution of a nickel(2+) salt leads, through a series of reactions (*see above* Aqua complexes), to the formation of the hexaamminenickel(2+) ion, which can be precipitated, for example, as the sulfate salt, $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$.

Complexes of metal ions in high oxidation states are sometimes more readily formed by adding the ligands to a solution of the metal ion in a lower oxidation state in the presence of an oxidizing agent. Thus, addition of ammonia to an aqueous solution of a cobalt(2+) salt in the presence of air or oxygen leads to the formation of cobalt(3+)-ammine complexes such as hexaamminecobalt(3+), $[\text{Co}(\text{NH}_3)_6]^{3+}$, and pentaammineaquacobalt(3+), $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$, ions.

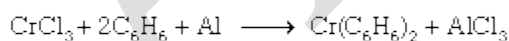
Complexes of metals in low oxidation states, such as the carbonyls of metals in their zero oxidation states, can sometimes be prepared by direct combination of the metal with the ligand, as, for example, in the reaction of nickel metal with carbon monoxide.



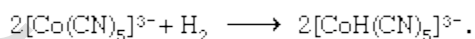
More commonly, a salt of the metal is reduced in the presence of the ligand. An example of this type of synthesis is the reduction of cobalt carbonate with hydrogen in the presence of carbon monoxide to give bis(tetracarbonylcobalt).



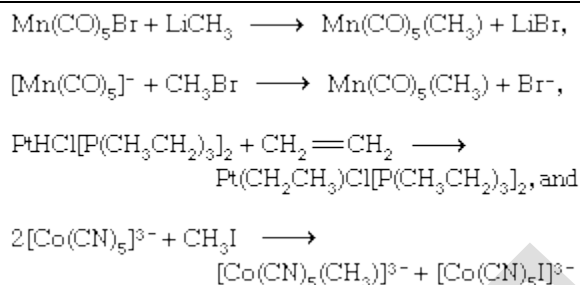
Similar procedures are applicable to the synthesis of metal sandwich compounds containing cyclopentadienyl and benzene ligands. Dibenzenechromium, for example, can be prepared from chromic chloride, benzene, and aluminum, as shown in the following equation.



Hydrido complexes of transition metals can be prepared by reactions of suitable precursors either with molecular hydrogen or with suitable reducing agents such as hydrazine or sodium borohydride; for example,

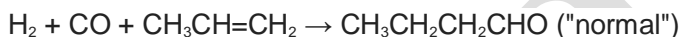


Transition metal complexes containing metal-carbon bonds can be prepared by a variety of routes, some of the more important of which are illustrated by the following examples

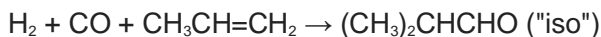


Hydroformylation:

The reaction of an alkene with carbonmonoxide and hydrogen, catalysed by cobalt or rhodium salts, to form an aldehyde is called hydroformylation (or sometimes the oxo process):



vs.



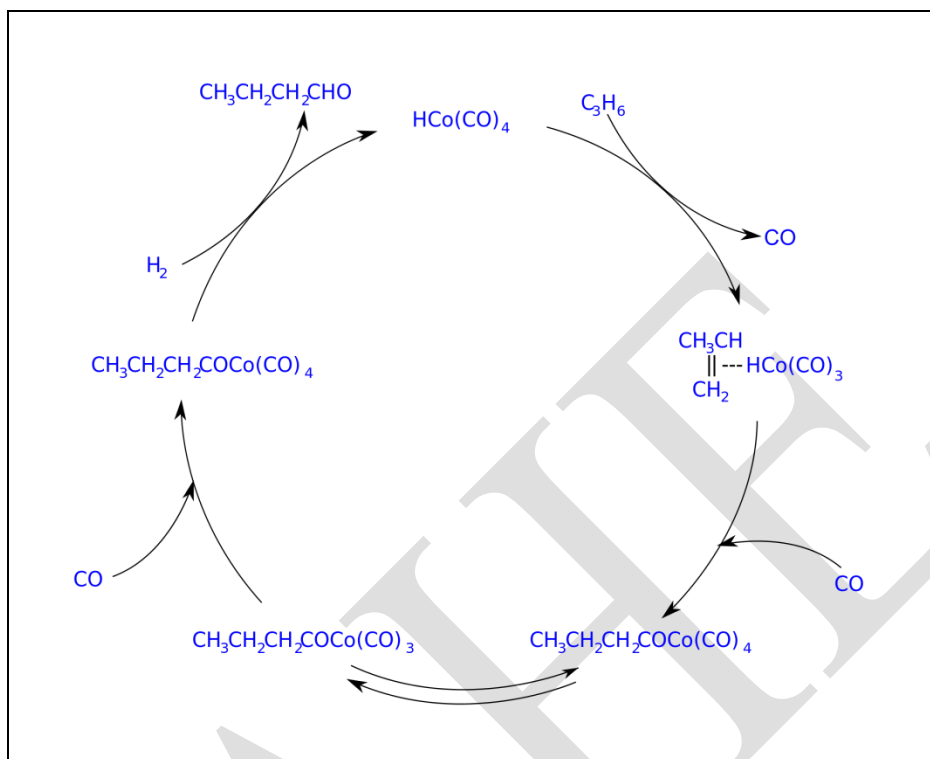
It was discovered by Roelin in 1938 and is the oldest and largest volume catalytic reaction of alkenes, with the conversion of propylene to butyraldehyde being the most important.

About 5 million tons of aldehydes and aldehyde derivatives (Mostly alcohols) are produced annually making the process the most important industrial synthesis using a metal carbonyl complex as a catalyst.

The name hydroformylation arises from the fact that in a formal sence a hydrogen atom and a formyl group are added across a double bond.

The net result of the process is extension of the carbon chain by one and introduction of oxygen into the molecule.

The most widely accepted mechanism for the catalytic cycle is the following one proposed by Heck and Breslow:



In equ(2) we see that $\text{Co}_2(\text{CO})_8$ reacts with H_2 to give $\text{HCo}(\text{CO})_3$ (a 16-electron species) and creating a vacant coordination site.

Alkene coordination recreates an 18- electron complex which undergoes migratory insertion of the olefin in to the the Co-H bond thereby creating another 16-electron complex and another vacant coordination site to which CO can become coordinated.

A carbon monoxide ligand of $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4$ migrates to a position between the cobalt atom and the alkyl group- this is the eritical step in the formation of the aldehyde.

Reaction with H_2 or $[\text{HCo}(\text{CO})_4]^-$ releases the aldehyde and regenerates the catalyticcobalt complex.

The process may be carried out so that the aldehyde products are reduced to give alcohols such as 1-butanol (which is used to make the plasticizer 2-ethyl -1-hexanol) or higher alcohols used for detergents or other plasticizers.

Some disadvantages are associated with the cobalt carbonyl catalyst when it is used to convert propylene to butyraldehyde.

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1) temperatures of 140-1750c and a pressure of 200 atmosphere catalyst when it is used to convert propylene to butyraldehyde.

2) branched chain aldehydes predominate over linear molecules which are more desirable (linear detergents are more biodegradable than are branched ones.).

A modified cobalt catalyst, $\text{HCo}(\text{CO})_3 \text{PBu}_3$, developed by shell improves the linear to branched ratio but gives a slower reaction and therefore is run at higher temperatures (1750c and 50-100 atm).

Union carbide has improved the ratio even more with various rhodium catalysts.

For example, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyzes the reaction at 90-1100c and 12 atm.

A few years ago the company announced a new low pressure hydroformylation rhodium catalyst modified with phosphites, $\text{P}(\text{OR})_3$, which works with less active alkenes such as 2-butene and 2-methyl propene.

The relatively high expense of rhodium requires that this catalysts be long lived and not lost from the reaction system.

It is expected that the use of rhodium catalyst will continue to increase in hydroformylation chemistry.

Monsanto acetic acid process:

Enormous quantities of methanol are produced commercially from synthesis gas:

Methanol in turn can be converted directly to other important chemicals such as acetic acid, formaldehyde, and even gasoline.

One of the great successes of homogeneous catalysis is in the conversion of methanol to acetic acid.

The mechanism for the reaction is believed to be as shown in equ (3) (start with CH_3OH , lower right, and end with CH_3COOH , lower left).

The reaction can be initiated with any rhodium salt, e.g. RhCl_3 and source of iodine, the two combining with CO to produce the active catalyst, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

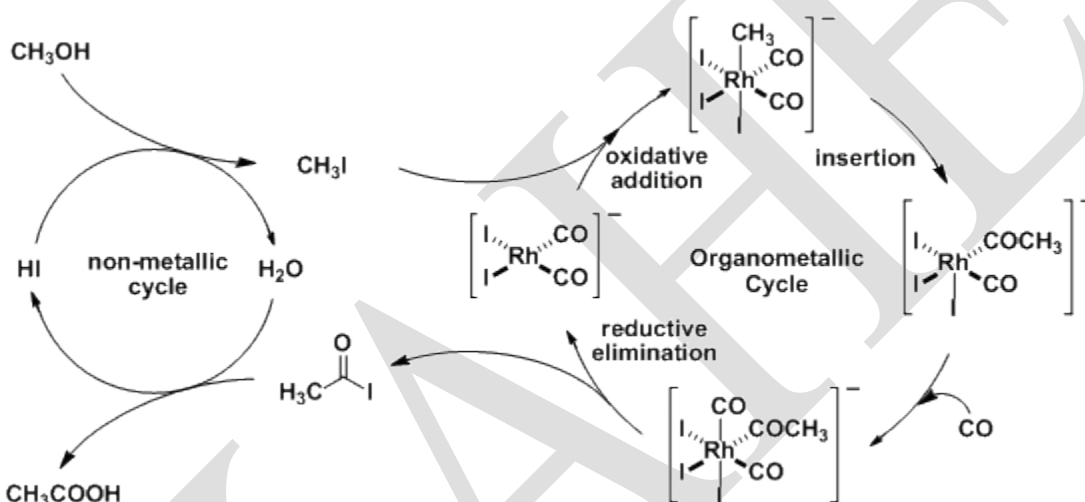
The methyl iodide arises from the reaction of methanol and hydrogen iodide.

Note that the catalytic loop involves oxidative addition, insertion, and reductive elimination, with a net production of acetic acid from the insertion of carbon monoxide into methanol.

The Rhodium shuttles between the +1 and +3 oxidation states.

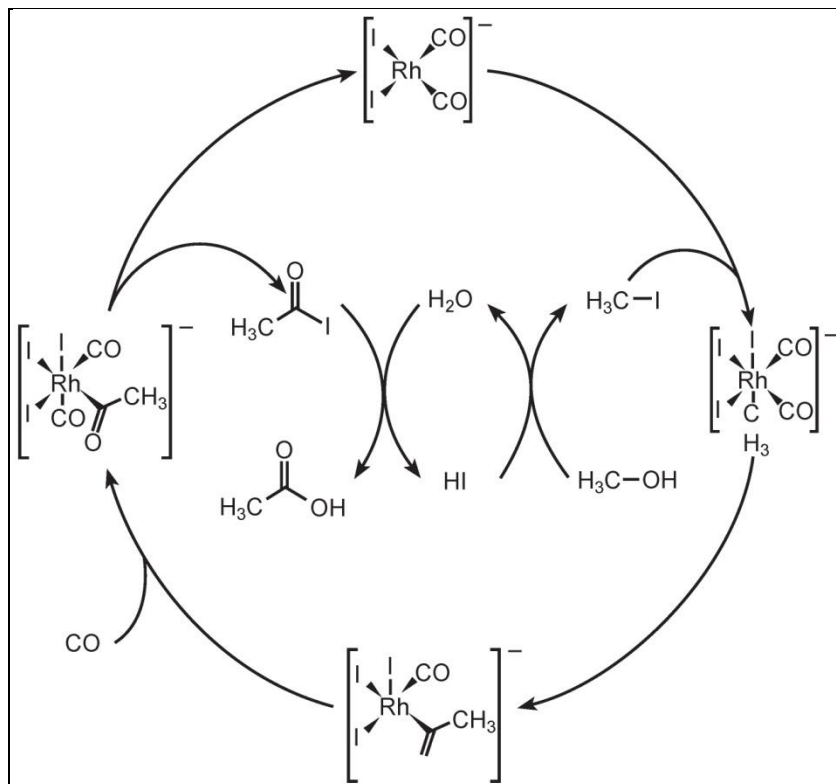
The catalyst is so efficient that the reaction will proceed at atmosphere pressure, although in practice the system is pressurized to increase the rate of the reaction.

The technology has been licensed worldwide, with over 1 million pounds of acetic acid being produced annually by this process.



In 1983, Tennessee Eastman began a similar process for producing acetic anhydride from methyl acetate.

The steps of this carboxylation reactions are very similar to these for the production of acetic acid.



Methyl iodide for oxidative addition to the rhodium complex is generated from the reaction of methyl acetate and lithium iodide.

Acetyl iodide is produced in the same manner as describe in the acetic acid cycle when it is eliminated in the presence of lithium acetate, acetic anhydride is formed.

The wacker process:

Adding oxygen to compounds on an industrial scale requires a cheap source of oxygen.

The three most important sources of sources of oxygen are carbon monoxide (e.g hydroformylation, acetic acid synthesis), water, and molecular oxygen.

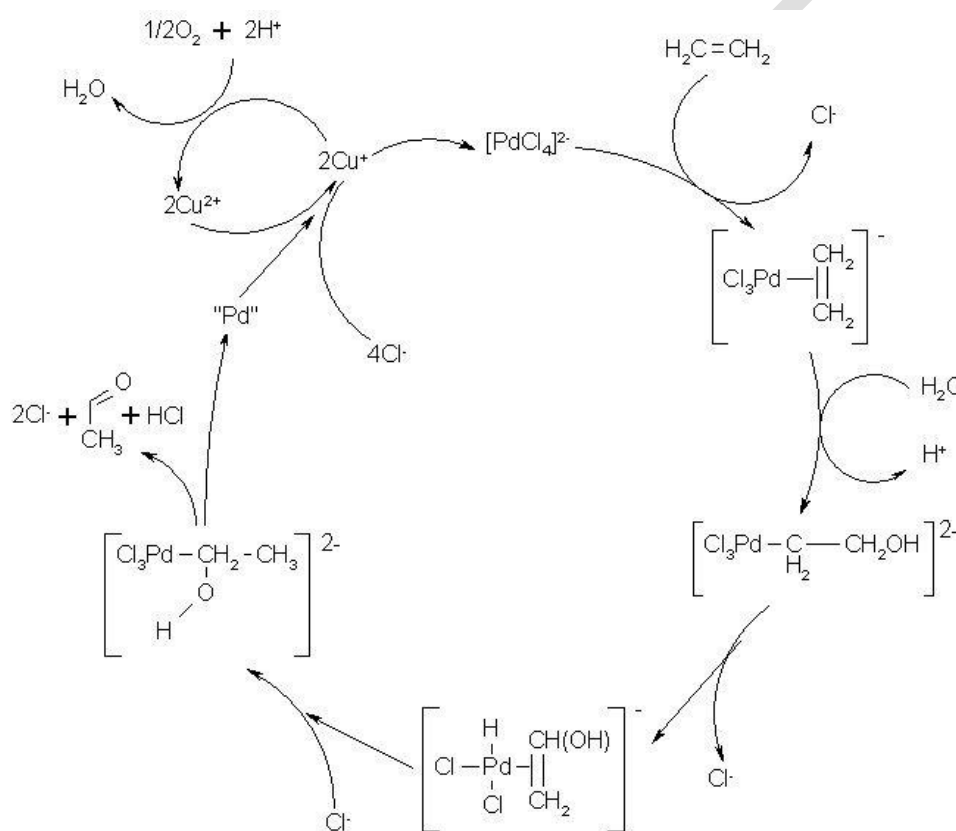
As discussed in most organic books, water can be added to propylene under acidic conditions to form isopropyl alcohol.

In this section we shall look at the catalytic addition of molecular oxygen to an alkene (the wacker process):

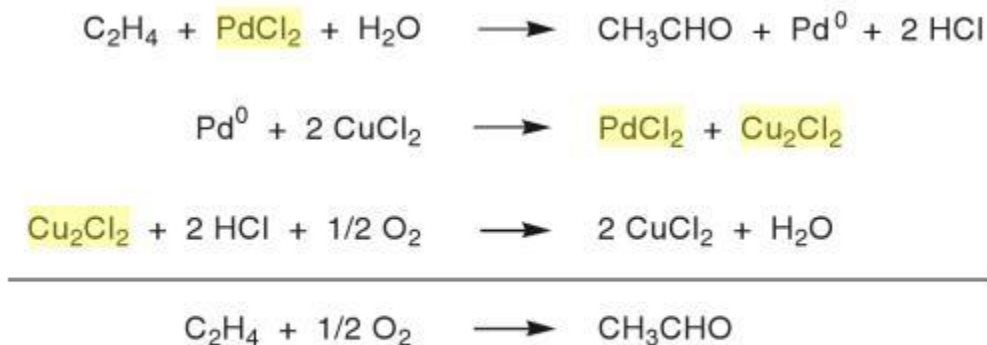
This process, developed in Germany, was one of the first to foretell the importance of alkenes following the world war II. About 4 million pounds of aldehydes are produced yearly by this method.

Acetaldehyde is easily oxidized to acetic acid and the overall conversion of ethylene to the acid represents a principal route to its synthesis.

It has been said that “the invention of the Wacker process was a triumph of common sense.



The cycle can be three reaction:



The sequence of reactions that, combined together, constitutes the Wacker process.

The first reaction is stoichiometric and would be of little value since palladium is expensive. In the presence of Cu^{2+} , palladium metal is oxidized back to Pd^{2+} before it precipitates (equ(4)).

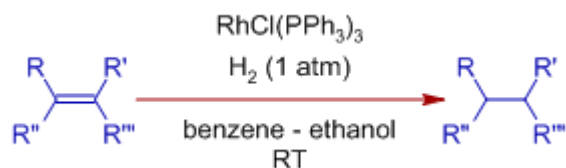
The Cu^+ produced is reoxidized by molecular oxygen.

The mechanism for conversion of ethylene to acetaldehyde has been extensively studied and the intermediates shown in the above cycle are now accepted by most chemists.

Hydrogenation of unsaturated organic compounds:

Alkene hydrogenation:

Although the reaction of hydrogen gas with ethylene is thermodynamically favorable, it does not take place at room temperature and pressure.



However, in the presence of metallic nickel, copper, palladium, or platinum, the reaction is fast and complete. The metal may be deposited on an inert solid support such as alumina or calcium carbonate, but the reaction is with the metal surface and therefore is heterogeneously catalyzed.

The first effective homogeneous catalyst to be discovered for hydrogenation was the square planar 16- electron d8 complex chlorotris (triphenyl phosphine) rhodium (I). $(\text{RhP}_3)\text{RhCl}$, which is known as wilkinson's catalyst.

We saw that this geometry and electron configuration are an especially favorable combination.

These species also have wide possibilities for oxidative addition.

They can become five coordinate through simple addition of a ligand or six coordinate through addition combined with oxidation.

In either case they become isoelectronic with the next noble gas, ie. They achieve an 18-electron Valence shell configuration. It is not surprising then that 16-electron square planar complexes have been regarded as very attractive catalyst candidates on the premise that they may oxidatively add two reactant molecules and thereby enhance their reactivity.

Wilkinson's catalyst is thought to behave as follows:

In solution one of the phosphine ligand dissociates, leaving $(\text{Ph}_3\text{P})_2\text{RhCl}$.

This tri coordinate complex is very reactive and has not as yet been isolated, but the closely related $[(\text{Ph}_3\text{P})_3\text{Rh}]^+$, which could form from the dissociation of a chloride ion from Wilkinson's catalyst has been studied and found to have an unusual structure.

Unlike most three coordinate complexes, it is more T- shaped than triangular

The evidence for dissociation of a Ph_3P ligand from $(\text{Ph}_3\text{P})_4\text{RhCl}$ is indirect but persuasive:

1)For complexes with less sterically hindered phosphines (e-g. Et_3P), the catalytic effect disappears apparently steric repulsion forcing dissociation is necessary: and,

2)With the corresponding iridium complex in which the metal- phosphorus bond is stronger, no dissociation takes place and no catalyst is observed.

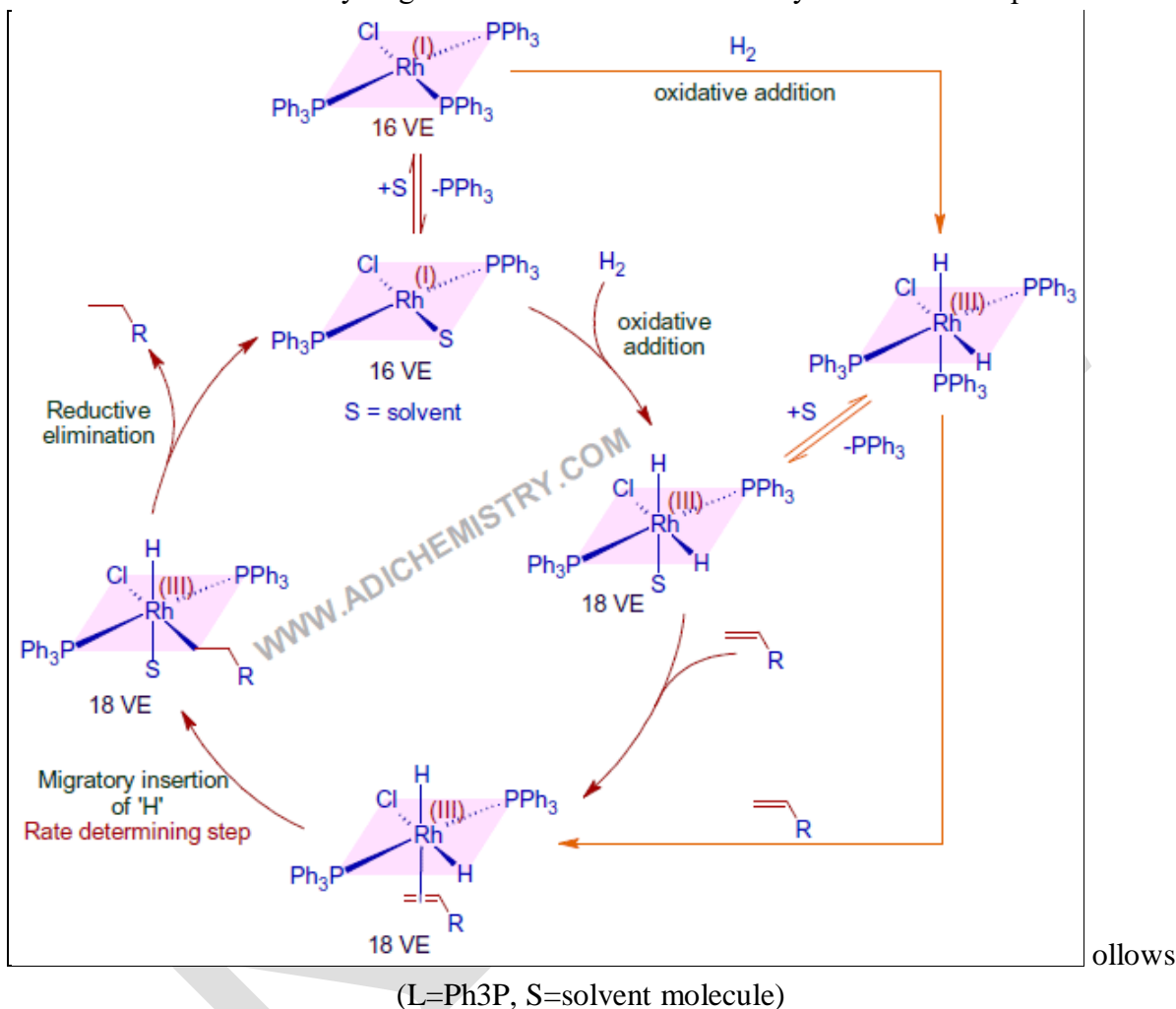
To return to the catalyst, the $(\text{Ph}_3\text{P})_2\text{RhCl}$ molecule, possibly solvated, can undergo oxidative addition of a molecule of hydrogen.

An alkene can then coordinate and react with a coordinated hydrogen ligand to form an alkyl group.

This reaction will result from a migration of a hydrogen from the metal to a carbon in the coordinated alkene.

Although the hydrogen atom does essentially all of the moving, this reaction is often called an alkene insertion reaction.

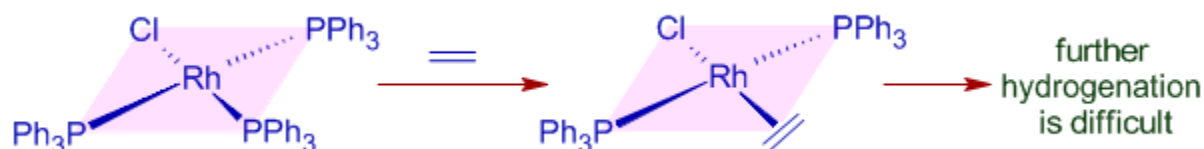
The reactions involved in hydrogenation with Wilkinson's catalyst thus can be represented as follows



Ethylene is commonly chosen to illustrate homogeneous hydrogenation with Wilkinson's catalyst, but the process is actually very slow with this alkene.

The explanation lies with the formation of a stable rhodium ethylene complex, which does not readily undergo reaction with H₂.

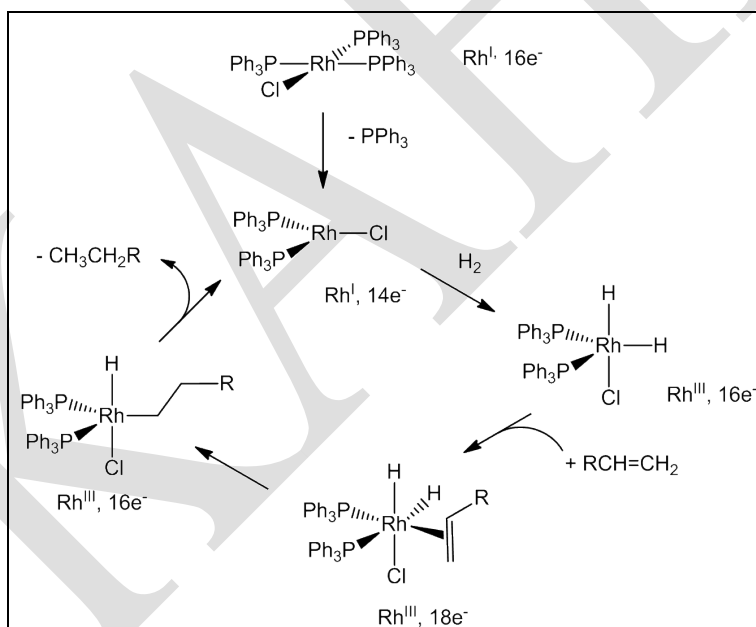
Ethylene competes effectively with the solvent for the vacant coordination site created when triphenylphosphine dissociates from Wilkinson's catalyst and thus serves as an indicator to hydrogenation.



Tolman catalytic loops:-

A reaction involving a trye catalyst can always be represented by a closed loop.

Thus we may comine Eqs 1-5 into a continuous cycle with the various catalytic species forming the main body of the loop and reactants and products entering and leaving the loop at appropriate places:



Synthesis Gas:-

The history of organic industrial chemistry can be organized around the relative reactivities of the organic feed stocks used are during a particular era.

The years 1910-1950 can be characterized as the “acetylene period” since readily available, highly reactive, but rather expensive acetylene was employed.

From 1950 to the present, alkene have predominated.

It now appears that alkenes in turn will be replaced by synthesis gas (H_2/Co) as the raw material, of choice, and we shall enter the era of one carbon feedstocks.

The evolution of homogeneous catalyst for industrial use has been extended to ever cheaper and less reactive feed stocks.

Synthesis gas can be produced from coal and was one of the reasons interest in coal rose markedly during the oil embargoes of the 1970s`

Enthusiasm toward coal as a resource waxes and wanes as the price of petroleum rises and falls.

The first H_2/Co mixture to be commercial importance was obtained from the action of steam on red-hot coke and, because of its origin, become known as water gas.

In the 19th century days of gas lamps, water gas was frequently used for domestic purposes, a practice fraught with danger because of the extreme toxicity of carbon monoxide.

The ratio of hydrogen to carbon monoxide in watergas can be altered with the water-gas shift reaction, which can be catalysed by a variety of heterogenous and homogenous catalysts.

There are several reasons for wishing to alter the hydrogen concentration.

First hydrogen is a more versatile industrial chemical than water gas.

atoms, so if the H_2/Co mole ratio can be changed to about two, a good feedstock is obtained.

Commercially, the water gas shift reaction is usually carried out over Fe_3O_4 .

However current interest centers on homogeneous catalyst.

Metal carbonyl complexes such as $[HFe(CO)_4]^-$, $[Rh(CO)_2I_2]^-$, and $[Ru(bpy)_2(CO)Cl]^+$ are effective and although all the mechanisms have not been worked out completely, the reactions may be nucleophilic attack on coordinated carbon monoxide.

The hydridic hydrogen can then attack water:

Alternatively (and equivalently) a water molecule can attack in equ(1) (freeing an H^+ ion) followed by attack of a proton on the hydridic ion in equ(2).



A scheme for the reaction catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ can be presented as:

This particular cycle is significant because all of the key intermediates have been isolated.

Substitution of H_2O for Cl^- in $[Ru(bpy)_2(CO)Cl]^+$ gives $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ which exists in equilibrium with $[Ru(bpy)(CO)(OH)]^+$.

Carbon monoxide displaces water give $[Ru(bpy)_2(CO)_2]^{2+}$ which undergoes nucleophilic attack to form a hydroxyl carbonyl complex.

Decarbonylation occurs with hydride formation followed by liberation of hydrogen gas and reformation of the catalyst.

The preferred route to synthesis gas currently is by reforming methane (Principal component of natural gas):

Whatever the source of synthetic gas, it is the starting point for many industrial chemicals.

Some examples to be discussed are the hydroformylation process for converting alkenes to aldehydes and alcohols, the “monsanto process” for the production of acetic acid from methanol from methane, and the preparation of gasoline by the mobil and Fisher-Tropsch methods.

Ziegler- Natta catalyst:

Ziegler- Natta polymerization:

The polymerization of olefins by catalyst of the Ziegler natta type represents a most important example of the insertion reaction.

The Ziegler catalyst formed from $TiCl_4$ and aluminium trialkyl.

These components may react in a following way.

In the inert hydrocarbon solvents used an insoluble mixed halide-alkyl complex of aluminium and titanium is formed of variable composition.

This material is the active catalyst for the polymerization of ethylene, presumably acting as a heterogeneous catalyst.

Natta and coworkers had produced stereospecific polymers.

For example, olefins like propylene have been polymerized in such a way as to yield long linear head to tail chains consisting of sequence of monomer units having the same steric structures.

These polymers are called isotactic polymers and they crystallize easily, whereas those monomeric units of different steric arrangement phased at random do not crystallize well.

These polymers are called atactic.

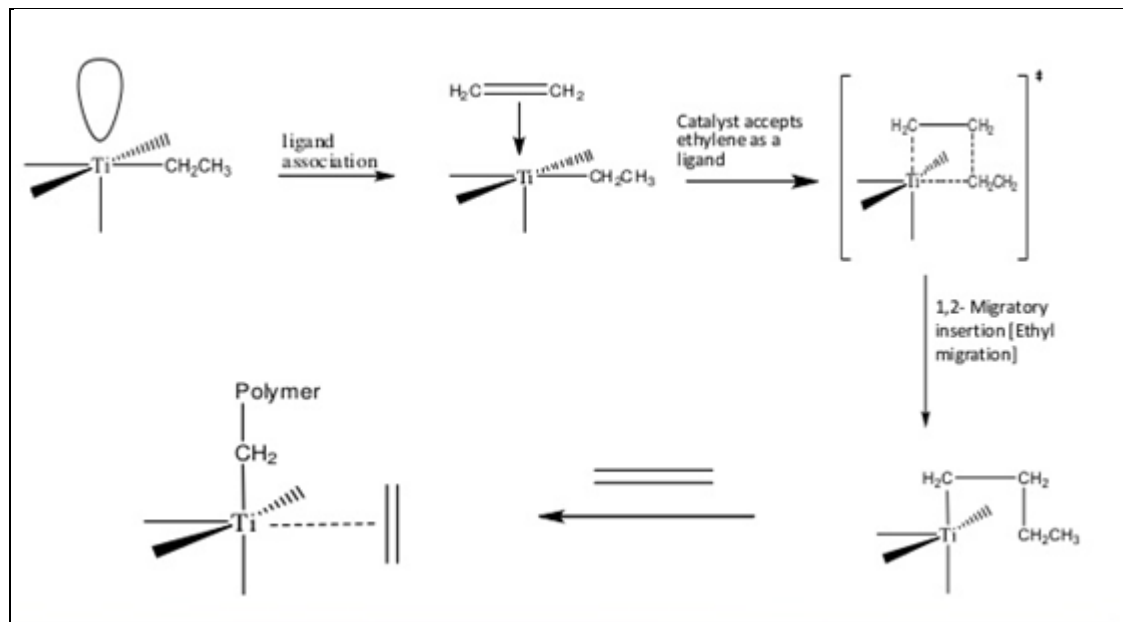
Polymers of regular, alternating structure are called syndiotactic polymers.

The Ziegler-Natta system is not homogeneous, it is heterogeneous and the active metal species is fibrous form of $TiCl_3$ formed in situ from $TiCl_4$ and $AlEt_3$ but preformed $TiCl_3$ can be used.

According to mechanism proposed by Cossee, the metal ion active site on the catalyst surface is octahedrally coordinated and which has a growing polymer chain R at one position and one position is vacant.

The alkene is coordinated to vacant site and an insertion reaction occurs.

After promotion of an electron from the Ti-alkyl bond to a molecular orbital of the complex, a four centre transition state is produced which enables an alkyl group to transfer to coordinated alkene.

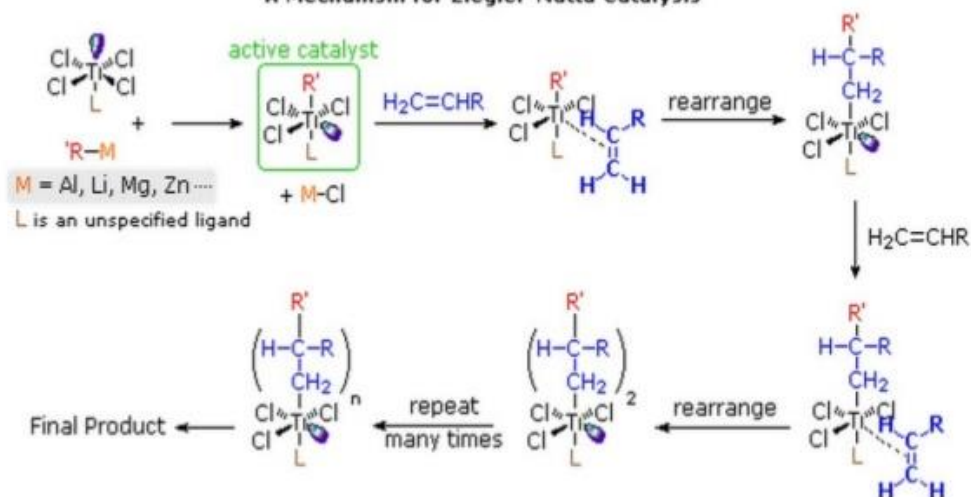


A further molecule of alkene is then bound to vacant site and the process is repeated.

The mechanism is then as follows:-

Mechanism Of Ziegler Natta Catalysis

A Mechanism for Ziegler-Natta Catalysis



The functions of aluminium alkyl are mainly-

- The formation of active metal species TiCl_3
- The replacement of one of the chloride ions in a Ti^{3+} ion at the surface by an alkyl radical derived from it.

The stereoregular polymerization of propene may arise because of the nature of the sterically hindered surface sites on the TiCl_3 lattice.

An important extension of Ziegler-Natta polymerization is the copolymerization of styrene, butadiene and a third component such as dicyclopentadiene or 1,4-hexadiene to give synthetic rubbers.

Vanadyl halides rather than titanium halides are then used as the metal catalyst.

Wilke and his coworkers have shown that zero –valent complexes, especially of nickel, obtained by reduction with aluminium alkyls can be used in a wide variety of polymerizations such as trimerization of butadiene to trans, trans, trans-cyclododecatriene.

References:-

1. Wahid U.Malik, G.D. Tuli, R.D. Madan, 2003. Selected topics in inorganic chemistry, schand & company, New Delhi.
2. Huheey, J. E, E.A. Keitter& R.L. Keitter 2002, Inorganic chemistry vol.IV, Pearson Education, Singapore.

Possible Questions:

Part A:

Each question carries one mark:

1. The reaction in aqueous medium in which a water molecule replaces a coordinated ligand from the complex species is termed as
 - a. Aquation reaction
 - b. Hydrolysis
 - c. Hydration
 - d. Dehydration
2. The reaction in aqueous medium in which the anion of water in OH^- ion replaces a coordinated ligand from the complex species is known as
 - a. Hydroxylation
 - b. Base hydrolysis
 - c. Neutralization
 - d. Acid hydrolysis
3. As the positive charge on the reacting species increases the rate of aquation
 - a. Increases
 - b. decreases
 - c. First decreases then increases
 - d. First increases then decreases
4. Rate of --- decreases with increases in the basicity of the leaving group
 - a. Hydration
 - b. hydrolysis

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c.Aquation

d.Base hydrolysis

5. Substitution process in complex cannot be carried out in presence of water due to --- reaction in aqueous medium

a.decomposition

b.Hydrolysis

c.Aquation

d.hydratation

6. In the presence of pi bonding inert ligand both cis and trans isomers will aquate to give the product with geometry --- as that of reactant

a.same

b.distorted

c.Different

d.None

7. In some cases solvent molecules act as nucleophiles form --- complexes

a.Solvation

b.Solvent encounter

c.Solvent cage

d.Solvent complexes

8. The ---- system will give square planar geometry in complex

a.d²

b. d⁴

c.d⁸

d.d⁶

9. IN order to get substituted product by the method of oxidative addition the process should be followed

a.reduction

b.Elimination

c.reductive elimination

d.Oxidation

10. Nucleophilic substitution in square planar complexes follows the mechanism usually

a.SN1

b.SN2

c.SN_i

d.SN_{cb}

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11. The ability of an attached group to direct substitution into a position opposite itself is called
a. Cis effect
b. Trans effect
c. both
d. None
12. If the substituting ligand is attached to central metal then the geometry of the intermediate complex will be
a. Square pyramidal
b. Square bipyramidal
c. trigonal pyramidal
d. tetrahedral
13. The orbital used by the attacking ligand in substitution reaction is
a. px
b. pz
c. py
d. s
14. Redox reaction involves transfer of ----- electron from one atom to another atom
a. 1
b. 2
c. 3
d. 4
15. In redox reaction change in ----- occurs
a. Oxidation state
b. Electron affinity
c. Electronegativity
d. Covalent bond
16. Two types of mechanism in redox reaction are
a. Inner and outer sphere mechanism
b. Bridge and electron transfer mechanism
c. Inner and bridge mechanism
d. Both a & b
17. In inner sphere mechanism the reaction is brought about by formation of a -----
a. Bridged activated complex
b. Complex ligand
c. Bridged unactivated complex
d. ligand

18. Inner sphere mechanism --- acts as bridge between two reacting complex

- a.free radical
- b. ions
- c.negative ion
- d.ligand**

19. Inner sphere mechanism is also called as

- a.Ligand bridged complex mechanism
- b.Atom transfer mechanism
- c.Bridged activated complex mechanism
- d.all the above**

20. In EDTA ----- acts as bridges

- a.Oxygen atom**
- b.Nitrogen atom
- c.Cl atom
- d.Flourine atom

Part-B

Each question carries six marks:

1. Explain Trans Effect Theory?
2. Illustrate with suitable example of Nucleophilic substitution reaction
3. Write a note on homogeneous catalysis
4. Write an account on Ziegler-Natta Polymerization?
5. Explain Carbonizations
6. Discuss about Hydroformylation reactions.
7. What is Kinetic Trans effect.Explain
8. Define heterogeneous catalysts.Explain
9. State and illustrate Substitution reactions in square planer complexes.
10. Discuss the theory of redox reactions using a typical example.

Part-C

Each question carries 10 marks:

1. Explain the mechanism of Wacker process in the synthesis of acetaldehyde.
2. Explain the inner sphere mechanism and outer sphere mechanism of redox reactions.

3. State and illustrate Trans effect. Explain the polarization theory of Trans effect.
4. Discuss the theory of redox reactions using a typical example.

18CHP202
Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2018 onwards)
Department of Chemistry
II- semester

Inorganic Chemistry -II (Coordination Chemistry)

UNIT V- Objective Questions for online examination (Each carry 1 Marks)

Question	Option-a	Option-b	Option-c	Option-d	Answer
The reaction in aqueous medium in which a water molecule replaces a coordinated ligand from the complex species in termed as	Aquation reaction	Hydrolysis	Hydration	Dehydration	Aquation reaction
The reaction in aqueous medium in which the anion of water in OH^- ion replaces a coordinated ligand from the complex species in known as	Hydroxylation	Base hydrolysis	Neutralization	Acid hydrolysis	Base hydrolysis
As the positive charge on the reacting species increases the rate of aquation	Increases	decreases	First decreases then increases	First increases then decreases	decreases
Rate of --- decreases with increases in the basicity of the leaving group	Hydration	hydrolysis	Aquation	Base hydrolysis	Aquation
Substitution process in complex cannot be carried out in presence of water due to --- reaction in aqueous medium	decomposition	Hydrolysis	Aquation	hydration	Aquation
In the presence of pi bonding inert ligand both cis and trans isomers will aquate to give the product with geometry --- as that of reactant	same	distorted	Different	None	same

In some cases solvent molecules act as nucleophiles form --- complexes	Solvation	Solvent encounter	Solvent cage	Solvento complexes	Solvento complexes
The ---- system will give square planar geometry in complex	d2	d4	d8	d6	d8
IN order to get substituted product by the method of oxidative addition the process should be followed	reduction	Elimination	reductive elimination	Oxidation	reductive elimination
Nucleophilic substitution in square planar complexes follows the mechanism usually	SN1	SN2	SNi	SNcb	SN2
The ability of an attached group to direct substitution into a position opposite itself is called	Cis effect	Trans effect	both	None	Trans effect
If the substituting ligand is attached to central metal then the geometry of the intermediate complex will be	Square pyramidal	Square bipyramidal	trigonal pyramidal	tetrahedral	Square pyramidal
The orbital used by the attacking ligand in substitution reaction is	px	pz	py	s	pz
Redox reaction involves transfer of ----- electron from one atom to another atom	1	2	3	4	1
In redox reaction change in ----- occurs	Oxidation state	Electron affinity	Electronegativity	Covalent bond	Oxidation state
Two types of mechanism in redox reaction are	Inner and outer sphere mechanism	Bridge and electron transfer mechanism	Inner and bridge mechanism	Both a & b	Both a & b
In inner sphere mechanism the reaction is brought about by formation of a -----	Bridged activated complex	Complex ligand	Bridged un activate complex	ligand	Bridged activated complex
Inner sphere mechanism --- acts as bridge between two reacting complex	free radical	ions	negative ion	ligand	ligand
Inner sphere mechanism is also called as	Ligand bridged complex mechanism	Atom transfer mechanism	Bridged activated complex mechanism	all the above	all the above

In EDTA ----- acts as bridges	Oxygen atom	Nitrogen atom	Cl atom	Flourine atom	Oxygen atom
In EDTA ---- oxygen atoms acts as bridge	1	2	3	4	3
In outersphere mechanism --- acts as electron conduction media.	Electrode	Position	Proton	Ligands	Ligands
Outersphere mechanism is appropriate to large ----- ligands	coordinated	Conjugated	Covalent	all	Conjugated
The requirements of outer, sphere mechanism is satisfactorily given by -----	frank-condon principle	Frank principle	Condon-wilkinsons principle	taube's principle	frank-condon principle
In outer spher mechanism, if the reactants are inert, the electron tranfer takes by --- mechanism.	Tunneling	Stunt	Spilitting	Coupling	Tunneling
In outer spin mechanism for an isotopic change ΔG is nearly	1	2	0	4	0
Outer sphere electron transfer reaction are faster for complexes having ---- ligands.	CN-	H2O	NH3	Cl-	CN-
Electron transfer reaction in which oxidant gains the same number of electrons as the reductant loses -----	Complementary electron transfer reaction	Elementary electron transfer reaction	Primary electron transfer reaction	Secondary electron transfer reaction	Complementary electron transfer reaction
The main success of homogeneous catalysis is the conversion of methanol to	Acetic acid	Oxalic acid	Sulphuric acid	hydrochloric acid	Acetic acid
The catalyst used for the conversion of methanol to acetic acid	Sr salt	Pt salt	Rh salt	Ag salt	Rh salt
The process of conversion of methanol to acetic acid using Rh salt as catalyst is called	Canizzaro reaction	Aldol condensation	Reformatsky reaction	Monsanto acetic acid process	Monsanto acetic acid process
In Monsanto acetic acid process inversion of takes place	CO	CO2	SO2	NO2	CO
Who proposed the conversion of acetic anhydride from methyl acetate in Monsanto manner	Bethe	Prevost	Mannich	tennesee eastman	tennesee eastman

The process in which the catalytic addition of molecular oxygen to alkene is called	Wacker process	Contact process	Heat process	Haber process	Wacker process
The product of wacker process is given as	Aldehydes	Ketones	Ozonide	Alkane	Aldehydes
The product formed , when the acidification of carbonylate ion	Carbonyl hydrido complex	Carbonyl complex	Carboxylate anion	none	Carbonyl hydrido complex
Which is the relatively expensive catalyst used in hydroformylation	Cobalt	Rhodium	Copper	Nickel	Rhodium
The uses of which catalyst will continue to increase in hydroformylation chemistry	Cobalt	Copper	Rhodium	Zinc	Rhodium
who proposed the most widely accepted mechanism for hydrofomylation	Watson and Crick	Cannzaro	Wittig	Heck and Breslow	Heck and Breslow
Hydroformylation is carried out in such a way that aldehydes are reducesd to give	Alcohols	Acids	ketones	none	Alcohols
The reaction of an alkene with carbnmonoxide and hydrogen, catalysed by cobalt or rhodium salt, to form an aldehyde is called	Hydroformylation	Hydroxylation	Hydrogenation	None	Hydroformylation
In hydroformylation cobalt and ----- are used as catalysis	Rhodium	Bismath	copper	Nickel	Rhodium
Many of the properties of metal complexes are dictated by which structure?	Chemical	Physical	Electron	Electronic	Electronic
Which isomerism occurs when the bonds are themselves different?	Stereo	Optical	Cis-trans	Structural	Structural
which is highest melting halide	NaCl	NaBr	NaF	NaOH	NaF
When the triphenyl phosphine ligands are replaced by chiral phosphines the catalyst becomes chiral and converts prochiral alkenes into enantiomerically enriched alkanes via the process called ?	Symmetric hydrogenation	Asymmetric hydrogenation	Hydrogenation	Desociation	Asymmetric hydrogenation

The original catalyst was $\text{HCo}(\text{CO})_4$, discovered by ?	Chernyaev	Wilkinson's	Otto Roelen	Flemming	Otto Roelen
Which one of the following is a carbonyl complex?	$\text{RhCl}(\text{PPh}_3)_3$	$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	PPh_3	$\text{HCo}(\text{CO})_3$	$\text{HCo}(\text{CO})_3$
Hydroformylation, also known as ?	oxo synthesis	Oxo production	Oxo reduction	Oxo decomposition	Oxo synthesis
Monsanto process operates at a pressure of ?	30-60 atm	40-70atm	20-60atm	30-50 atm	30-60 atm
Which speed up inner sphere reactions?	Increasable ligands	Ligand	Reducible ligands	Metal	Reducible ligands
Ligands that are able to bridge are required for ?	Inner sphere mechanism	Rates of reaction	Sphere mechanism	Outer sphere mechanism	Inner sphere mechanism
Which one of the following depend on the ability of the electron to “tunnel” through the ligands from one metal to the other?	Speed of reaction	Ability of reaction	Rates of reaction	Catalyst	Rates of reaction
In reduction the metal ion becomes ?	Less positively charged	More positively charged	Negatively charged	Less negatively charged	Less positively charged
Chloride is said to have a stronger trans effect than ?	Iodine	Ammonia	CN	NO_2	Ammonia
Who introduced the concept of the trans effect in platinum chemistry?	Chernyaev	Wilkinson's	Otto Roelen	Jahn-Teller	Chernyaev
In an interchange (I) reaction, a rapid equilibrium between the incoming ligand and the 6- coordinate reactant forms an ?	Ion	Too loosely bonded molecular combination	Ion pairs	Tightly bonded molecular combination	Ion pairs
Larger electrostatic attraction between the positive metal ion and the negative ligand should?	Speeds the dissociation	slow the dissociation	Does not affect the dissociation	Not react with dissociation	Slow the dissociation
Dissociative mechanisms generally result in which values for Δv_{act} ?	Positive	Alkaline	Neutral	Negative	Positive

In which year highly active rhodium catalysts were discovered?	1940	1950	1960	1970	1980

Subject Code: 18CHP202

Reg.No.....

KARPAGAM ACADEMY OF HIGHER EDUCATION

COIMBATORE-21

(For the candidates admitted from 2018& onwards)

DEPARTMENT OF CHEMISTRY

M.Sc Degree Examination

Semester-II

INTERNAL TEST-I(FEBRUARY-2019)

SUBJECT TITLE: INORGANIC CHEMISTRY-II (COORDINATION CHEMISTRY)

Date: 4. 2.2019 AN

Subject Code : 18CHP202

Time : 2 Hours

Maximum : 50 marks

Part-A (20 x1= 20 Marks)

Answer all the questions

1. In a bidentate ligand if the two coordinating atoms are same means it is known as ----
a. Flexidentate ligands b. Ambidentate ligands c. Symmetrical ligands d. Unsymmetrical ligands
2. The geometry of the complex which is having coordination number 3 is
a. Tetrahedral b. Linear c. Square planar d. Trigonalpyramidal
3. Polydentate ligands in which two are more donar atoms are attached with the same metal ion and produce rings are called -----
a. Briged ligand b. Chelating ligand c. Flexidentate ligand d. Ambidentate ligand
4. The ligands which are having only one donar atom and can coordinate to the central metal ion at one site only are called -----
a. Unidentate b. Bidentate c. Tridentate d. Flexidentate
5. The combination of ligand-to-metal σ -bonding and metal-to-ligand π -bonding is ?,
a. Magnetic effect b. Synergic effect c. Paramagnetic effect d. Diamagnetic effect
6. The LFT analysis is highly dependent on the geometry of the ?,
a. Bonds b. Ligands c. Electrons d. Complex
7. The d orbitals of the ligands are usually?
a. Too high in energy b. Low energy c.High energy d.Too low in energy
8. Tanabe-Sugano diagrams are helpful in understanding
a. Spectral behaviour of metal complexes b.Magnetic character of complexes
c.Identification of molecular structure d.The mechanism of reactions

9. The electronic transition of two energy levels of a molecule which are not having same spin multiplicity is -----
 a. Spin allowed b. Spin forbidden c. Laporte allowed d. Laporte forbidden
10. The electronic transition of two energy levels having same spin multiplicity is -----
 a. Spin allowed b. Spin forbidden c. Laporte allowed d. Laporte forbidden
11. The ground state term symbol for Ni^{2+} is
 a. ^3P b. ^2D c. ^1D d. ^3F
12. Example for d^2 metal ion octahedral environment
 a. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ b. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ c. $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ d. $[\text{Cu}(\text{H}_2\text{O})_6]^{3+}$
13. which is not possible for the charge transfer transitions of d^6 configuration
 a. $t_{1u}, t_{2u} \rightarrow t_{2g}$ b. $t_{1u}, t_{2u} \rightarrow t_{2g}^*$ c. $t_{1u}, t_{2u} \rightarrow e_g$ d. $t_{1u}, t_{2u} \rightarrow e_g^*$
14. The Nephelauxetic ratio β is given by,
 a. $\beta = B'/B$ b. $\beta = B/B'$ c. $\beta = C/B'$ d. $\beta = 1/B$
15. There are no d-d electron transitions in which metal complexes?
 a. d^{10} b. d^{11} c. d^{12} d. d^{13}
16. Tanabe-Sugano diagrams are utilized in determining?
 a. Atom placements b. Element placements c. Electron placements d. Spin
17. In the $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ metal complex, manganese has an oxidation state of +2, thus it is a ?
 a. d^6 ion b. d^4 ion c. d^3 ion d. d^5 ion
18. The Carbonyls which contain more than one metallic atoms are known as ----
 a. Polydentate b. Polynuclear c. Bidentate d. Mononuclear
19. When Co reacted directly with Co at 2000C, 100 atm. pressure it gives
 a. $\text{Co}_2(\text{CO})_8$ b. $\text{Co}(\text{CO})_8$ c. $\text{Co}_3(\text{CO})_8$ d. $\text{Co}_2(\text{CO})_6$
20. The hybridization involved in the complex $[\text{Ni}(\text{CO})_4]$ is
 a. sp^3 b. sp^2 c. dsp^2 d. dsp^3

PART-B (3 X 2= 6 MARKS)

ANSWER ALL THE QUESTIONS

21. What is meant by coordination sphere?
22. Assign ground state term symbol for carbon?
23. What is Vaska's compound?

PART-C (3 X 8 = 28 MARKS)

ANSWER ALL THE QUESTIONS

24. a). Write a note on Crystal field theory?

OR

(b). Discuss the types of isomerism exhibited by coordination complexes, giving suitable examples.

25. a). Sketch and explain the splitting of d-orbital in tetrahedral and octahedral Complexes

OR

(b). What is Jahn-Teller effect? Illustrate with an example?

26.a). Explain the Tanabe-Sugano diagram of a metal complex with d^2 and d^8 configurations.

OR

(b). How do you prepare $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$? Give their structural formulae.

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3. Polydentate ligands in which two are more donar atoms are attached with the same metal ion and produce rings are called -----
a. Briged ligand **b. Chelating ligand** c. Flexidentate ligand d. Ambidentate ligand
4. The ligands which are having only one donar atom and can coordinate to the central metal ion at one site only are called -----
a. **Unidentate** b. Bidentate c. Tridentate d. Flexidentate
5. The combination of ligand-to-metal σ -bonding and metal-to-ligand π -bonding is ?,
a. Magnetic effect **b. Synergic effect** c. Paramagnetic effect d. Diamagnetic effect
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20. The hybridization involved in the complex $[\text{Ni}(\text{CO})_4]$ is
 a. **sp^3** b. sp^2 c. dsp^2 d. dsp^3

PART-B (3 X 2= 6 MARKS)

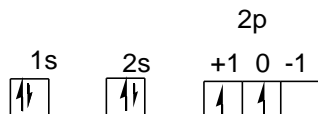
ANSWER ALL THE QUESTIONS

21. What is meant by coordination sphere?

The central metal ion and the ligands that are directly to it are enclosed in a square bracket which Werner has called coordination sphere or first sphere of attraction. The anions being outside the square bracket form the second sphere of attraction.

22. Assign ground state term symbol for carbon?

- The box diagram for carbon is;



And the term symbol to be determined is $^3\text{P}_0$.

23. What is Vaska's compound?

Vaska's complex is the trivial name for the chemical compound *trans*-carbonylchlorobis(triphenylphosphine)iridium(I), which has the formula $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$. This square planar diamagnetic organometallic complex consists of a central iridium atom bound to two mutually *trans* triphenylphosphine ligands, carbon monoxide, and a chloride ion. The complex was first reported by J. W. DiLuzio and Lauri Vaska in 1961. Vaska's complex can undergo oxidative addition and is notable for its ability to bind to O_2 reversibly. It is a bright yellow crystalline solid.

PART-C (3 X 8 = 28 MARKS)

ANSWER ALL THE QUESTIONS

24. a). Write a note on Crystal field theory?

Crystal Field Theory (CFT) is a model that describes the breaking of degeneracies of electron orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution (anion neighbors). This theory has been used to describe various spectroscopies of transition metal coordination complexes, in particular optical spectra (colors). CFT successfully accounts for some magnetic properties, colors, hydration enthalpies, and spinel structures of transition metal complexes, but it does not attempt to describe bonding. CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleck in the 1930s. CFT was subsequently combined with molecular orbital theory to form the more realistic and complex ligand field theory (LFT), which delivers insight into the process of chemical bonding in transition metal complexes.

According to crystal field theory, the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and the negative charge on the non-bonding electrons of the ligand. The theory is developed by considering energy changes of the five degenerate *d*-orbitals upon being surrounded by an array of point charges consisting of the ligands. As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of the *d*-orbitals and farther away from others, causing a loss of degeneracy. The electrons in the *d*-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the *d*-electrons closer to the ligands will have a higher energy than those further away which results in the *d*-orbitals splitting in energy. This splitting is affected by the following factors:

- the nature of the metal ion.
- the metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.
- the arrangement of the ligands around the metal ion.
- the coordination number of the metal (i.e. tetrahedral, octahedral...)
- the nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy *d* groups.

The most common type of complex is octahedral; here six ligands form an octahedron around the metal ion. In octahedral symmetry the *d*-orbitals split into two sets with an energy difference,

Δ_{oct} (the crystal-field splitting parameter) where the d_{xy} , d_{xz} and d_{yz} orbitals will be lower in energy than the d_z^2 and $d_{x^2-y^2}$, which will have higher energy, because the former group is farther from the ligands than the latter and therefore experiences less repulsion. The three lower-energy orbitals are collectively referred to as t_{2g} , and the two higher-energy orbitals as e_g . (These labels are based on the theory of molecular symmetry). Typical orbital energy diagrams are given below in the section High-spin and low-spin.

Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal ion. In a tetrahedral crystal field splitting, the d -orbitals again split into two groups, with an energy difference of Δ_{tet} . The lower energy orbitals will be d_z^2 and $d_{x^2-y^2}$, and the higher energy orbitals will be d_{xy} , d_{xz} and d_{yz} - opposite to the octahedral case. Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the d -orbitals, the energy splitting will be lower than in the octahedral case. Square planar and other complex geometries can also be described by CFT.

The size of the gap Δ between the two or more sets of orbitals depends on several factors, including the ligands and geometry of the complex. Some ligands always produce a small value of Δ , while others always give a large splitting. The reasons behind this can be explained by ligand field theory. The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ that they produce (small Δ to large Δ ; see also this table):

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^-$ (S-bonded) $< \text{Cl}^- < \text{NO}_3^- < \text{N}_3^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^-$ (N-bonded) $< \text{CH}_3\text{CN} < \text{py} < \text{NH}_3 < \text{en} < 2,2\text{'-bipyridine} < \text{phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$.

It is useful to note that the ligands producing the most splitting are those that can engage in metal to ligand back-bonding.

The oxidation state of the metal also contributes to the size of Δ between the high and low energy levels. As the oxidation state increases for a given metal, the magnitude of Δ increases. A V^{3+} complex will have a larger Δ than a V^{2+} complex for a given set of ligands, as the difference in charge density allows the ligands to be closer to a V^{3+} ion than to a V^{2+} ion. The smaller distance between the ligand and the metal ion results in a larger Δ , because the ligand and metal electrons are closer together and therefore repel more.

OR

(b). Discuss the types of isomerism exhibited by coordination complexes, giving suitable examples.

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique. Isomers are compounds with the same molecular formula but different structural formulas and do not necessarily share similar properties. There are many different classes of isomers, like stereoisomers, enantiomers, geometrical isomers, etc. (see chart below). There are two main forms of isomerism: **structural isomerism** and **stereoisomerism** (spatial isomerism).

Class I: Structural Isomers

Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers, which differ in structure or bond type. For inorganic complexes, there are three types of structural isomers: *ionization*, *coordination* and *linkage*. Structural isomers, as their name implies, differ in their structure or bonding, which are separate from stereoisomers that differ in the spatial arrangement of the ligands are attached, but still have the bonding properties. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms. When determining a structural isomer, you look at (1) the ligands that are bonded to the central metal and (2) which atom of the ligands attach to the central metal.

Structural Isomers: Ionization Isomerism

Ionization isomers are identical except for a ligand has exchanging places with an anion or neutral molecule that was originally outside the coordination complex. The central ion and the other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different. A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.

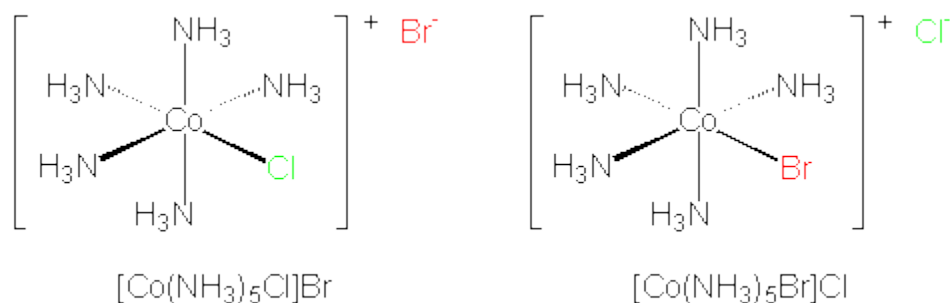


Figure 24.4.124.4.1: Two Ionization isomers. The two isomers differ only which ligands are actually bound to the center metal. (left) The chloride atom is bound to the cobalt as a chloro-ligand with the bromine atom as the bromide counter ion. (right) In the other ionization isomer the bromine atom is acting as a bromo- ligand to the cobalt with the chlorine atom acting as the chloride counter ion. These two isomers are called *pentaamminechlorocobalt(II) bromide* (left) and *pentaamminebromocobalt(II) chloride* (right).

The difference between the ionization isomers can be view within the context of the ions generated when each are dissolved in solution. For example, when pentaamminbromocobalt(II) chloride is dissolved in water, Cl^- ions are generated:



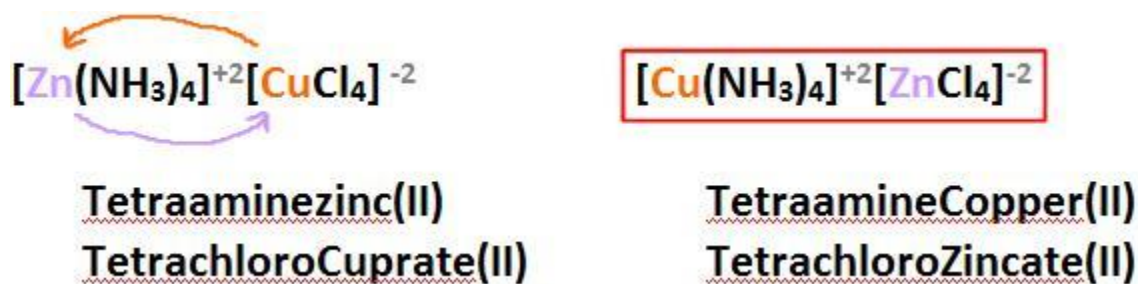
whereas when pentaquachlorocobalt(II) bromide is dissolved, Br^- ions are generated:



Notice that both anions are necessary to balance the charge of the complex, and that they differ in that one ion is directly attached to the central metal, but the other is not.

Structural Isomers: Coordination Isomerism

Coordination isomerism occurs compounds containing complex anionic and cationic parts can be thought of as occurring by interchange of some ligands from the cationic part to the anionic part. Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge. In coordination isomers, the anion and cation complexes of a coordination compound exchange one or more ligands. For example, the $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$ compounds and $[\text{Co}(\text{C}_2\text{O}_4)_3][\text{Cr}(\text{NH}_3)_6]$ compound are coordination isomers.



Structural Isomers: Linkage Isomerism

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: $\text{SCN}^-/\text{NCS}^-$ and NO_2^-/ONO . The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a *polydentate* rather than an *ambidentate* ligand.

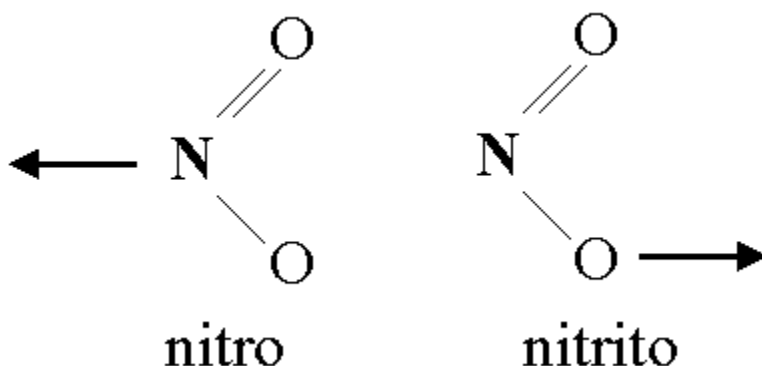


Figure 24.4.224.4.2: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. Image used with permission from Angel C. de Dios.

As with all structural isomers, the formula of the complex is unchanged for each isomer, but the properties may differ. The names used to specify the changed ligands are changed as well. For example, the NO_2^- ion is called *nitro* when it binds with the NN atom and is called *nitrito* when it binds with the O atom.

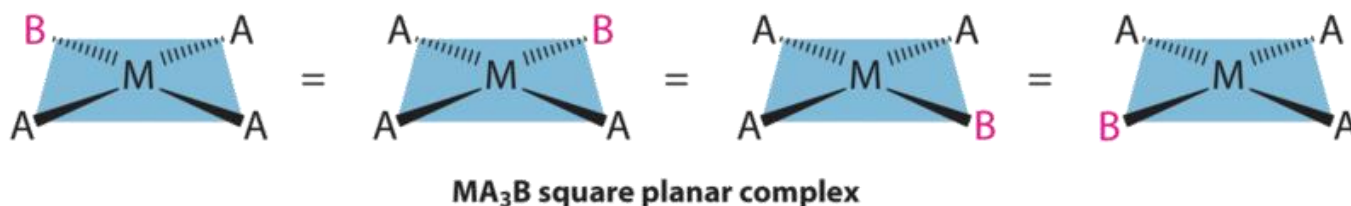
Class 2: Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

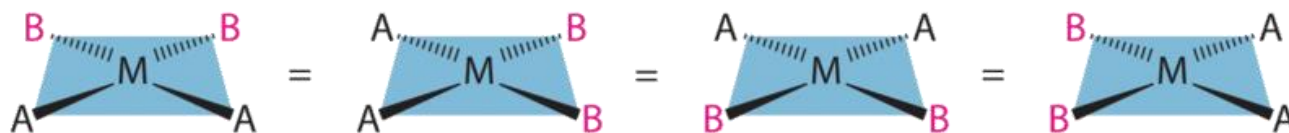
Geometric Isomers: Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

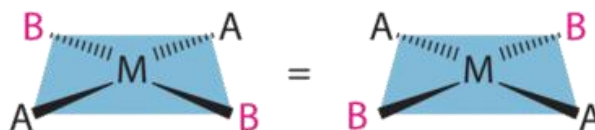
Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (**cis**), in which case the B ligands must also be **cis**, or the A ligands can be across from one another (**trans**), in which case the B ligands must also be **trans**. Even though it is possible to draw the **cis** isomer in four different ways and the **trans** isomer in two different ways, all members of each set are chemically equivalent:



MA₂B₂ square planar complex, *cis* isomer



MA₂B₂ square planar complex, *trans* isomer

Because there is no way to convert the *cis* structure to the *trans* by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of *cis* and *trans* isomers of an MA₂B₂ square planar complex are *cis*-Pt(NH₃)₂Cl₂, also known as cisplatin, and *trans*-Pt(NH₃)₂Cl₂, which is actually toxic rather than therapeutic.

25. a). Sketch and explain the splitting of d-orbital in tetrahedral and octahedral Complexes
OR

Description of *d*-Orbitals

To understand CFT, one must understand the description of the lobes:

- d_{xy} : lobes lie in-between the x and the y axes.
- d_{xz} : lobes lie in-between the x and the z axes.
- d_{yz} : lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z^2} : there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

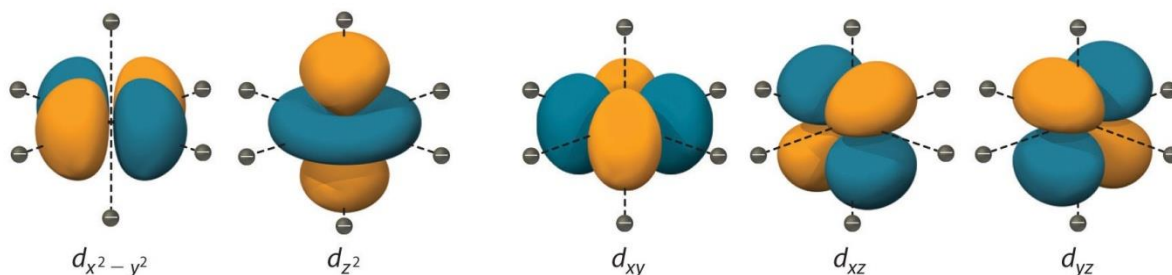


Figure 3: Spatial arrangement of ligands in the an octahedral ligand field with respect to the five *d*-orbitals.

Octahedral Complexes

In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels. The bottom three energy levels are named d_{xy} , d_{xz} , and d_{yz} (collectively referred to as t_{2g}). The two upper energy levels are named $d_{x^2-y^2}$ and d_{z^2} (collectively referred to as e_g).

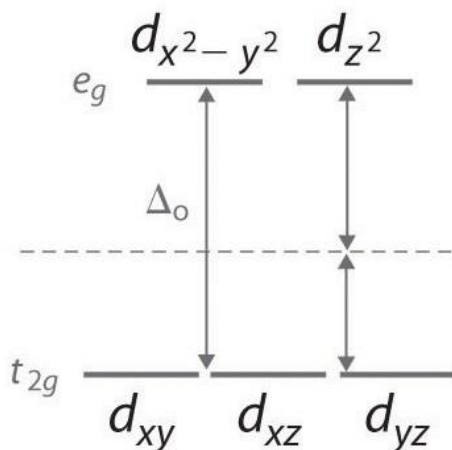


Figure 4: Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field shown in Figure 3.

The reason they split is because of the electrostatic interactions between the electrons of the ligand and the lobes of the d-orbital. In an octahedral, the electrons are attracted to the axes. Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of e_g are higher ($0.6\Delta_o$) while t_{2g} is lower ($0.4\Delta_o$). The distance that the electrons have to move from t_{2g} to e_g and it dictates the energy that the complex will absorb from white light, which will determine the color. Whether the complex is paramagnetic or diamagnetic will be determined by the spin state. If there are unpaired electrons, the complex is paramagnetic; if all electrons are paired, the complex is diamagnetic.

Tetrahedral Complexes

In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three consist of the d_{xy} , d_{xz} , and d_{yz} orbitals. The bottom two consist of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not.

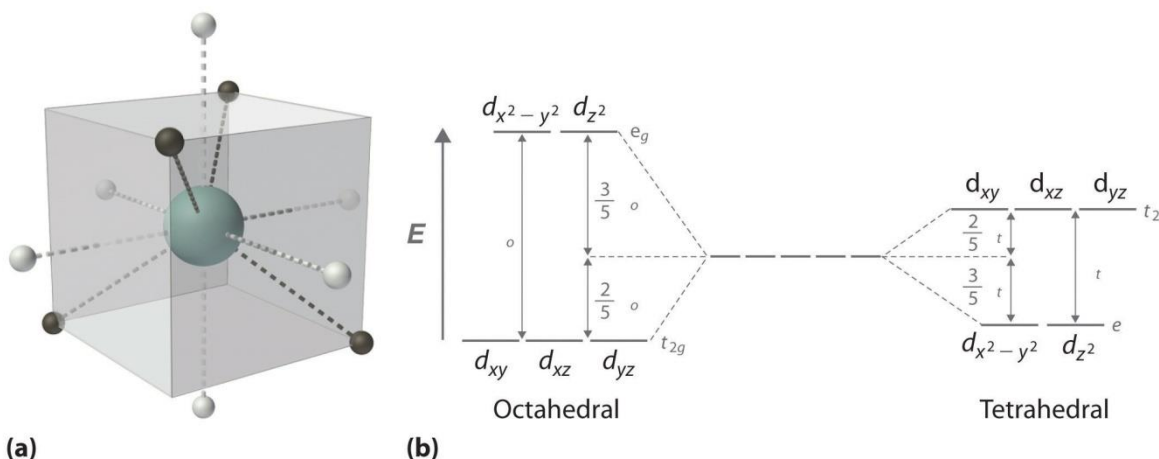


Figure 5: (a) Tetrahedral ligand field surrounding a central transition metal (blue sphere). (b) Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field (left diagram) and the tetrahedral field (right diagram).

The difference in the splitting energy is tetrahedral splitting constant (Δt), which is less than (Δo) for the same ligands:

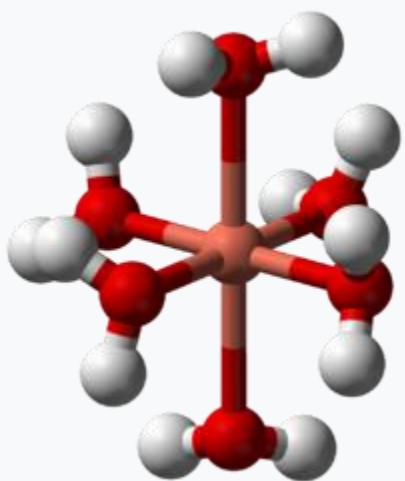
$$\Delta t = 0.44 \Delta o$$

Consequently, Δt is typically smaller than the spin pairing energy, so tetrahedral complexes are usually **high spin**.

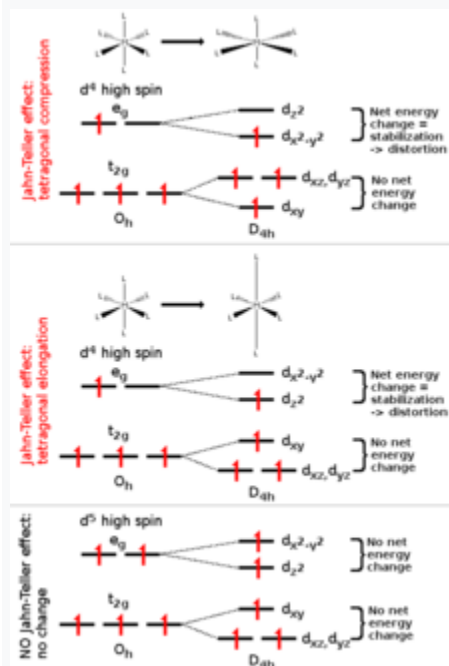
(b). What is Jahn-Teller effect? Illustrate with an example?

The **Jahn-Teller effect**, sometimes also referred to as **Jahn-Teller distortion**, describes the geometrical distortion of molecules and ions that result from certain electron configurations. The **Jahn-Teller theorem** essentially states that any non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species. For a description of another type of geometrical distortion that occurs in crystals with substitutional impurities see article off-center ions.

Transition metal chemistry



The Jahn–Teller effect is responsible for the tetragonal distortion of the hexaaquacopper(II) complex ion, $[\text{Cu}(\text{OH}_2)_6]^{2+}$, which might otherwise possess regular octahedral geometry. The two axial Cu–O distances are 238 pm, whereas the four equatorial Cu–O distances are ~195 pm. This geometry is common in crystal structures; the geometry in solution is uncertain.



Above: JT effect is observed as tetragonal elongation and compression in octahedral high-spin d^4 complexes due to net change in the energy of electrons (notice odd amount of electrons in e_g -orbital). **Below:** JT effect doesn't occur if there is no net change in energy (notice even amount of electrons in e_g -orbital).

The Jahn–Teller effect is most often encountered in octahedral complexes of the transition metals. The phenomenon is very common in six-coordinate copper(II) complexes. The d^9 electronic configuration of this ion gives three electrons in the two degenerate e_g orbitals, leading to a doubly degenerate electronic ground state. Such complexes distort along one of the molecular fourfold axes (always labelled the z axis), which has the effect of removing the orbital and electronic degeneracies and lowering the overall energy. The distortion normally takes the form of elongating the bonds to the ligands lying along the z axis, but occasionally occurs as a shortening of these bonds instead (the Jahn–Teller theorem does not predict the direction of the distortion, only the presence of an unstable geometry). When such an elongation occurs, the effect is to lower the electrostatic repulsion between the electron-pair on the Lewis basic ligand and any electrons in orbitals with a z component, thus lowering the energy of the complex. The inversion centre is preserved after the distortion.

In octahedral complexes, the Jahn–Teller effect is most pronounced when an odd number of electrons occupy the e_g orbitals. This situation arises in complexes with the configurations d^9 , low-spin d^7 or high-spin d^4 complexes, all of which have doubly degenerate ground states. In such compounds the e_g orbitals involved in the degeneracy point directly at the ligands, so distortion can result in a large energetic stabilisation. Strictly speaking, the effect also occurs when there is a degeneracy due to the electrons in the t_{2g} orbitals (*i.e.* configurations such as d^1 or d^2 , both of which are triply degenerate). In such cases, however, the effect is much less noticeable, because there is a much smaller lowering of repulsion on taking ligands further away from the t_{2g} orbitals, which do not point *directly* at the ligands (see the table below). The same is true in tetrahedral complexes (e.g. manganate: distortion is very subtle because there is less stabilisation to be gained because the ligands are not pointing directly at the orbitals).

The expected effects for octahedral coordination are given in the following table:

Jahn–Teller effect														
Number of d electrons	1	2	3	4		5		6		7		8	9	10
High/Low Spin				HS	LS	HS	LS	HS	LS	HS	LS			
Strength of J-T Effect	w	w		s	w		w	w		w	s		s	

w: weak Jahn–Teller effect (t_{2g} orbitals unevenly occupied)

s: strong Jahn–Teller effect expected (e_g orbitals unevenly occupied)

blank: no Jahn–Teller effect expected.

The Jahn–Teller effect is manifested in the UV-VIS absorbance spectra of some compounds, where it often causes splitting of bands. It is readily apparent in the structures of many copper(II) complexes. Additional, detailed information about the anisotropy of such complexes and the

nature of the ligand binding can be however obtained from the fine structure of the low-temperature electron spin resonance spectra.

26.a). Explain the Tanabe-Sugano diagram of a metal complex with d^2 and d^8 configurations.

OR

TANABE-SUGANO DIAGRAMS

An alternative method is to use Tanabe Sugano diagrams, which are able to predict the transition energies for both spin-allowed and spin-forbidden transitions, as well as for both strong field (low spin), and weak field (high spin) complexes.

Note however that most textbooks only give Tanabe-Sugano diagrams for octahedral complexes and a separate diagram is required for each configuration.

In this method the energy of the electronic states are given on the vertical axis and the ligand field strength increases on the horizontal axis from left to right.

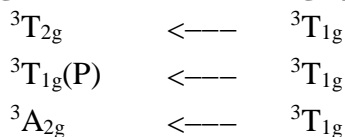
Linear lines are found when there are no other terms of the same type and curved lines are found when 2 or more terms are repeated. This is as a result of the "non-crossing rule".

The baseline in the Tanabe-Sugano diagram represents the lowest energy or ground term state.

The d^2 case (not many examples documented).

The electronic spectrum of the V^{3+} ion, where V(III) is doped into alumina (Al_2O_3), shows three major peaks with frequencies of: $\nu_1=17400\text{ cm}^{-1}$, $\nu_2=25400\text{ cm}^{-1}$ and $\nu_3=34500\text{ cm}^{-1}$.

These have been assigned to the following spin-allowed transitions.

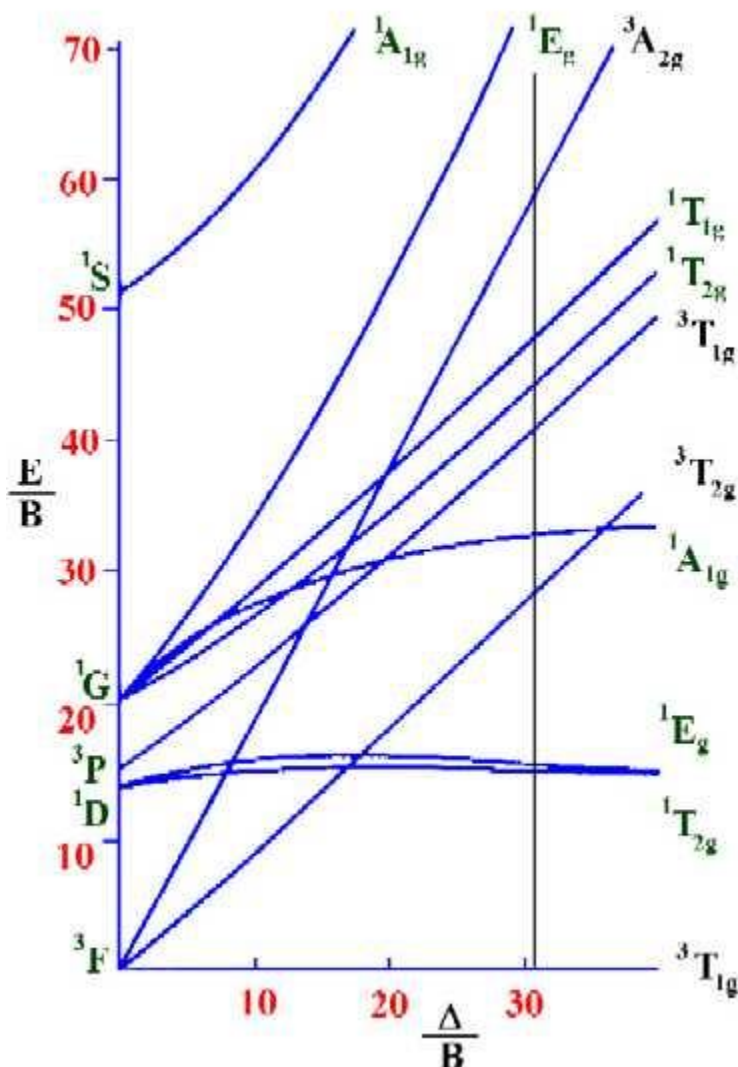


The ratio between the first two transitions is calculated as ν_2 / ν_1 which is equal to $25400 / 17400 = 1.448$.

In order to calculate the Racah parameter, **B**, the position on the horizontal axis where the ratio between the lines representing ν_2 and ν_1 is equal to 1.448, has to be

determined. On the diagram below, this occurs at $\Delta/B=30.9$. Having found this value, a vertical line is drawn at this position.

Tanabe-Sugano diagram for d2 octahedral complexes



On moving up the line from the ground term to where lines from the other terms cross it, we are able to identify both the spin-forbidden and spin-allowed transition and hence the total number of transitions that are possible in the electronic spectrum.

Next, find the values on the vertical axis that correspond to the spin-allowed transitions so as to determine the values of ν_1/B , ν_2/B and ν_3/B . From the diagram above these are 28.78, 41.67 and 59.68 respectively.

Knowing the values of ν_1 , ν_2 and ν_3 , we can now calculate the value of B.

Since $\nu_1/B=28.78$ and ν_1 is equal to $17,400\text{ cm}^{-1}$, then $B=\nu_1/28.78 = 17400/28.78$
or $B=604.5\text{cm}^{-1}$

Then it is possible to calculate the value of Δ .

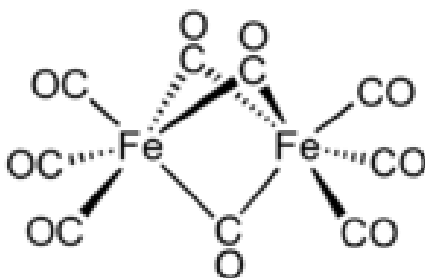
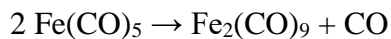
Since $\Delta/B=30.9$, then: $\Delta=B*30.9$ and hence: $\Delta = 604.5 * 30.9 = 18680\text{ cm}^{-1}$

(b). How do you prepare $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$? Give their structural formulae.

Diiron nonacarbonyl is an inorganic compound with the formula $\text{Fe}_2(\text{CO})_9$. This metal carbonyl is an important reagent in organometallic chemistry and of occasional use in organic synthesis. It is a more reactive source of Fe(0) than $\text{Fe}(\text{CO})_5$ and less dangerous to handle because it is nonvolatile. This micaceous orange solid is virtually insoluble in all common solvents.

Synthesis and structure:

Following the original method, photolysis of an acetic acid solution of $\text{Fe}(\text{CO})_5$ produces $\text{Fe}_2(\text{CO})_9$ in good yield:



$\text{Fe}_2(\text{CO})_9$ consists of a pair of $\text{Fe}(\text{CO})_3$ centers linked by three bridging CO ligands. Although older textbooks show an Fe-Fe bond consistent with the 18 electron rule (8 valence electrons from Fe, two each from the terminal carbonyls, one each from the bridging carbonyls and one from the other Fe atom in the metal-metal bond), theoretical analyses have consistently indicated the absence of a direct Fe-Fe bond this latter model proposes an Fe-C-Fe three-center-two-electron "banana bond" for one of the bridging carbonyls. The minor isomer has been crystallized together with C_{60} . The iron atoms are equivalent and octahedral molecular geometry. Elucidation of the structure of $\text{Fe}_2(\text{CO})_9$ proved to be challenging because its low solubility inhibits growth of crystals. The Mößbauer spectrum reveals one quadrupole doublet, consistent with the D_{3h} -symmetric structure.

Reactions

$\text{Fe}_2(\text{CO})_9$ is a precursor to compounds of the type $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3(\text{diene})$. Such syntheses are typically conducted in THF solution. In these conversions, it is proposed that small amounts of $\text{Fe}_2(\text{CO})_9$ dissolve according to the following reaction:^[6]



Cyclobutadieneiron tricarbonyl is prepared using $\text{Fe}_2(\text{CO})_9$. $\text{Fe}_2(\text{CO})_9$ has also been employed in the synthesis of cyclopentadienones via a net [2+3]-cycloaddition from dibromoketones, known as the Noyori [3+2] reaction.

Low temperature UV/vis photolysis of $\text{Fe}_2(\text{CO})_9$ yields the $\text{Fe}_2(\text{CO})_8$ unsaturated complex, producing both CO-bridged and unbridged isomers.

Triiron dodecarbonyl is the organoiron compound with the formula $\text{Fe}_3(\text{CO})_{12}$. It is a dark green solid that sublimes under vacuum. It is soluble in nonpolar organic solvents to give intensely green solutions. Most low-nuclearity clusters are pale yellow or orange. Hot solutions of $\text{Fe}_3(\text{CO})_{12}$ decompose to an iron mirror, which can be pyrophoric in air. The solid decomposes slowly in air, and thus samples are typically stored cold under an inert atmosphere. It is a more reactive source of iron(0) than iron pentacarbonyl.

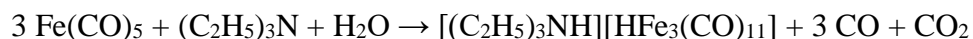
Synthesis

It was one of the first metal carbonyl clusters synthesized. It was occasionally obtained from the thermolysis of $\text{Fe}(\text{CO})_5$:



Traces of the compound are easily detected because of its characteristic deep green colour. UV-photolysis of $\text{Fe}(\text{CO})_5$ produces $\text{Fe}_2(\text{CO})_9$, not $\text{Fe}_3(\text{CO})_{12}$.

The usual synthesis of $\text{Fe}_3(\text{CO})_{12}$ starts with the reaction of $\text{Fe}(\text{CO})_5$ with base:

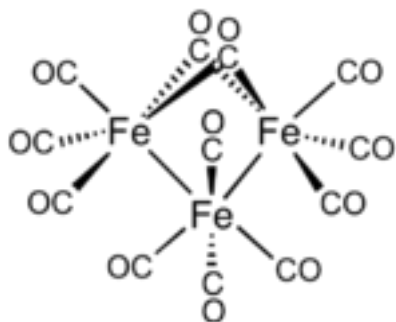


followed by oxidation of the resulting hydrido cluster with acid:



The original synthesis by Walter Hieber et al. entailed the oxidation of $\text{H}_2\text{Fe}(\text{CO})_4$ with MnO_2 . The cluster was originally formulated incorrectly as " $\text{Fe}(\text{CO})_4$ ".

Structure



Elucidation of the structure of $\text{Fe}_3(\text{CO})_{12}$ proved to be challenging because the CO ligands are disordered in the crystals. Early evidence for its distinctive C_{2v} structure came from Mössbauer spectroscopic measurements that revealed two quadrupole doublets with similar isomer shifts but different (1.13 and 0.13 mm s^{-1}) quadrupolar coupling constants.

$\text{Fe}_3(\text{CO})_{12}$ consists of a triangle of iron atoms surrounded by 12 CO ligands. Ten of the CO ligands are terminal and two span an Fe---Fe edge, resulting in C_{2v} point group symmetry. By contrast, $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ adopt D_{3h} -symmetric structures, wherein all 12 CO ligands are terminally bound to the metals. Spectroscopic evidence indicates that the two carbonyl groups may be unsymmetrical, in which case the idealized C_{2v} symmetry is reduced to C_2 .^[citation needed] In solution $\text{Fe}_3(\text{CO})_{12}$ is fluxional, resulting in equivalencing all 12 CO groups. Overall, it can be appreciated that these three clusters formally arise from condensation of three 16-electron $\text{M}(\text{CO})_4$ fragments, akin to the theoretical condensation of three methylene ($:\text{CH}_2$) molecules into cyclopropane.

The anion $[\text{HFe}_3(\text{CO})_{11}]^-$ is structurally related to $\text{Fe}_3(\text{CO})_{12}$, with the hydride replacing one bridging CO ligand. The bonding in the Fe-H-Fe subunit is described using concepts developed for diborane.

Reg.No.....

**KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21**

(For the candidates admitted from 2018& onwards)

M.Sc DEGREE EXAMINATION-APRIL-2019

SECOND SEMESTER

CHEMISTRY

INORGANIC CHEMISTRY –II (COORDINATION CHEMISTRY)

DATE: 11.3.2019 AN SUBJECT CODE: 18CHP202

TIME: 2 HRS

TOTAL: 50 MARKS

Internal Test-II

PART-A (20x1=20 Marks)

ANSWER ALL THE QUESTIONS

1. Give example for the compound which contain more than two cyclopentadienyl rings
a. Tetrakis(cyclopentadienyl) uranium b. Ferrocene c. Sodium cyclopentadienide
d. Thallium
2. Give an example for the compound which containing only one cyclopentadienyl ring
a. Tetrakis(cyclopentadienyl) uranium b. Ferrocene
c. Sodium cyclopentadienide d. Thallium
3. The compounds having only one cyclopentadienyl ring are commonly known as ----
a. Sandwich compound b. Open-faced sandwich compound
c. Closed faced sandwich compound d. Tripledeckers
4. Ferrocene undergoes Vilsmeier reaction to yield-----
a. Amino ferrocene b. Ferrocenecarboxaldehyde c. Nitro ferrocene
d. Chloroferrocene
5. The product formed, on acidification of the carbonylate ion
a. Carbonyl hydride complex b. Carbonyl complex c. Carboxylate anion
d. Carboxylate cation
6. Which is the relatively expensive catalyst used in hydroformylation
a. Cobalt b. Rhodium c. Copper d. Nickel
7. The uses of which catalyst will continue to increase in hydroformylation chemistry
a. Cobalt b. Copper c. Rhodium d. Zinc
8. Who proposed the most widely accepted mechanism for hydroformylation
a. Watson and Crick b. Cannizzaro c. Wittig d. Heck and Breslow
9. Arene complexes are mostly synthesized by ----- reaction
a. Aldol condensation b. Beckmann rearrangement c. Reduction reaction
d. Friedel Crafts reaction

10. During the preparation of Arene complexes ---- is used to reduce the metal salt to a lower oxidation state.

- a. Aluminium b. Palladium c. Chromium d. Nickel

11. Benzene is coordinated to chromium in arene complexes with the assistance of ----

- a. AlCl_3 b. LiCl_3 c. TiCl_4 d. H-Pd

12. The melting point of Dibenzene chromium is ----- $^{\circ}\text{C}$

- a. 270 b. 170 c. 280 d. 260

13. Who proposed the most widely accepted mechanism for hydroformylation

- a. Watson and Crick b. Cannizzaro c. Wittig d. Heck and Breslow

14. Hydroformylation is carried out in such a way that aldehydes are reduced to give

- a. Alcohols b. Acids c. Ketones d. Amines

15. The reaction of an alkene with carbon monoxide and hydrogen, catalysed by cobalt or rhodium salt, to form an aldehyde is called

- a. Hydroformylation b. Hydroxylation c. Hydrogenation d. Acetylation

16. The orbital used by the attacking ligand in substitution reaction is

- a. p_x b. p_z c. p_y d. s

17. The active center of the cytochromes is

- a. Amino group b. Haeme group c. Nitro group d. Sulphur group

18. Cobalt is mainly ----- in its salt

- a. Positive b. Negative c. Dipositive d. Tripositive

19. If the substituting ligand is attached to central metal then the geometry of the intermediate complex will be

- a. Square pyramidal b. Square bipyramidal c. trigonal pyramidal
d. tetrahedral

20. In inner sphere mechanism the reaction is brought about by formation of a -----

- a. Bridged activated complex b. Complex ligand c. Bridged unactivated complex d. ligand

PART-B (3x2=6 Marks)

ANSWER ALL THE QUESTIONS:

21. What is meant by hydroformylation reactions?

22. Differentiate between the terms hemoglobin and myoglobin.

23. Explain Wacker Process?

PART-C(3x8 = 24 Marks)

ANSWER ALL THE QUESTIONS:

24. a. Explain the difference between ionic and covalent bonding?

OR

b. Write notes on alkene complexes?

26. a. Write an account on carbonylate ions?

OR

b. Discuss various methods of synthesis of cyclopentadienyl complexes?

26. a. Write a note on heterogeneous catalyst?

OR

b. What is Trans-effect? Explain the uses of Trans-effect?

Reg.No.....

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M.Sc DEGREE EXAMINATION-APRIL-2019

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DATE: 11.3.2019 AN

TIME: 2 HRS

SUBJECT CODE: 18CHP202

TOTAL: 50 MARKS

Internal Test-II

Answer key

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ANSWER ALL THE QUESTIONS

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- a. **Tetrakis(cyclopentadienyl) uranium** b. Ferrocene c. Sodium
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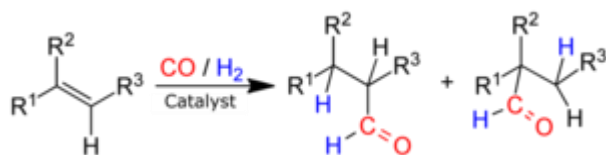
PART-B (3x2=6 Marks)

ANSWER ALL THE QUESTIONS:

21. What is meant by hydroformylation reactions?

Hydroformylation, also known as **oxo synthesis** or **oxo process**, is an industrial process for the production of aldehydes from alkenes. This chemical reaction entails the net addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. This process has undergone continuous growth since its invention: Production capacity reached 6.6×10⁶ tons in 1995. It is important because aldehydes are easily converted into many secondary products. For example, the resulting aldehydes are hydrogenated to alcohols that are converted to detergents. Hydroformylation is also used in speciality

chemicals, relevant to the organic synthesis of fragrances and drugs. The development of hydroformylation is one of the premier achievements of 20th-century industrial chemistry.



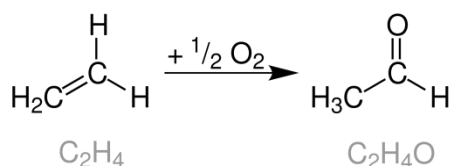
22. Differentiate between the terms hemoglobin and myoglobin.

BASIS FOR COMPARISON	HEMOGLOBIN	MYOGLOBIN
Number of chains	Haemoglobin has 4 chains of two different types- alpha and beta, delta, gamma, or epsilon (depending on the type of hemoglobin).	It contains single polypeptide chains.
Type of structure	A tetramer.	A monomer.
Binds	Binds CO ₂ , CO, NO, O ₂ and H ⁺ .	Binds to O ₂ , tightly and firmly.
Their presence	Systemically all over the body.	In muscles cells.
Types of curve	Sigmoid binding curve.	Hyperbolic curve.
Also known as	Hb.	Mb.
Role	Haemoglobin is transported along with blood to whole body and carry oxygen.	Myoglobin supplies oxygen to muscles only, which is helpful at the starving time of oxygen.
Concentration in blood	High in RBC.	Low.

23. Explain wacker Process?

The **Wacker process** or the **Hoechst-Wacker process** (named after the chemical companies of the same name) refers to the oxidation of ethylene to acetaldehyde in the presence

of palladium(II) chloride as the catalyst. This chemical reaction was one of the first homogeneous catalysis with organopalladium chemistry applied on an industrial scale.



PART-C(3x8 = 24 Marks)

ANSWER ALL THE QUESTIONS:

24. a. Explain the difference between ionic and covalent bonding?

Ionic bonds	Covalent bonds
Ionic bond is formed by the transfer of electrons from one atom to another atom. It is also known as electrovalent bond.	Covalent bond is formed by the sharing of valence electrons between atoms of similar electronegativity
Occurs between a metal and a non-metal	Occurs between two non-metals.
Ionic bonds do not have definite shape	Covalent bonds have definite shape
They exist in solid state at room temperature	They exist in liquid or gaseous state at room temperature
They have high boiling and melting points	They have low boiling and melting points.

OR

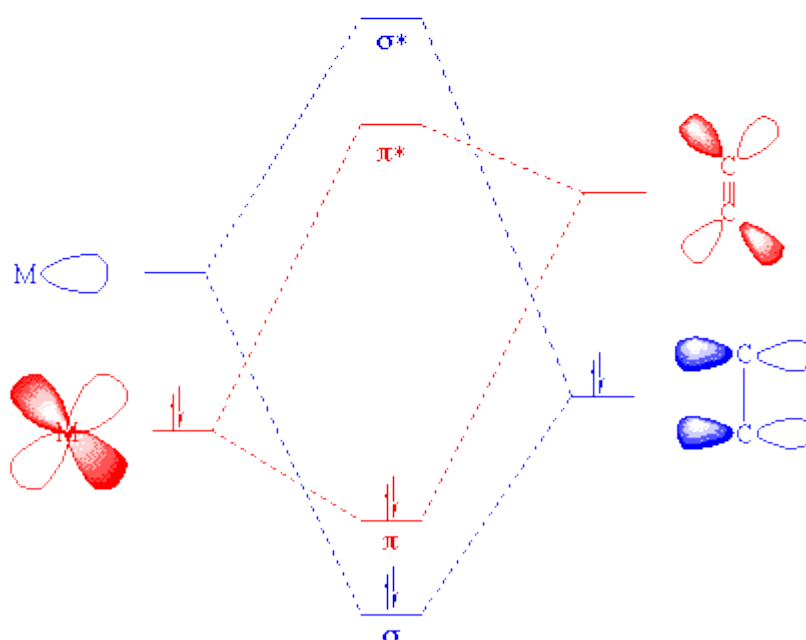
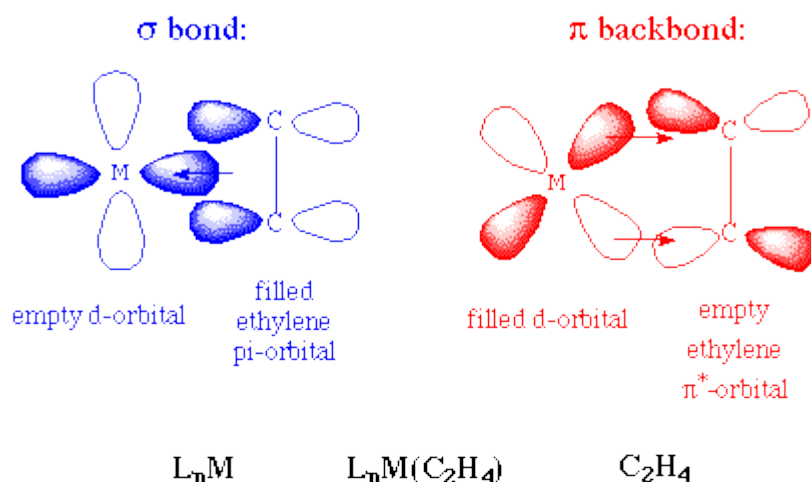
b. Write notes on alkene complexes?

Alkene or olefin ligands are common in organotransition metal chemistry. In fact, the first organotransition metal complex, Zeise's salt ($\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$) was an alkene complex although its true nature was not unambiguously determined until about 100 years after its discovery.

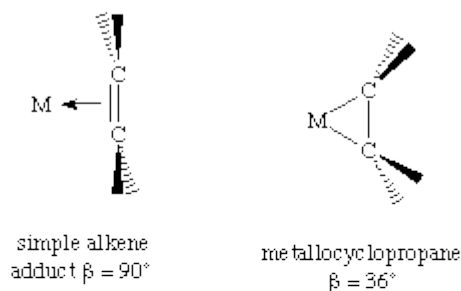
Bonding and Structure in Alkene Complexes

The bonding in alkene complexes is described by the **Dewar-Chatt-Duncanson model**, which provides us with a bonding picture not unlike that seen in carbonyl or phosphine complexes. A sigma-type donation from the C=C pi orbital with concomitant pi-backbonding into an empty pi* orbital on the ethylene presents us with a

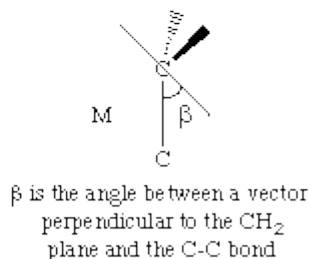
synergistic bonding situation: the greater the sigma donation to the metal, the greater the pi-backbonding:



The greater the electron density back-donated into the π^* orbital on the alkene, the greater the reduction in the C=C bond order. An alternative way of stating this would be to say that the hybridization of the alkene carbon changes from sp^2 to sp^3 as back-donation increases. Either formalism describes two limiting structures: a planar olefin adduct and a metallocyclopropane. X-ray crystallographic studies confirm that as the C-C bond length increases, the CH_2 plane is distorted from the ideal planar geometry of an alkene:



	$d_{C=C}$	β
C_2H_4	1.337	90°
$K[PtCl_3(C_2H_4)]$	1.375	74°
$Cp^*_2Ti(C_2H_4)$	1.438	55°
$(PPh_3)_2Pt(C_2F_4)$	1.44	50°
C_2H_6	1.54	36°



The structural distortion of a bound alkene can also be detected by NMR: the J_{CH} of alkene-like sp^2 carbons is typically around 160 Hz whereas sp^3 -like carbons have a J_{CH} around 120 Hz. Unlike carbonyl stretching frequencies, the $C=C$ IR band (around 1500 cm^{-1}) is usually weak and not well-correlated to C-C bond length.

Electronic factors play a large role in the binding of alkenes to transition metals. For example, tetrafluoroethylene will bind more tightly than ethylene to a low valent metal complex because the presence of electron-withdrawing groups on the olefin results in poorer sigma donation and lowers the energy of the π^* orbital (providing better overlap for backbonding). Likewise, ethylene (like carbon monoxide) is a poor ligand for d^0 metal complexes because there are no d-electrons to engage in back-bonding.

The stability of alkene complexes also depends on steric factors as well. An empirical ordering of relative stability would be:

tetrasubstituted < trisubstituted < trans-disubstituted < cis-disubstituted < monosubstituted < ethylene.

Synthesis of Alkene Complexes

Alkene complexes can be synthesized by several methods:

1. Ligand substitution reactions.
2. Reduction of a higher valent metal in the presence of an alkene.
3. From alkyls and related species:
 - reductive elimination (of an allyl and hydride, for example).
 - hydride abstraction from alkyls
 - protonation of sigma-alkyls
 - from epoxides (indirectly)

Reactions of Alkene Complexes

The bonding of an alkene to a transition metal can activate the ligand to electrophilic or nucleophilic attack depending on the nature and charge of the metal center. For example, if there is a high formal charge on the metal center then the olefin is subject to attack by **nucleophiles** at the face opposite the metal (giving trans addition). Likewise, electron rich metal centers in low oxidation states are activated for attack by **electrophiles** at the C-C bond.

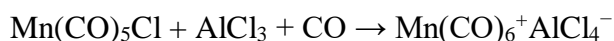
The reaction chemistry of these complexes is quite broad and could form another textbook in itself. For some other examples of alkene reactivity look at the sections on olefin metathesis, olefin polymerization and insertion reactions.

26. a. Write an account on carbonylate ions?

Metal carbonyl cations and carbonylates

The synthesis of ionic carbonyl complexes is possible by oxidation or reduction of the neutral complexes. Anionic metal carbonylates can be obtained for example by reduction of dinuclear complexes with sodium. A familiar example is the sodium salt of iron tetracarbonylate ($\text{Na}_2\text{Fe}(\text{CO})_4$, *Collman's reagent*), which is used in organic synthesis.

The cationic hexacarbonyl salts of manganese, technetium and rhenium can be prepared from the carbonyl halides under carbon monoxide pressure by reaction with a Lewis acid.



The use of strong acids succeeded in preparing gold carbonyl cations such as $[\text{Au}(\text{CO})_2]^+$, which is used as a catalyst for the carbonylation of olefins. The cationic platinum carbonyl complex $[\text{Pt}(\text{CO})_4]^{2+}$ can be prepared by working in so-called superacids such as antimony pentafluoride. Although CO is considered generally as a ligand for low-valent metal ions, the tetravalent iron complex $[\text{Cp}^*_2\text{Fe}]^{2+}$ (16-valence electron complex) quantitatively binds CO to give the diamagnetic Fe(IV)-carbonyl $[\text{Cp}^*_2\text{FeCO}]^{2+}$ (18-valence electron complex).

OR

b. Discuss various methods of synthesis of cyclopentadienyl complexes?

A **cyclopentadienyl complex** is a metal complex with one or more cyclopentadienyl groups (C_5H_5^- , abbreviated as Cp^-). Cyclopentadienyl ligands almost invariably bind to metals as pentahapto (η^5 -) bonding mode. The metal–cyclopentadienyl interaction is typically drawn as a single line from the metal center to the center of the Cp ring.

Examples

Biscyclopentadienyl complexes are called metallocenes. A famous example of this type of complex is ferrocene (FeCp_2), which has many analogues for other metals, such as chromocene (CrCp_2), cobaltocene (CoCp_2), and nickelocene (NiCp_2). When the Cp rings are mutually parallel the compound is known as a sandwich complex. This area of organometallic chemistry was first developed in the 1950s. Bent metallocenes are represented by compounds of the type $[\text{MCp}_2\text{L}_x]$. Some are catalysts for ethylene polymerization. Metallocenes are often thermally stable, and find use as catalysts in various types of reactions.

Mixed-ligand Cp complexes containing Cp ligand and one or more other ligands. They are more numerous. One widely studied example is the Fp dimer, $(\text{Cp}_2\text{Fe}_2(\text{CO})_4)$. Monometallic compounds featuring only one Cp ring are often known as half sandwich compounds or as piano stool compounds, one example being cyclopentadienylmanganese tricarbonyl $(\text{CpMn}(\text{CO})_3)$.

Bonding modes

All 5 carbon atoms of a Cp ligand are bound to the metal in the vast majority of M–Cp complexes. This bonding mode is called η^5 -coordination. The M–Cp bonding arises from overlap of the five π molecular orbitals of the Cp ligand with the s, p, and d orbitals on the metal. This π bonding is significant, hence these complexes are referred to as π -complexes. Almost all of the transition metals, that is, group 4 to 10 metals, employ this coordination mode.

In relatively rare cases, Cp binds to metals via only one carbon center. These types of interactions are described as σ -complexes because they only have a σ bond between the metal and the cyclopentadienyl group. Typical examples of this type of complex are group 14 metal complexes such as CpSiMe_3 . An example of both is $(\text{Cp}_2\text{Fe}(\text{CO})_2)$. It is probable that η^1 -Cp complexes are intermediates in the formation of η^5 -Cp complexes.

Still rarer, the Cp unit can bond to the metal via a three-carbons. In these η^3 -Cp complexes, the bonding resembles that in allyl ligands. Such complexes, sometimes called "slipped Cp complexes", are invoked as intermediates in ring slipping reactions.

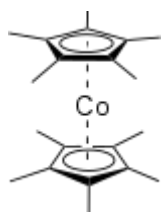
Synthesis of Cp complexes

The compounds are generally prepared by salt metathesis reactions of alkali-metal cyclopentadienyl compounds with transition metal chlorides. Sodium cyclopentadienide (NaCp) and lithium cyclopentadienide are commonly used. Trimethylsilylcyclopentadiene cyclopentadienylthallium (CpTl) are alternative sources. For the preparation of some particularly robust complexes, e.g. nickelocene, cyclopentadiene is employed in the presence of a conventional base such as KOH. When only a single Cp ligand is installed, the other ligand typically carbonyl, halogen, alkyl, and hydride.

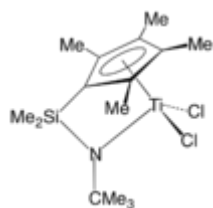
Most Cp complexes are prepared by substitution of preformed Cp complexes by replacement of halide, CO, and other simple ligands.

Variations of Cp complexes

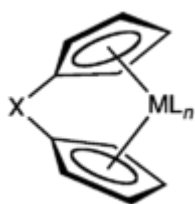
Variations of Cyclopentadienyl complexes



decamethylcobaltocene, a powerful reducing agent



A constrained geometry organotitanium complex, related to commercial catalysts



An ansa-metallocene

Ansa Cp ligands

A pair of cyclopentadienyl ligands can be covalently linked giving rise to so-called ansa metallocenes. The angle between the two Cp rings is fixed. Rotation of the rings about the metal-centroid axis is stopped as well. A related class of derivatives give rise to the constrained geometry complexes. In these cases, a Cp ligand is linked to a non-Cp ligand. Such complexes have been commercialized for the production of polypropylene.

Cp* complexes

Pentamethylcyclopentadiene gives rise to pentamethylcyclopentadienyl complexes. These ligands are bulkier and more basic, which results in distinctive properties.

Constrained geometry complexes

Constrained geometry complexes are related to ansa-metallocenes except that one ligand is not Cp-related.

Applications

Cp metal complexes are mainly used as stoichiometric reagents in chemical research. Ferrocenium reagents are oxidants. Cobaltocene is a strong, soluble reductant.

Derivatives of Cp_2TiCl_2 and Cp_2ZrCl_2 are the basis of some reagents in organic synthesis. Upon treatment with aluminoxane, these dihalides give catalysts for olefin polymerization. Such species are called Kaminsky-type catalysts.

26. a. Write a note on heterogeneous catalyst?

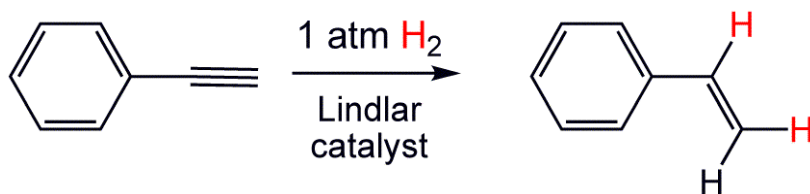
Heterogeneous catalysts

Heterogeneous catalysts for hydrogenation are more common industrially. In industry, precious metal hydrogenation catalysts are deposited from solution as a fine powder on the support, which is a cheap, bulky, porous, usually granular material, such as activated carbon, alumina, calcium carbonate or barium sulfate. For example, platinum on carbon is produced by reduction of chloroplatinic acid *in situ* in carbon. Examples of these catalysts are 5% ruthenium on activated carbon, or 1% platinum on alumina. Base metal catalysts, such as Raney nickel, are typically much cheaper and do not need a support. Also, in the laboratory, unsupported (massive) precious metal catalysts such as platinum black are still used, despite the cost.

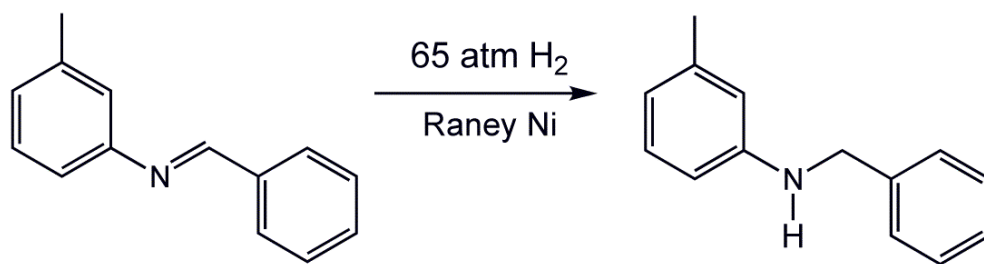
As in homogeneous catalysts, the activity is adjusted through changes in the environment around the metal, i.e. the coordination sphere. Different faces of a crystalline heterogeneous catalyst display distinct activities, for example. This can be modified by mixing metals or using different preparation techniques. Similarly, heterogeneous catalysts are affected by their supports.

In many cases, highly empirical modifications involve selective "poisons". Thus, a carefully chosen catalyst can be used to hydrogenate some functional groups without affecting others, such as the hydrogenation of alkenes without touching aromatic rings, or the selective hydrogenation of alkynes to alkenes using Lindlar's catalyst. For example, when the catalyst palladium is placed on barium sulfate and then treated with quinoline, the resulting catalyst reduces alkynes only as far as alkenes. The Lindlar catalyst has been applied to the conversion of phenylacetylene to styrene.

Partial hydrogenation of phenylacetylene using the Lindlar catalyst.



- Hydrogenation of an imine using a Raney nickel catalyst, a popular heterogeneous catalyst.



OR

b. What is Trans-effect? Explain the uses of Trans-effect?

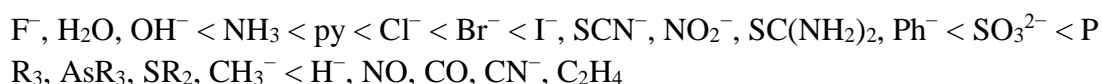
In inorganic chemistry, the **trans effect** is the labilization (making more reactive) of ligands that are trans to certain other ligands, which can thus be regarded as trans-directing ligands. It is attributed to electronic effects and it is most notable in square planar complexes, although it can also be observed for octahedral complexes.^[1] The cis effect is most often observed in octahedral transition metal complexes.

In addition to this *kinetic trans effect*, trans ligands also have an influence on the ground state of the molecule, the most notable ones being bond lengths and stability. Some authors prefer the term **trans influence** to distinguish it from the kinetic effect, while others use more specific terms such as **structural trans effect** or **thermodynamic trans effect**.

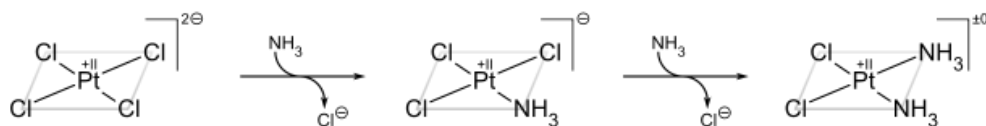
The discovery of the trans effect is attributed to Ilya Ilich Chernyaev, who recognized it and gave it a name in 1926.

Kinetic trans effect

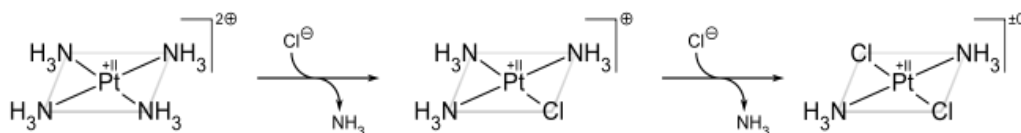
The intensity of the trans effect (as measured by the increase in rate of substitution of the trans ligand) follows this sequence:



The classic example of the trans effect is the synthesis of cisplatin and its trans isomer. Starting from PtCl_4^{2-} , the first NH_3 ligand is added to any of the four equivalent positions at random. However, since Cl^- has a greater trans effect than NH_3 , the second NH_3 is added trans to a Cl^- and therefore cis to the first NH_3 .



If, on the other hand, one starts from $\text{Pt}(\text{NH}_3)_4^{2+}$, the *trans* product is obtained instead:



The trans effect in square complexes can be explained in terms of an addition/elimination mechanism that goes through a trigonal bipyramidal intermediate. Ligands with a high trans effect are in general those with high π acidity (as in the case of phosphines) or low-ligand lone-pair- d_π repulsions (as in the case of hydride), which prefer the more π -basic equatorial sites in the intermediate. The second equatorial position is occupied by the incoming ligand; due to the principle of microscopic reversibility, the departing ligand must also leave from an equatorial position. The third and final equatorial site is occupied by the trans ligand, so the net result is that the kinetically favored product is the one in which the ligand trans to the one with the largest trans effect is eliminated.

Structural trans effect

The structural trans effect can be measured experimentally using X-ray crystallography, and is observed as a stretching of the bonds between the metal and the ligand trans to a trans-influencing ligand. Stretching by as much as 0.2 Å occurs with strong trans-influencing

ligands such as hydride. A *cis influence* can also be observed, but is smaller than the trans influence. The relative importance of the cis and trans influences depends on the formal electron configuration of the metal center, and explanations have been proposed based on the involvement of the atomic orbitals.