



Karpagam Academy of Higher Education
(Deemed University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

DEPARTMENT OF CHEMISTRY

B.Sc Chemistry

Semester-III

16CHU 302

INORGANIC CHEMISTRY III
(Coordination Chemistry)

4H 4C

Instruction Hours/week: L:4 0 T:0 P:0
Total:100

Marks: Internal: 40 External: 60

Scope

The course deals with the coordination compounds, various theories explaining the structure of coordination compounds, transition metals, lanthanides and actinides and reactions of coordination compounds.

Course outcome

1. To understand the key features of coordination compounds, including: the variety of structures, oxidation numbers and electronic configurations, - coordination numbers, ligands, chelates bonding and stability of complexes
2. Able to use Crystal Field Theory to understand the magnetic properties (and in simple terms the colour) of coordination compounds.
3. To describe the shapes and structures of coordination complexes with coordination numbers 4 and 6.
4. To recognize the types of isomers in coordination compounds.
5. To name coordination compounds and to be able to draw the structure based on it's name.
6. To become familiar with some reactions and applications of coordination compounds.

Course Learning outcome

The students know the fundamentals of coordination compounds and the theories behind it to understand nomenclature, the shapes, structures, magnetic properties and colour of coordination compounds. They also know the reactions and applications of coordination compounds.

UNIT I

Coordination Chemistry:

Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of $10 Dq$ (Δ_o), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of $10 Dq$ (Δ_o , Δ_t). Octahedral vs.

tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

UNIT II

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

UNIT III

Transition Elements:

General group trends with special reference to electronic configuration, colour, variable valency, magnetic and catalytic properties, ability to form complexes. Stability of various oxidation states and e.m.f. (Latimer diagrams) Different between the first, second and third transition series. Chemistry of Cr, Mn, Fe and Co in various oxidation states with special reference to the following compounds: peroxo compounds of chromium, potassium dichromate, potassium permanganate, potassium ferrocyanide, potassium ferricyanide, sodium nitroprusside and sodium cobaltinitrite.

UNIT IV

Lanthanoids and Actinoids:

Electronic configuration, oxidation states, colour, spectral and magnetic properties, lanthanide contraction, separation of lanthanides (ion-exchange method only).

UNIT V

Inorganic Reaction Mechanism

Introduction to inorganic reaction mechanisms. Substitution reactions in square planar complexes, Trans- effect, theories of trans effect. Thermodynamic and Kinetic stability.

Suggested Readings

Text Books:

1. Purcell, K.F & Kotz, J.C. (1977). *Inorganic Chemistry*. W.B. Saunders Co.
2. Huheey, J.E. (2016). *Inorganic Chemistry*. Prentice Hall.
3. Puri, Sharma, Kalia. 2016. Principles of Inorganic Chemistry, Milestone publishers, Delhi.

Reference Books

1. Cotton, F.A. & Wilkinson, G. (2013). *Advanced Inorganic Chemistry*. Wiley-VCH.
2. Basolo, F. & Pearson, R.C. (1967). *Mechanisms of Inorganic Chemistry*. NY: John Wiley & Sons.
3. Greenwood, N.N. & Earnshaw A. (1997). *Chemistry of the Elements*. Butterworth-Heinemann.
4. Miessler, G. L. & Tarr, Donald A. (2009). *Inorganic Chemistry*. 3rd Ed.(adapted), Pearson.



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DEPARTMENT OF CHEMISTRY
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LECTURE PLAN

ODD SEMESTER- JUNE 2017

CLASS : II- B. Sc-CHEMISTRY (A Section)
STAFF INCHARGE : Dr. G.Ayyannan
TITLE OF THE PAPER : Inorganic Chemistry-III(Coordination Chemistry)
PAPER CODE : 16CHU302
YEAR / SEMESTER : II / III
TOTAL HOURS : 62 Hrs

UNIT-I

Hours required: 14

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Werner's theory,	T1: 928
2.	1	Valence bond theory	T1: 959
3.	1	Valence bond theory	T1: 959
4.	1	Electroneutrality principle and back bonding	T1: 965
5.	1	Crystal field theory, measurement of $10 Dq$ (Δ_o),	T1: 966
6.	1	CFSE in weak and strong fields, pairing energies,	T1: 969
7	1	Factors affecting the magnitude of $10 Dq$ (Δ_o , Δ_t)	T1: 975

8	1	Octahedral vs. tetrahedral coordination	T1: 971
9	1	Tetragonal distortions from octahedral geometry	T1: 1011
10.	1	Jahn-Teller theorem	T1: 1011
11.	1	Square planar geometry,	T1: 945, 978, 981
12.	1	Qualitative aspect of Ligand field Theory	T1: 978, 981
13.	1	Qualitative aspect of MO Theory	T1: 978, 981
14.	1	Recapitulation and Discussion of important questions	

Text book:

T1 : Puri, Sharma, Kalia. 2016. Principles of Inorganic Chemistry, Milestone publishers, Delhi.

UNIT-II

Hours required: 11

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	IUPAC nomenclature of coordination compounds	T1: 920, 933
2.	1	IUPAC nomenclature of coordination compounds	T1: 920, 933
3.	1	Isomerism in coordination compounds.	T1: 947
4.	1	Isomerism in coordination compounds.	T1: 947
5.	1	Stereochemistry of complexes with 4 coordination numbers.	T1: 951
6.	1	Stereochemistry of complexes with 6 coordination numbers.	T1: 951
7.	1	Stereochemistry of complexes with 4 and 6 coordination numbers.	T1: 951
8.	1	Chelate effect,	T1: 925, 937, 1135
9.	1	Polynuclear complexes,	T1: 937, 1135

10.	1	Labile and inert complexes.	T1: 1135
11.	1	Recapitulation and Discussion of important questions	

Text book:

T1: Puri, Sharma, Kalia. 2016. Principles of Inorganic Chemistry, Milestone publishers, Delhi.

UNIT-III

Hours required: 14

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Transition Elements: General group trends with special reference to electronic configuration	T1: 762
2.	1	Transition Elements: General group trends with special reference to electronic configuration	T1: 762
3.	1	colour	T1: 771
4.	1	variable valency and magnetic properties,	T1: 768, 772
5.	1	variable valency and magnetic properties,	T1: 768, 772
6.	1	catalytic properties and ability to form complexes	T1: 774, 775
7.	1	Stability of various oxidation states and e.m.f.	T1: 770
8.	1	Different between the first, second and third transition series.	T1: 770
9.	1	Chemistry of Cr in various oxidation states and peroxo compounds of chromium,	T1: 792, 798, 799
10.		Chemistry of Mn and potassium permanganate	T1: 801, 802, 804
11.	1	Chemistry of Fe and compounds of Fe,	T1: 815-819
12.	1	potassium ferrocyanide, potassium ferricyanide, sodium nitroprusside,	T1: 823
13.	1	Chemistry of Cobalt and compounds of cobalt-sodium cobaltinitrite.	T1: 823
14.	1	Recapitulation and Discussion of important questions	

Text book:

T1: Puri, Sharma, Kalia. 2016. Principles of Inorganic Chemistry, Milestone publishers, Delhi.

UNIT-IV**Hours required: 11**

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Lanthanoids and Actinoids: Introduction	T1: 886 , 903
2.	1	Lanthanoids and Actinoids: Electronic configuration	T1: 886 , 903
3.	1	Oxidation states	T1: 887, 905
4.	1	Oxidation states	T1: 887, 905
5.	1	Colour	T1: 891, 906
6.	1	Spectral properties	T1: 893, 905
7.	1	Magnetic properties	T1: 891
8.	1	Lanthanide contraction	T1: 889
9.	1	Separation of lanthanides	T1: 897
10	1	Seperation of lanthanides-ion exchange method	T1: 897
11	1	Recapitulation and Discussion of important questions	

Text book:

T1: Puri, Sharma, Kalia. 2016. Principles of Inorganic Chemistry, Milestone publishers, Delhi.

UNIT-V

Hours required: 12

S.No	Lecture Hour	Topics to be Covered	Support Materials
1.	1	Inorganic Reaction Mechanism Introduction to inorganic reaction mechanisms.	T1: 1132
2.	1	Substitution reactions in square planar complexes,	T1: 1161
3.	1	Substitution reactions in square planar complexes,	T1: 1161
4.	1	Trans- effect,	T1: 1164-1165
5.	1	Theories of trans effect.	T1: 1164-1165
6.	1	Thermodynamic stability of complexes	T1: 1166
7.		Kinetic stability of complexes	T1: 1166
8.	1	Recapitulation and Discussion of important questions	
9.	1	End semester question paper discussion	
10	1	End semester question paper discussion	
11	1	End semester question paper discussion	
12	1	End semester question paper discussion	

Text book:

T1: Puri, Sharma, Kalia. 2016. Principles of Inorganic Chemistry, Milestone publishers, Delhi.

UNIT-I

Coordination Chemistry:

Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of $10 Dq$ (Δ_o), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of $10 Dq$ (Δ_o , Δ_t). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

Werner's Coordination Chemistry

Postulates of werner's theory

Coordination compounds were known in eighteenth century. It was a mystery for the chemist, of those days to understand as to why a stable salt like CoCl_3 reacts with varying number of stable molecules or compounds such as ammonia to give several new compounds: $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$; and what are their structures? These compounds differed from each other in their chloride ion reactivity. Conductivity measurements on solutions of these compounds showed that the number of ions present in solution for each compound is different. Several theories were proposed, but none could satisfactorily explain all the observable properties of these compounds and similar other series of compounds which had been prepared by then. It was only in 1893 that Werner put forward a set of ideas which are known as Werner's coordination theory, to explain the nature of bonding in complexes. His theory has been a guiding principle in inorganic chemistry and in the concept of valence. The important postulates of Werner's theory are:

1. Metals exhibit two types of valence:

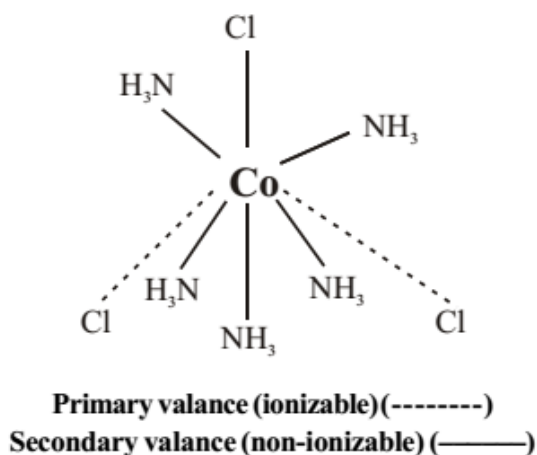
- (a) Primary valence (ionizable)
- (b) Secondary valence (non-ionizable).

Primary or ionizable valence is satisfied by negative ions and corresponds to oxidation state of the metal. The secondary or non-ionizable valence, which is satisfied by negative, positive or neutral groups, is equal to the coordination number of metal ion.

Every metal tends to satisfy both its primary and secondary valence.

2. The secondary valence is directed toward fixed positions in space i.e. this has spatial arrangement corresponding to different coordination number. For the complexes $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$, the number of ionizable ions in these complexes are three, two and one, respectively. It has been proved by precipitation reactions and conductivity measurements. On the basis of Werner's postulate these compounds are formulated as:

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, respectively, the species inside the square brackets being the complex ion and outside the square brackets the ionisable ions. On the basis of Werner's theory the structure of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is:



Naming complexes

The basic procedure for naming a complex:

1. When naming a complex ion, the ligands are named before the metal ion.
2. Write the names of the ligands in alphabetical order. (Numerical prefixes do not affect the order.)
 - Multiple occurring monodentate ligands receive a prefix according to the number of occurrences: *di-*, *tri-*, *tetra-*, *penta-*, or *hexa-*. Polydentate ligands (e.g., ethylenediamine, oxalate) receive *bis-*, *tris-*, *tetrakis-*, etc.
 - Anions end in *ido*. This replaces the final 'e' when the anion ends with '-ate', e.g. *sulfate* becomes *sulfato*. It replaces 'ide': *cyanide* becomes *cyanido*.

- Neutral ligands are given their usual name, with some exceptions: NH_3 becomes *ammine*; H_2O becomes *aqua* or *aquo*; CO becomes *carbonyl*; NO becomes *nitrosyl*.
3. Write the name of the central atom/ion. If the complex is an anion, the central atom's name will end in *-ate*, and its Latin name will be used if available (except for mercury).
 4. If the central atom's oxidation state needs to be specified (when it is one of several possible, or zero), write it as a Roman numeral (or 0) in parentheses.
 5. Name cation then anion as separate words (if applicable, as in last example)

Examples:

$[\text{NiCl}_4]^{2-} \rightarrow \text{tetrachloridonickelate(II) ion}$

$[\text{CuNH}_3\text{Cl}_5]^{3-} \rightarrow \text{amminepentachloridocuprate(II) ion}$

$[\text{Cd}(\text{en})_2(\text{CN})_2] \rightarrow \text{dicyanidobis(ethylenediamine)cadmium(II)}$

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4 \rightarrow \text{pentaamminechloridocobalt(III) sulfate}$

The coordination number of ligands attached to more than one metal (bridging ligands) is indicated by a subscript to the Greek symbol μ placed before the ligand name. Thus the dimer of aluminium trichloride is described by $\text{Al}_2\text{Cl}_4(\mu_2\text{-Cl})_2$.

Application of coordination compounds

- (1) They are used in photography, i.e., AgBr forms soluble complex with sodium thiosulfate in photography.
- (2) $\text{K}[\text{Ag}(\text{CN})_2]$ is used for electroplating of silver, and $\text{K}[\text{Au}(\text{CN})_2]$ is used for gold plating.
- (3) Some ligands oxidise Co^{2+} to Co^{3+} ion.
- (4) EDTA is used for estimation of Ca^{2+} and Mg^{2+} in hard water.
- (5) Silver and gold are extracted by treating zinc with their cyanide complexes.

Valence Bond Theory

Linus Pauling of the California Institute of Technology developed the valence bond theory. He was awarded the Nobel prize in chemistry in 1954. Pauling's ideas have had an important impact on all areas of chemistry. He applied valence bond theory to coordination compounds. This theory can account reasonably well for the structure and

magnetic properties of metal complexes. The basic principles, which are involved in the valence bond treatment of coordination compounds are:

- Hybridization of valence orbitals of the central metal/ ion
- Bonding between ligand and the metal ion/atom.
- Relation between the type of bond and the observed magnetic behaviour.

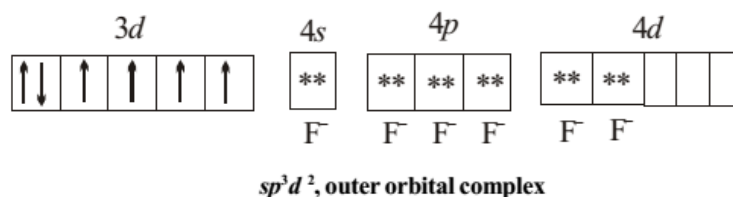
Six Coordinate Complexes

Let us explain by taking simple examples such as $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$. Although in both the complexes, the oxidation state of cobalt is +3, but $[\text{CoF}_6]^{3-}$ is paramagnetic and $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic, why? The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken e.g. Co^{3+} . Cobalt atom has the outer electronic configuration $3d^7 4s^2$. Thus Co^{3+} ion will have the configuration $3d^6$ and the electrons will be arranged as:



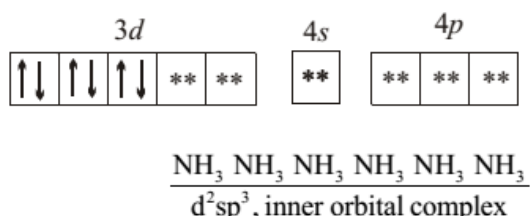
Co^{3+} ion forms both paramagnetic (outer orbital) and diamagnetic (inner orbital) complexes depending upon the nature of ligands as illustrated below.

As Co^{3+} ion combines with six fluoride ligands in $[\text{CoF}_6]^{3-}$, empty atomic orbitals are required on the metal ion to receive the coordinated lone pair of electrons. The orbitals used are one $4s$, three $4p$ and two $4d$. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. A ligand orbital containing a lone pair of electron forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a σ -bond is formed with each ligand. The d -orbitals used are the $4d_{x^2-y^2}$ and $4d_{z^2}$. It is shown below:



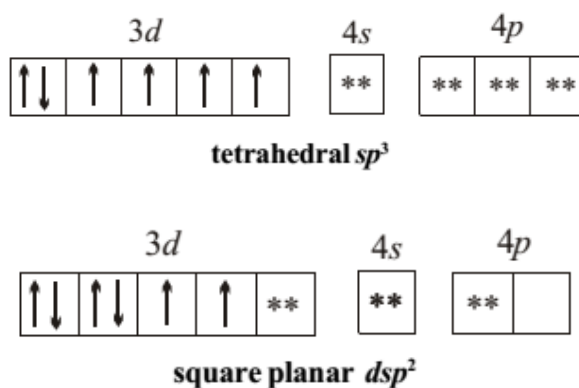
Since the outer $4d$ orbitals are used for bonding, this is called an outer orbital complex. The energy of these orbitals is quite high, so the complex will be reactive. This complex

will be high-spin paramagnetic, because it has four unpaired electrons. An alternative octahedral arrangement in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is possible when the electrons on metal ion are rearranged as shown below:



Since inner d-orbitals are used this is called an inner orbital complex. There is no unpaired electron; the complex will be low-spin diamagnetic.

The metal ion can also form 4-coordinate complexes. For such complexes two different arrangements are possible i.e. tetrahedral (sp^3) and square planar (dsp^2):



Let us illustrate six coordinate complexes with more examples:

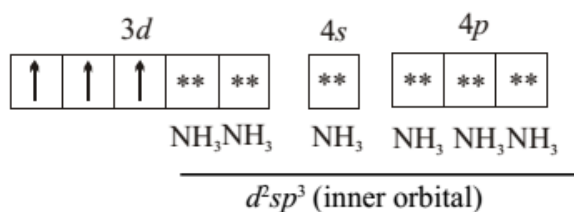
1. $\text{Cr}(\text{NH}_3)_6]^{3+}$

The electronic configuration of only 3d, 4s and 4p orbitals are taken into account. The following steps are involved. The electronic configuration of Cr atom and Cr^{3+} ion are given in (i) and (ii) below:

(i) Cr ground state:



(ii) Cr^{3+}

 (iii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$


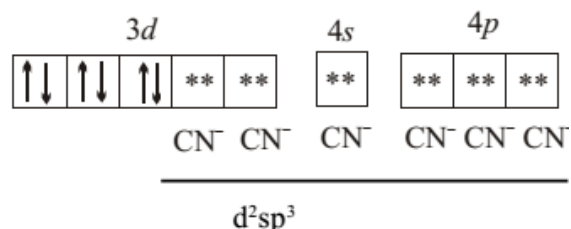
The 12 electrons for bond formation come from six ligands, each donating a lone pair of electrons. The resulting complex will be paramagnetic because it has three unpaired electrons. Its magnetic moment will be:

$$\sqrt{n(n+2)} = \sqrt{3(\sqrt{3+2})} = \sqrt{15} = 3.87 \text{ B.M}$$

 2. $[\text{Fe}(\text{CN})_6]^{4-}$

(i) Fe


 (ii) Fe^{2+}

 (iii) $[\text{Fe}(\text{CN})_6]^{4-}$


The resulting complex is inner orbital, octahedral and due to the absence of unpaired electron, it will be diamagnetic.

3. $[\text{Fe}(\text{CN})_6]^{3-}$

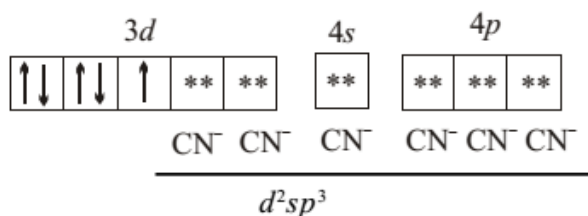
(i) Fe



(ii) Fe^{3+}



(iii) $[\text{Fe}(\text{CN})_6]^{3-}$



The resulting complex is inner orbital, octahedral. Due to presence of one unpaired electron, it will be paramagnetic.

Four coordinate complexes:

1. $[\text{NiCl}_4]^{2-}$

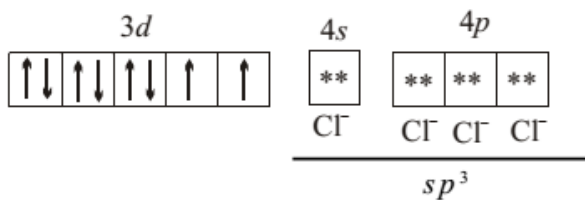
(i) Ni



(ii) Ni^{2+}



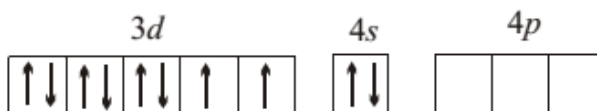
(iii) $[\text{NiCl}_4]^{2-}$



The resulting complex will be tetrahedral with two unpaired electrons. It will be paramagnetic.

2. $\text{Ni}(\text{CO})_4$

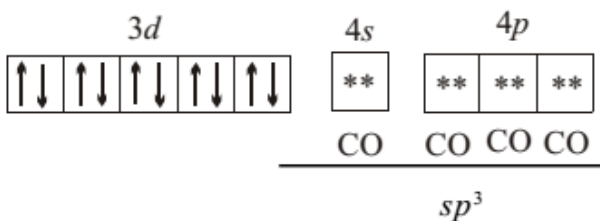
(i) Ni



(ii) $\text{Ni}(\text{O})$



(iii) $\text{Ni}(\text{CO})_4$



The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.

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

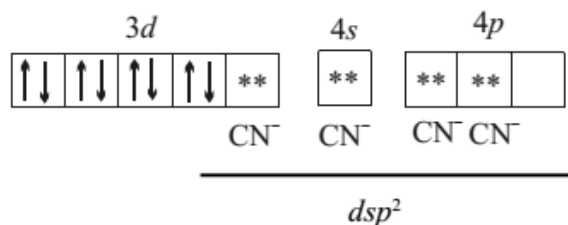
(i) Ni



(ii) Ni^{2+}



(iii) $[\text{Ni}(\text{CN})_4]^{2-}$



The resulting complex is square planar and diamagnetic.

Coordination number	Type of hybridisation	Geometry	Example	
4	sp^3	tetrahedral	$[\text{Ni}(\text{CO})_4]$	$[\text{ZnCl}_4]^{2-}$
4	dsp^2	square planar	$[\text{Ni}(\text{CN})_4]^{2-}$	$[\text{Pt}(\text{NH}_3)_4]^{2+}$
6	d^2sp^3	octahedral	$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$[\text{Fe}(\text{CN})_6]^{4-}$
6	$sp^3 d^2$	octahedral	$[\text{FeF}_6]^{3-}$	$[\text{CoF}_6]^{3-}$

Electroneutrality principle

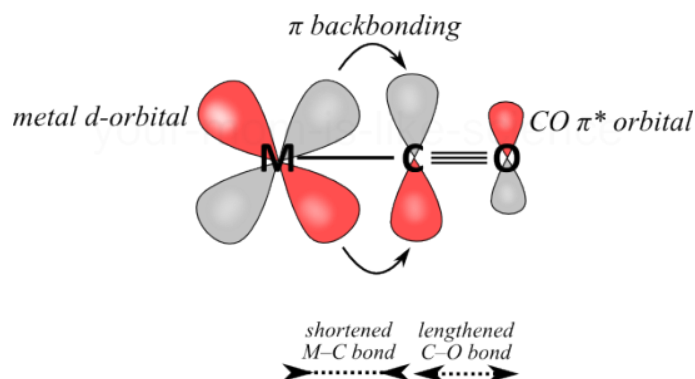
Pauling's principle of electroneutrality states that each atom in a stable substance has a charge close to zero. It was formulated by Linus Pauling in 1948 and later revised. The principle has been used to predict which of a set of molecular resonance structures would be the most significant, to explain the stability of inorganic complexes and to explain the existence of π -bonding in compounds and polyatomic anions containing silicon, phosphorus or sulfur bonded to oxygen; it is still invoked in the context of coordination complexes. However, modern computational techniques indicate many stable compounds have a greater charge distribution than the principle predicts (they contain bonds with greater ionic character).

“Stable molecules and crystals have electronic structures such that the electric charge of each atom is close to zero. Close to zero means between -1 and +1.”

The large difference in electronegativity gives a calculated ionic character of 9%. In the crystal (CsF has the NaCl structure with both ions being 6-coordinate) if each bond has 9% covalent character the total covalency of Cs and F would be 54%. This would be represented by one bond resonating between the six positions and the overall effect would be to reduce the charge on Cs to about + 0.5 and fluoride to -0.5. It seemed reasonable to him that such a reduction would be general.

Back bonding

π **back bonding**, also called π back donation, is a concept from chemistry in which electrons move from an atomic orbital on one atom to a π^* antibonding orbital on a π -acceptor ligand.



Crystal Field theory

This theory (CFT) largely replaced VB Theory for interpreting the chemistry of coordination compounds. It was proposed by the physicist Hans Bethe in 1929. Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions. These modifications are often referred to as Ligand Field Theory.

The assumptions were are

- The interaction between the metal ion and the ligands are electrostatic in nature
- The ligands are regarded as point charges
- If the ligand is negatively charged: ion-ion interaction, if the ligand is neutral then ion-dipole interaction.
- The electrons in the metal are under repulsive from those on the ligands
- The electrons on the metal occupy those d -orbitals that are farthest away the direction of approach of ligands.

The 5 d orbitals in an isolated gaseous metal are degenerate. If a spherically symmetric field of negative charges is placed around the metal, these orbitals

remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and electrons present in the d orbitals.

In an octahedral field not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, y, +y, +z and -z axes respectively. The orbitals which lie along these axes (i.e. x^2-y^2 and z^2) will be destabilized more than the orbitals which lie in-between the axes (i.e. xy, xz, yz). The extent to which these two sets of orbitals are split is denoted by Δ_o or alternatively $10Dq$. As the barycenter must be conserved on going from a spherical field to an octahedral field the t_{2g} set must be stabilized as much as the e_g set is destabilized.

What happens for more than 1 electron in d orbitals? The electron-electron interactions must be taken into account. For d^1 - d^3 systems: Hund's rule predicts that the electrons will not pair and occupy the t_{2g} set. For d^4 - d^7 systems (there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (low spin case or strong field situation). Or put the electrons in the e_g set, which lies higher in energy, but the electrons do not pair (the electrons do not pair (high spin case or weak field high spin case or weak field situation). Therefore there are two important parameters to consider:

Therefore, there are two important parameters to consider:

- The Pairing energy (P) [is a repulsive energy], and
- the e_g - t_{2g} Splitting (referred to as Δ_o , $10Dq$)

For both the high spin (H.S.) and low spin (L.S.) situations, it is possible to compute the CFSE.

Δ_o is dependent on:

- Nature of the ligands
- The charge on the metal ion
- Whether the metal is a 3d 4d or 5d element

Crystal field splitting

In an octahedral complex, the d orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy, Δ_o .

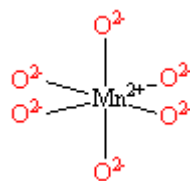
(A). When Δ is large, it is energetically more favorable for electrons to occupy the lower set of orbitals.

Crystal field stabilization energy

Crystal Field Stabilisation Energy (CFSE) A consequence of Crystal Field Theory is that the distribution of electrons in the d orbitals can lead to stabilisation for some electron configurations. It is a simple matter to calculate this stabilization since all that is needed is the electron configuration.

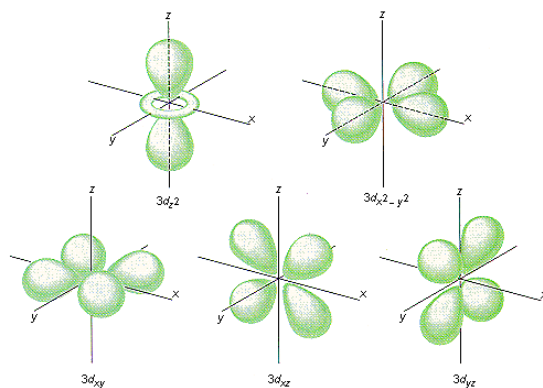
Octahedral Crystal Fields

Each Mn^{2+} ion in manganese (II) oxide is surrounded by six O^{2-} ions arranged toward the corners of an octahedron, as shown in the figure below. MnO is therefore a model for an *octahedral* complex in which a transition-metal ion is coordinated to six ligands.

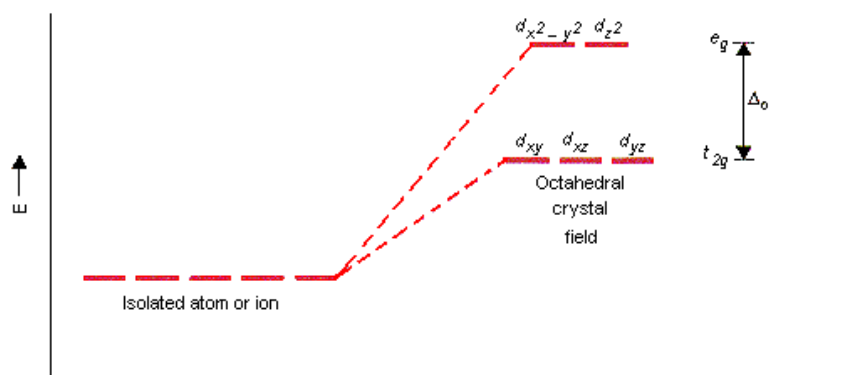


What happens to the energies of the $4s$ and $4p$ orbitals on an Mn^{2+} ion when this ion is buried in an MnO crystal? Repulsion between electrons that might be added to these orbitals and the electrons on the six O^{2-} ions that surround the metal ion in MnO increase the energies of these orbitals. The three $4p$ orbitals are still degenerate, however. These orbitals still have the same energy because each $4p$ orbital points toward two O^{2-} ions at the corners of the octahedron.

Repulsion between electrons on the O^{2-} ions and electrons in the $3d$ orbitals on the metal ion in MnO also increases the energy of these orbitals. But the five $3d$ orbitals on the Mn^{2+} ion are no longer degenerate. Let's assume that the six O^{2-} ions that surround each Mn^{2+} ion define an XYZ coordinate system. Two of the $3d$ orbitals ($3d_{x^2-y^2}$ and $3d_{z^2}$) on the Mn^{2+} ion point directly toward the six O^{2-} ions, as shown in the figure below. The other three orbitals ($3d_{xy}$, $3d_{xz}$, and $3d_{yz}$) lie between the O^{2-} ions.



The energy of the five $3d$ orbitals increases when the six O^{2-} ions are brought close to the Mn^{2+} ion. However, the energy of two of these orbitals ($3d_{x^2-y^2}$ and $3d_{z^2}$) increases much more than the energy of the other three ($3d_{xy}$, $3d_{xz}$, and $3d_{yz}$), as shown in the figure below. The crystal field of the six O^{2-} ions in MnO therefore splits the degeneracy of the five $3d$ orbitals. Three of these orbitals are now lower in energy than the other two.



By convention, the d_{xy} , d_{xz} , and d_{yz} orbitals in an octahedral complex are called the t_{2g} orbitals. The $d_{x^2-y^2}$ and d_{z^2} orbitals, on the other hand, are called the e_g orbitals. The easiest way to remember this convention is to note that there are three orbitals in the t_{2g} set.

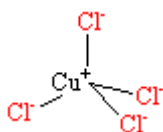
$$t_{2g}: d_{xy}, d_{xz}, \text{ and } d_{yz} \quad e_g: d_{x^2-y^2} \text{ and } d_{z^2}$$

The difference between the energies of the t_{2g} and e_g orbitals in an octahedral complex is represented by the symbol Δ_o . This splitting of the energy of the d orbitals is not trivial; Δ_o for the $Ti(H_2O)_6^{3+}$ ion, for example, is 242 kJ/mol.

The magnitude of the splitting of the t_{2g} and e_g orbitals changes from one octahedral complex to another. It depends on the identity of the metal ion, the charge on this ion, and the nature of the ligands coordinated to the metal ion.

Tetrahedral Crystal Fields

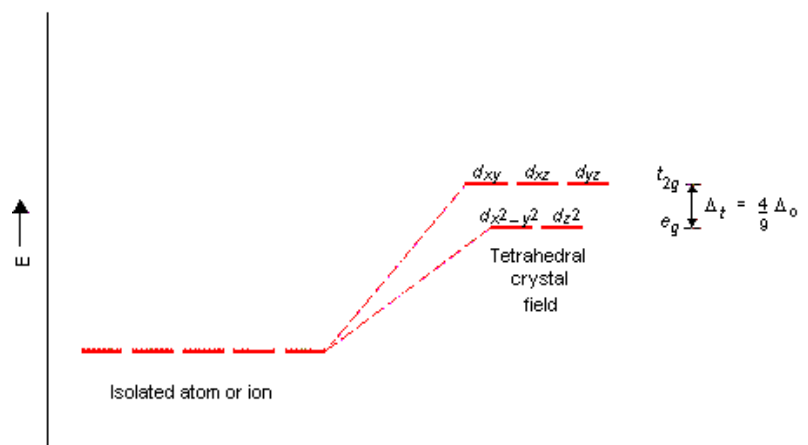
Each Cu^+ ion in copper(I) chloride is surrounded by four Cl^- ions arranged toward the corners of a tetrahedron, as shown in the figure below. CuCl is therefore a model for a *tetrahedral* complex in which a transition-metal ion is coordinated to four ligands.



Once again, the negative ions in the crystal split the energy of the d atomic orbitals on the transition-metal ion. The tetrahedral crystal field splits these orbitals into the same t_{2g} and e_g sets of orbitals as does the octahedral crystal field.

$$t_{2g}: d_{xy}, d_{xz}, \text{ and } d_{yz} \quad e_g: d_{x^2-y^2} \text{ and } d_{z^2}$$

But the two orbitals in the e_g set are now lower in energy than the three orbitals in the t_{2g} set, as shown in the figure below.



To understand the splitting of d orbital in a tetrahedral crystal field, imagine four ligands lying at alternating corners of a cube to form a tetrahedral geometry, as shown in the figure below. The $d_{x^2-y^2}$ and d_{z^2} orbitals on the metal ion at the center of the cube lie between the ligands, and the d_{xy} , d_{xz} , and d_{yz} orbitals point toward the ligands. As a result,

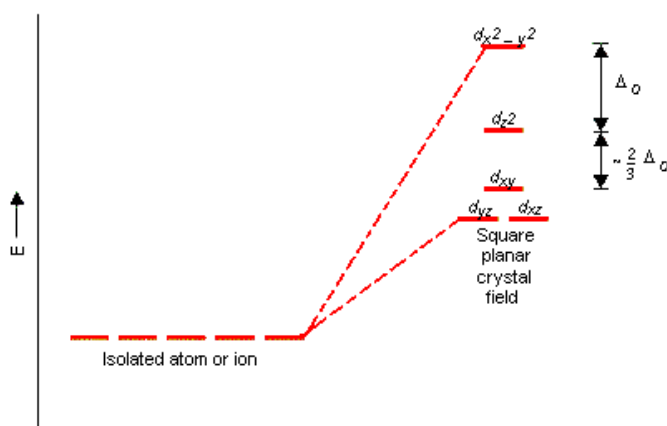
the splitting observed in a tetrahedral crystal field is the opposite of the splitting in an octahedral complex.

Because a tetrahedral complex has fewer ligands, the magnitude of the splitting is smaller. The difference between the energies of the t_{2g} and e_g orbitals in a tetrahedral complex (Δ_t) is slightly less than half as large as the splitting in analogous octahedral complexes (Δ_o).

$$\Delta_t = \frac{4}{9} \Delta_o$$

Square Planar complexes

The crystal field theory can be extended to square-planar complexes, such as $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. The splitting of the d orbitals in these compounds is shown in the figure below.



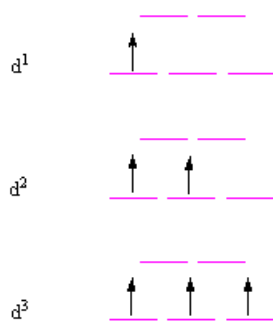
Ligands that give rise to large differences between the energies of the t_{2g} and e_g orbitals are called *strong-field ligands*. Those at the opposite extreme are known as *weak-field ligands*. Because they result from studies of the absorption spectra of transition-metal complexes, these generalizations are known as the spectrochemical series. The range of values of Δ for a given geometry is remarkably large. The value of Δ_o is 100 kJ/mol in the $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ion, for example, and 520 kJ/mol in the $\text{Rh}(\text{CN})_6^{3-}$ ion.

High-spin versus Low-spin complexes

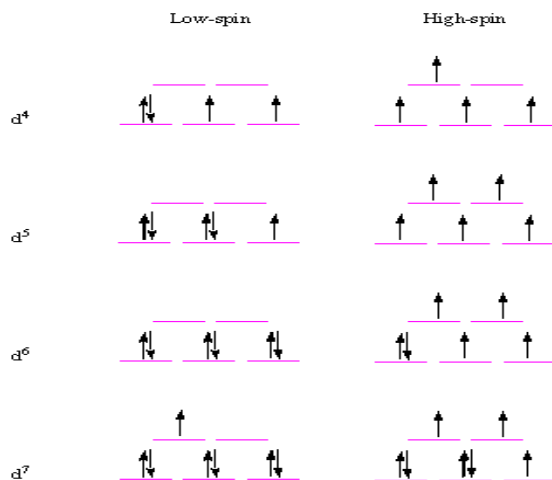
Once we know the relative energies of the d orbitals in a transition-metal complex, we have to worry about how these orbitals are filled. Degenerate orbitals are filled according to Hund's rules.

- One electron is added to each of the degenerate orbitals in a subshell before a second electron is added to any orbital in the subshell.
- Electrons are added to a subshell with the same value of the spin quantum number until each orbital in the subshell has at least one electron.

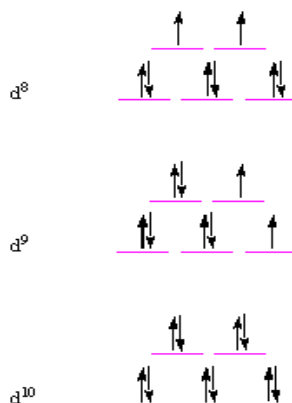
Octahedral transition-metal ions with d^1 , d^2 , or d^3 configurations can therefore be described by the following diagrams.



When we try to add a fourth electron, we are faced with a problem. This electron could be used to pair one of the electrons in the lower energy (t_{2g}) set of orbitals or it could be placed in one of the higher energy (e_g) orbitals. One of these configurations is called high-spin because it contains four unpaired electrons with the same spin. The other is called low-spin because it contains only two unpaired electrons. The same problem occurs with octahedral d^5 , d^6 , and d^7 complexes.

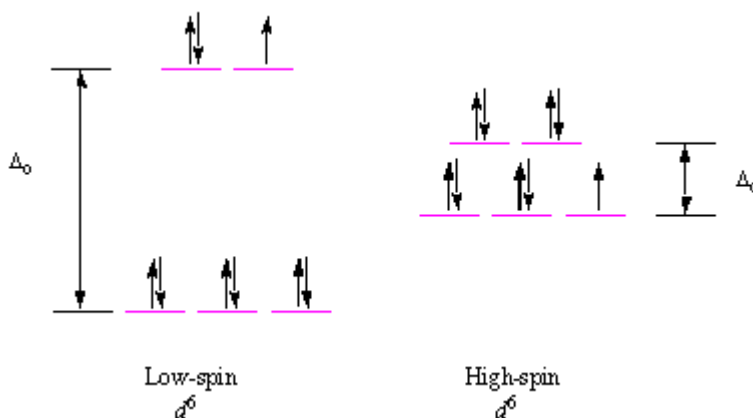


For octahedral d^8 , d^9 , and d^{10} complexes, there is only one way to write satisfactory configurations.



As a result, we have to worry about high-spin versus low-spin octahedral complexes only when there are four, five, six, or seven electrons in the d orbitals.

The choice between high-spin and low-spin configurations for octahedral d^4 , d^5 , d^6 , or d^7 complexes is easy. All we have to do is compare the energy it takes to pair electrons with the energy it takes to excite an electron to the higher energy (e_g) orbitals. If it takes less energy to pair the electrons, the complex is low-spin. If it takes less energy to excite the electron, the complex is high-spin. The amount of energy required to pair electrons in the t_{2g} orbitals of an octahedral complex is more or less constant. The amount of energy needed to excite an electron into the higher energy (e_g) orbitals, however, depends on the value of Δ_o for the complex. As a result, we expect to find low-spin complexes among metal ions and ligands that lie toward the high-field end of the spectrochemical series. High-spin complexes are expected among metal ions and ligands that lie toward the low-field end of these series.



Compounds in which all of the electrons are paired are diamagnetic — they are repelled by both poles of a magnet. Compounds that contain one or more unpaired electrons are paramagnetic — they are attracted to the poles of a magnet. The force of attraction between paramagnetic complexes and a magnetic field is proportional to the number of unpaired electrons in the complex. We can therefore determine whether a complex is high-spin or low-spin by measuring the strength of the interaction between the complex and a magnetic field.

Factors Affecting the Magnitude of Δ

1. Higher oxidation states of the metal atom correspond to larger Δ .

$$\Delta = 10,200 \text{ cm}^{-1} \text{ for } [\text{CoII}(\text{NH}_3)_6]^{2+} \text{ and } 22,870 \text{ cm}^{-1} \text{ for } [\text{CoIII}(\text{NH}_3)_6]^{3+}$$

$$\Delta = 32,200 \text{ cm}^{-1} \text{ for } [\text{FeII}(\text{CN})_6]^{4-} \text{ and } 35,000 \text{ cm}^{-1} \text{ for } [\text{FeIII}(\text{CN})_6]^{3-}$$

2. In groups, heavier analogues have larger Δ .

For hexa ammine complexes $[\text{MIII}(\text{NH}_3)_6]^{3+}$:

$$\Delta = 22,870 \text{ cm}^{-1} \text{ (Co)}$$

$$34,100 \text{ cm}^{-1} \text{ (Rh)}$$

$$41,200 \text{ cm}^{-1} \text{ (Ir)}$$

3. Geometry of the metal coordination unit affects Δ greatly.

Tetrahedral complexes ML_4 have smaller Δ than octahedral ones ML_6 :

$$\Delta = 10,200 \text{ cm}^{-1} \text{ for } [\text{CoII}(\text{NH}_3)_6]^{2+}$$

$$5,900 \text{ cm}^{-1} \text{ for } [\text{CoII}(\text{NH}_3)_4]^{2+}$$

4. Nature of the ligands.

For $[\text{CoIII}\text{L}_6]$ Δ in cm^{-1} : 13 100 (F^-); 20 760 (H_2O); 22 870 (NH_3)

For $[\text{CrIII}\text{L}_6]$, Δ in cm^{-1} : 15,060 (F^-); 17,400 (H_2O); 26,600 (CN^-)

Hybridization of atomic orbitals

The solution to the Schrodinger Equation provides the wavefunctions for the following atomic orbitals:

1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, etc.

For atoms containing two or more electrons, the energy levels are shifted with respect to those of the H atom. An atomic orbital is really the energy state of an electron bound to an atomic nucleus. The energy state changes when one atom is bonded to another atom.

Quantum mechanical approaches by combining the wave functions to give new wavefunctions are called **hybridization** of atomic orbitals. Hybridization has a sound mathematical foundation, but it is a little too complicated to show the details here. Leaving out the jargons, we can say that an imaginary mixing process converts a set of atomic orbitals to a new set of **hybrid atomic orbitals** or **hybrid orbitals**.

At this level, we consider the following hybrid orbitals:

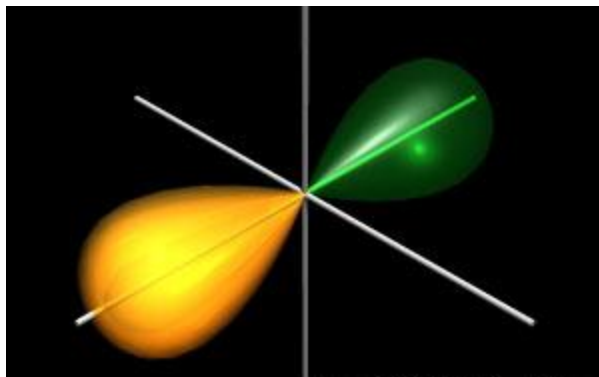
$$Sp, sp^2, sp^3, sp^3d, sp^3d^2$$

The *sp* hybrid atomic orbitals

The *sp* hybrid atomic orbitals are possible states of electron in an atom, especially when it is bonded to others. These electron states have half *2s* and half *2p* characters. From a mathematical view point, there are two ways to combine the *2s* and *2p* atomic orbitals:

$$sp_1 = 2s + 2p$$

$$sp_2 = 2s - 2p$$



These energy states (*sp*₁ and *sp*₂) have a region of high electron probability each, and the two atomic orbitals are located opposite to each other, centered on the atom. The *sp* hybrid orbitals are represented by this photograph.

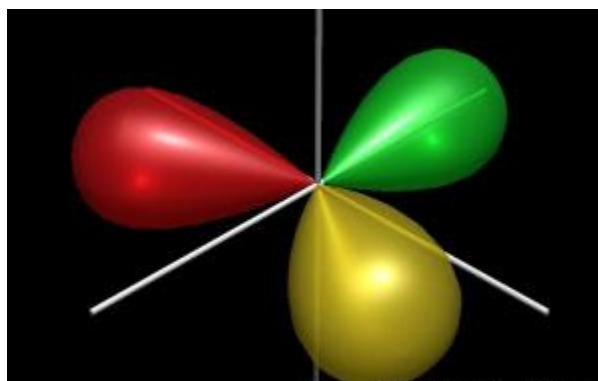
For example, the molecule H-Be-H is formed due to the overlapping of two $1s$ orbitals of 2 H atoms and the two sp hybridized orbitals of Be. Thus, the H-Be-H molecule is linear. The diagram here shows the overlapping of AOs in the molecule H-Be-H.

The ground state electronic configuration of Be is $1s^2 2s^2$, and one may think of the electronic configuration "before" bonding as $1s^2 sp^2$. The two electrons in the sp hybrid orbitals have the same energy.

You may say that the concept of hybridizing AOs for the bonding is just a story made up to explain the molecular shape of Cl-Be-Cl. You are right! The story is lovely and interesting, though.

In general, when two and only two atoms bond to a third atom and the third atom makes use of the sp hybridized orbitals, the three atoms are on a straight line. For example, sp hybrid orbitals are used in the central atoms in the molecules shown on the right.

The sp^2 hybrid orbitals



The energy states of the valence electrons in atoms of the second period are in the $2s$ and $2p$ orbitals. If we mix two of the $2p$ orbitals with a $2s$ orbital, we end up with **three sp^2 hybridized orbitals**. These three orbitals lie on a plane, and they point to the vertices of an equilateral triangle as shown here.

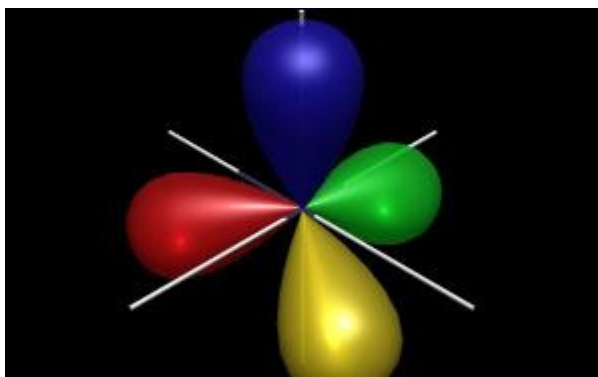
When the central atom makes use of sp^2 hybridized orbitals, the compound so formed has a trigonal shape. BF_3 is such a molecule:

Not all three sp^2 hybridized orbitals have to be used in bonding. One of the orbitals may be occupied by a pair or a single electron. If we do not count the unshared electrons, these molecules are bent, rather than linear. The three molecules shown together with the BF_3 molecule are such molecules.

Carbon atoms also makes use of the sp^2 hybrid orbitals in the compound $\text{H}_2\text{C}=\text{CH}_2$. In this molecule, the remaining p orbital from each of the carbon overlap to form the additional π σ , bond. Other ions such as CO_3^{2-} , and NO_3^- , can also be explained in the same way.

The sp^3 hybrid orbitals

Mixing one s and all three p atomic orbitals produces a set of four equivalent sp^3 hybrid atomic orbitals. The four sp^3 hybrid orbitals points towards the vertices of a tetrahedron, as shown here in this photograph.



When sp^3 hybrid orbitals are used for the central atom in the formation of molecule, the molecule is said to have the shape of a tetrahedron.

The typical molecule is CH_4 , in which the $1s$ orbital of a H atom overlap with one of the sp^3 hybrid orbitals to form a C-H bond. Four H atoms form four such bonds, and they are all equivalent. The CH_4 molecule is the most cited molecule to have a tetrahedral shape. Other molecules and ions having tetrahedral shapes are SiO_4^{4-} , SO_4^{2-} ,

As are the cases with sp^2 , hybrid orbitals, one or two of the sp^3 hybrid orbitals may be occupied by non-bonding electrons. Water and ammonia are such molecules.

The C, N and O atoms in CH_4 , NH_3 , OH_2 (or H_2O) molecules use the sp^3 hybrid orbitals, however, a lone pair occupies one of the orbitals in NH_3 , and two lone pairs occupy two of the sp^3 hybrid orbitals in OH_2 . The lone pairs must be considered in the VSEPR model, and we can represent a lone pair by E, and two lone pairs by E_2 . Thus, we have NH_3E and OH_2E_2 respectively.

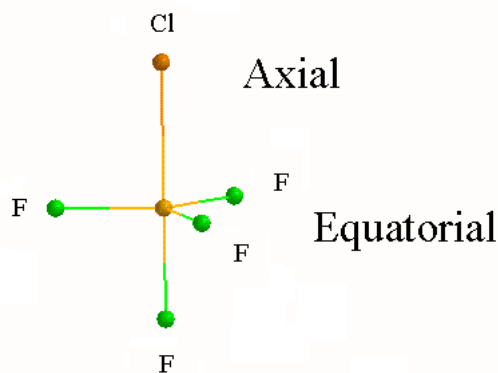
The *VSEPR number* is equal to the number of bonds plus the number of lone pair electrons. Does not matter what is the order of the bond, any bonded pair is considered on bond. Thus, the *VSEPR number* is 4 for all of CH_4 , $:\text{NH}_3$, $::\text{OH}_2$.

According to the VSEPR theory, the lone electron pairs require more space, and the H-O-H angle is 105 degrees, less than the ideal tetrahedral angle of 109.5 degrees.

The dsp^3 hybrid orbitals

The five dsp^3 hybrid orbitals resulted when one $3d$, one $3s$, and three $3p$ atomic orbitals are mixed. When an atom makes use of five dsp^3 hybrid orbitals to bond to five other atoms, the geometry of the molecule is often a **trigonalbipyramidal**.

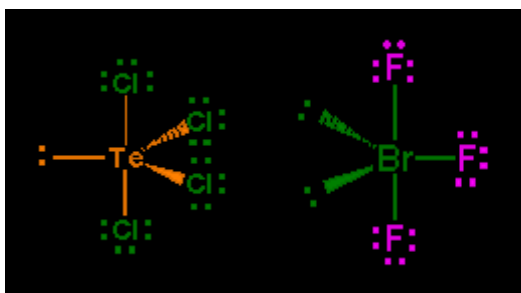
For example, the molecule PClF_4 displayed here forms such a structure. In this diagram, the Cl atom takes up an axial



position of the trigonalbipyramid. There are structures in which the Cl atom may take up the equatorial position. The change in arrangement is accomplished by simply change the bond angles. This link discusses this type of configuration changes of this molecule.

Some of the dsp^3 hybrid orbitals may be occupied by electron pairs. The shapes of these molecules are interesting. In TeCl_4 , only one of the hybrid dsp^3 orbitals is occupied by a lone pair. This structure may be represented by TeCl_4E , where E represents a lone

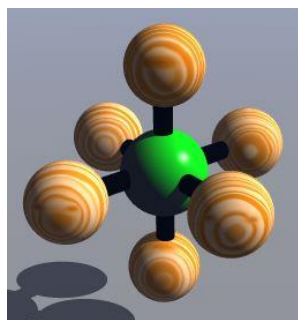
pair of electrons. Two lone pairs occupy two such orbitals in the molecule BrF_3 , or BrF_3E_2 . These structures are given in a VSEPR table of 5 and 6 coordinations.



The compound SF_4 is another AX_4E type, and many interhalogen compounds ClF_3 and IF_3 are AX_3E_2 type. The ion I_3^- is of the type AX_2E_3 .

The d^2sp^3 hybrid orbitals

The six d^2sp^3 hybrid orbitals resulted when two $3d$, one $3s$, and three $3p$ atomic orbitals are mixed. When an atom makes use of six d^2sp^3 hybrid orbitals to bond to six other atoms, the molecule takes the shape of an octahedron, in terms of molecular geometry. The gas compound SF_6 is a typical such structure. This link provides other shapes as well.



There are also cases that some of the d^2sp^3 hybrid orbitals are occupied by lone pair electrons leading to the structures of the following types:

AX_6 , AX_5E , AX_4E_2 , AX_3E_3 and AX_2E_4
 IOF_5 , IF_5E , XeF_4E_2

No known compounds of AX_3E_3 and AX_2E_4 are known or recognized, because they are predicted to have a T shape and linear shape respectively when the lone pairs of electrons are ignored.

Molecular shapes of compounds

While the hybridized orbitals were introduced, in the foregoing discussion, Valence-shell Electron-pair Repulsion (VSEPR) Model was included to suggest the shapes of various molecules. Specifically, the VSEPR model counts unshared electron pairs and the bonded atoms as the *VSEPR number*. A single-, double- and tripple-bond is considered as 1. After having considered the hybridized orbitals and the VSEPR model, we can not take a systematic approach to rationalize the shapes of many molecules based on the number of valence electrons.

A summary in the form of a table is given here to account for the concepts of **hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule**. In this table, the geometric shapes of the molecules are described by **linear, trigonal planar, tetrahedral, trigonal bypyramidal, and octahedral**. The hybrid orbitals use are sp , sp^2 , sp^3 , dsp^3 , and d^2sp^3 .

The *VSEPR number* is the same for all molecules of each group. Instead of using NH_3E , and OH_2E_2 , we use: NH_3 , $::OH_2$ to emphasize the unshared (or lone) electron pairs.

A summary of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule.				
Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
sp	sp^2	sp^3	dsp^3	d^2sp^3
BeH_2	BH_3	CH_4	PF_5	SF_6
BeF_2	BF_3	CF_4	PCl_5	IOF_5
CO_2	CH_2O	CCl_4	$PFCl_4$	PF_6^-
HCN	$(>C=O)$	CH_3Cl	$:SF_4$	SiF_6^{2-}
$HC\equiv CH$	$>C=C<$	NH_4^+	$:TeF_4$	$:BrF_5$
	CO_3^{2-}	$:NH_3$	$::ClF_3$	$:IF_5$
	benzene	$:PF_3$	$::BrF_3$	$::XeF_4$
	graphite	$:SOF_2$	$:::XeF_2$	
	fullerenes	$::OH_2$	$:::I_3^-$	
	$\bullet NO_2$	$::SF_2$	$(:::I \quad I_2^-)$	

	N_3^-		$:::\text{ICl}_2^-$	
	$:\text{OO}_2$ (O_3)	SiO_4^{4-}		
	$:\text{SO}_2$	PO_4^{3-}		
	SO_3	SO_4^{2-}		
		ClO_4^-		
• a lone odd electron : a lone electron pair				

This table correlates a lot of interesting chemical concepts in order to understand the molecular structures of these compounds or ions. There are some intriguing chemical relationships among the molecules in each column for you to ponder.

Only Be and C atoms are involved in linear molecules. In gas phase, BeH_2 and BeF_2 are stable, and these molecules do not satisfy the octet rule. The element C makes use of sp hybridized orbitals and it has the ability to form double and triple bonds in these linear molecules.

Carbon compounds are present in trigonal planar and tetrahedral molecules, using different hybrid orbitals. The extra electron in nitrogen for its compounds in these groups appears as lone unpaired electron or lone electron pairs. More electrons in O and S lead to compounds with lone electron pairs. The five-atom anions are tetrahedral, and many resonance structures can be written for them.

Trigonal bipyramidal and octahedral molecules have 5 and 6 VSEPR pairs. When the central atoms contain more than 5 or 6 electrons, the extra electrons form lone pairs. The number of lone pairs can easily be derived using Lewis dot structures for the valence electrons.

In describing the shapes of these molecules, we often ignore the lone pairs. Thus, $\bullet\text{NO}_2$, N_3^- , $:\text{OO}_2$ (O_3), and $:\text{SO}_2$ are **bent molecules** whereas $:\text{NH}_3$, $:\text{PF}_3$, and $:\text{SOF}_2$ are pyramidal. You already know that water and sulphur difluoride contain two lone pairs each and are bent molecules.

The lone electron pair takes up the equatorial location in: SF_4 , which has the same structure as $:\text{TeF}_4$ described earlier. If you lay a model of this molecule on the side, it looks like a *butterfly*. By the same reason, ClF_3 and BrF_3 have a *T* shape, and XeF_2 , I_3^- , and ICl_2^- are linear.

Similarly, $:\text{BrF}_5$ and $:\text{IF}_5$ are square pyramidal whereas XeF_4 is square planar.

The Center Atom

Usually, the atom in the center is more electropositive than the terminal atoms. However, the H and halogen atoms are usually at the terminal positions because they form only one bond.

However, the application of VSEPR theory can be expanded to complicated molecules also.

By applying the VSEPR theory, one deduces the following results:

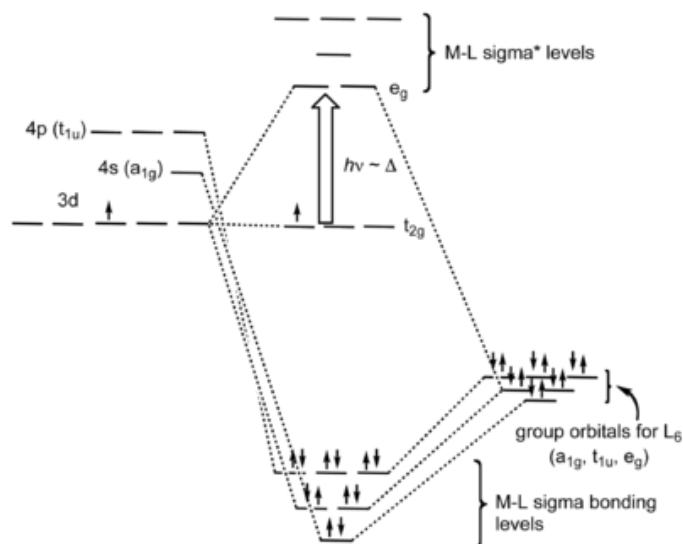
- H-C-C bond angle = 109°
- H-C=C bond angle = 120° , geometry around C trigonal planar
- C=C=C bond angle = 180° , in other words linear
- H-N-C bond angle = 109° , tetrahedral around N
- C-O-H bond angle = 105 or 109° , 2 lone electron pairs around O

Ligand field theory:

Ligand field theory (LFT) describes the bonding, orbital arrangement, and other characteristics of coordination complexes. It represents an application of molecular orbital theory to transition metal complexes. A transition metal ion has nine valence atomic orbitals, five nd , one $(n+1)s$, and three $(n+1)p$ orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The LFT analysis is highly dependent on the geometry of the complex, but most explanations begin by describing octahedral complexes, where six ligands coordinate to the metal.

σ -Bonding

The molecular orbitals created by coordination can be seen as resulting from the donation of two electrons by each of six σ -donor ligands to the d -orbitals on the metal. In octahedral complexes, ligands approach along the x -, y - and z -axes, so their σ -symmetry orbitals form bonding and anti-bonding combinations with the d_z^2 and $d_{x^2-y^2}$ orbitals. The d_{xy} , d_{xz} and d_{yz} orbitals remain non-bonding orbitals. Some weak bonding (and anti-bonding) interactions with the s and p orbitals of the metal also occur, to make a total of 6 bonding (and 6 anti-bonding) molecular orbitals.



Ligand-Field scheme summarizing σ -bonding in the octahedral complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

In molecular symmetry terms, the six lone pair orbitals from the ligands (one from each ligand) form six symmetry adapted linear combinations (SALCs) of orbitals, also sometimes called ligand group orbitals (LGOs). The irreducible representations that these span are a_{1g} , t_{1u} and e_g . The metal also has six valence orbitals that span these irreducible representations - the s orbital is labeled a_{1g} , a set of three p-orbitals is labeled t_{1u} , and the d_z^2 and $d_{x^2-y^2}$ orbitals are labeled e_g . The six σ -bonding molecular orbitals result from the combinations of ligand SALC's with metal orbitals of the same symmetry.

π -bonding

π bonding in octahedral complexes occurs in two ways: via any ligand p -orbitals that are not being used in σ bonding, and via any π or π^* molecular orbitals present on the ligand.

The p -orbitals of the metal are used for σ bonding (and are the wrong symmetry to overlap with the ligand p or π or π^* orbitals anyway), so the π interactions take place with the appropriate metal d -orbitals, i.e. d_{xy} , d_{xz} and d_{yz} . These are the orbitals that are non-bonding when only σ bonding takes place.

One important π bonding in coordination complexes is metal-to-ligand π bonding, also called π back bonding. It occurs when the LUMOs of the ligand are anti-bonding π^*

orbitals. These orbitals are close in energy to the d_{xy} , d_{xz} and d_{yz} orbitals, with which they combine to form bonding orbitals (i.e. orbitals of lower energy than the aforementioned set of d -orbitals). The corresponding anti-bonding orbitals are higher in energy than the anti-bonding orbitals from σ bonding so, after the new π bonding orbitals are filled with electrons from the metal d -orbitals, Δ_O has increased and the bond between the ligand and the metal strengthens. The ligands end up with electrons in their π^* molecular orbital, so the corresponding π bond within the ligand weakens.

The other form of coordination π bonding is ligand-to-metal bonding. This situation arises when the π -symmetry p or π orbitals on the ligands are filled. They combine with the d_{xy} , d_{xz} and d_{yz} orbitals on the metal and donate electrons to the resulting π -symmetry bonding orbital between them and the metal. The metal-ligand bond is somewhat strengthened by this interaction, but the complementary anti-bonding molecular orbital from ligand-to-metal bonding is not higher in energy than the anti-bonding molecular orbital from the σ bonding. It is filled with electrons from the metal d -orbitals, however, becoming the HOMO of the complex. For that reason, Δ_O decreases when ligand-to-metal bonding occurs.

The greater stabilization that results from metal-to-ligand bonding is caused by the donation of negative charge away from the metal ion, towards the ligands. This allows the metal to accept the σ bonds more easily. The combination of ligand-to-metal σ -bonding and metal-to-ligand π -bonding is a synergic effect, as each enhances the other.

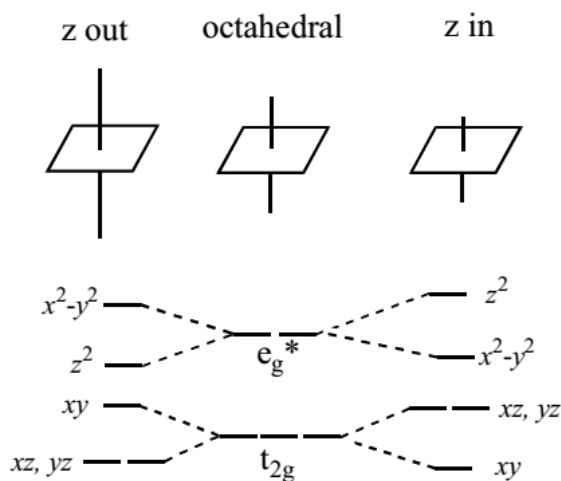
As each of the six ligands has two orbitals of π -symmetry, there are twelve in total. The symmetry adapted linear combinations of this fall into four triply degenerate irreducible representations, one of which is of t_{2g} symmetry. The d_{xy} , d_{xz} and d_{yz} orbitals on the metal also have this symmetry, and so the π -bonds formed between a central metal and six ligands also have it (as these π -bonds are just formed by the overlap of two sets of orbitals with t_{2g} symmetry.)

Tetragonal distortions from octahedral symmetry

The sections we just passed over, discussed how energy levels are affected by having different ligands bound to the central metal atom or ion. As I said earlier, this is more complex than we need to get into, however energy level distortions can occur even if the

ligands are all the same. The Jahn-Teller theorem predicts these distortions. It states that for a non-linear molecule in a non-degenerate state, the molecule must distort such that the symmetry of the molecule is lowered, the degeneracy is removed, and the energy of the molecule is lowered.

So what does this mean? First, a non-degenerate state is one in which all sets of orbitals are not full, empty, or half-full (e.g. 1 or 2 electrons in t_{2g} or 1 electron in e_g^*). Let's assume for a moment you have 1 electron in an e_g set. That electron spends 50% of the time in the z^2 and 50% of the time in the x^2-y^2 . Now what would happen if the two z -axis ligands were pulled slightly away from the metal? The x and y axis ligands would be pulled in a little closer to replace lost electron density. With the z^2 ligands further away the z^2 drops in energy. The x^2-y^2 will rise in energy by an equal amount because its ligands are drawn closer. The reverse may also happen. That is: z ligands move in and x , y ligands move out. There will also be an effect on the t_{2g} set. This is shown graphically below.

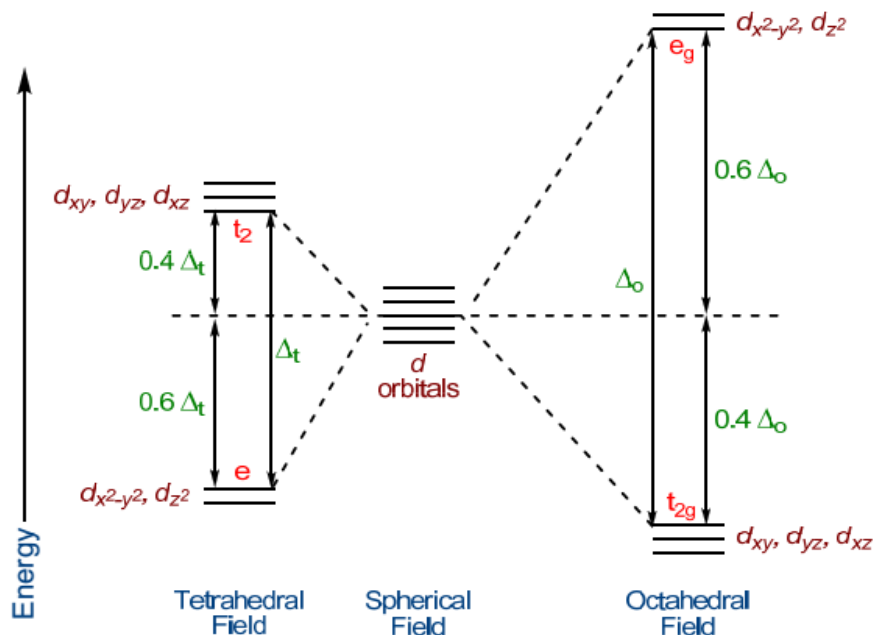


Note the average energy of each split set equals the energy of the unsplit set. These splittings are quite small and so do not affect pairings. Altering spin pairings could conceivably happen in a d^4 case where to avoid spin pairing energy the fourth electron moved into a lowered e_g^* orbital. However, the square planar geometry can be viewed as an extreme Jahn-Teller distortion with the z -ligands moved to infinite distance.

Finally, the number of electrons in a t_{2g} set will govern the type of distortion: $1e^-$, $4e^-$ (LS), or $6e^-$ (HS) z out and $2e^-$, $5e^-$ (LS), or $7e^-$ (HS) z in. What about the e_g^* set? This brings us to an important point about the Jahn-Teller theorem. It tells us neither the type,

nor the size of the distortion, only that it will occur with the proviso that the center of symmetry will remain. For the e_g set, either distortion can occur, depending on the complex.

Octahedral Vs Tetrahedral



High and low spin and the spectrochemical series

The six bonding molecular orbitals that are formed are "filled" with the electrons from the ligands, and electrons from the d -orbitals of the metal ion occupy the non-bonding and, in some cases, anti-bonding MO's. The energy difference between the latter two types of MO's is called Δ_o (O stands for octahedral) and is determined by the nature of the π -interaction between the ligand orbitals with the d -orbitals on the central atom. As described above, π -donor ligands lead to a small Δ_o and are called weak- or low-field ligands, whereas π -acceptor ligands lead to a large value of Δ_o and are called strong- or high-field ligands. Ligands that are neither π -donor nor π -acceptor give a value of Δ_o somewhere in-between.

The size of Δ_o determines the electronic structure of the $d^4 - d^7$ ions. In complexes of metals with these d -electron configurations, the non-bonding and anti-bonding molecular orbitals can be filled in two ways: one in which as many electrons as possible are put in the non-bonding orbitals before filling the anti-bonding orbitals, and one in

which as many unpaired electrons as possible are put in. The former case is called low-spin, while the latter is called high-spin. A small Δ_O can be overcome by the energetic gain from not pairing the electrons, leading to high-spin. When Δ_O is large, however, the spin-pairing energy becomes negligible by comparison and a low-spin state arises.

The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ that they produce. It can be seen that the low-field ligands are all π -donors (such as I^-), the high field ligands are π -acceptors (such as CN^- and CO), and ligands such as H_2O and NH_3 , which are neither, are in the middle.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < py$ (pyridine) $< NH_3 < en$ (ethylenediamine) $< bipy$ (2,2'-bipyridine) $< phen$ (1,10-phenanthroline) $< NO_2^- < PPh_3 < CN^- < CO$.

UNIT I

POSSIBLE QUESTIONS**PART A** (objective type questions- each carry one mark)

- Primary Valency indicates----- of the metal ion
 - Coordination number
 - Neutral ligands
 - Negative ligands
 - b). Oxidation state**
- Werner's theory explain the
 - Colour of the complex
 - Magnetic property of the complex
 - hybridization
 - b). Geometry of the complex**
- Bonding and orbital arrangement is described by
 - CFT
 - b). LFT**
 - VBT
 - MOT
- The axial Orbitals are known as
 - d- Orbitals
 - t_{2g} -Orbitals
 - b). e_g -Orbitals**
 - none
- The number of unpaired electrons present in $[\text{MnCl}_4]^{2-}$ complex ion is 5, the hybridisation of the complex is ----
 - sp
 - sp^2
 - c). sp^3**
 - dsp^2
- Crystal field theory is also called as
 - Weak field theory
 - Strong field theory
 - c). ligand field theory**
 - None
- The CFSE for a high spin d^4 octahedral complex ion is
 - 14Dq
 - b). -6Dq**
 - 12Dq
 - Zero
- The largest crystal field splitting will be for the ligand (same metal ion)
 - Ox^{2-}
 - NO^{2-}
 - NH_3
 - d). CN^-**
- Which of the following is a ligand which causes maximum crystal field splitting?
 - NH_3
 - F^-
 - c). CO**
 - Ox^{2-}
- Among the following which is known as the chelating agent
 - NH_3
 - b). DMG**
 - Cl
 - ONO
- The order of splitting in cubic geometry is same as that in
 - a. tetrahedral**
 - Square planar
 - Octahedral
 - distorted octahedral
- The number of unpaired electron in d^7 tetrahedral configuration is
 - a. 3**
 - 2
 - 1
 - 7
- Stability of a complex does not depend upon
 - nature of the central metal ion
 - Number of chelate rings

- c. steric effects **d. mass of the complex**
14. Maximum value of $\log \beta$ is that of
a. **AgI** b. AgCl c. AgBr d. AgF
15. Who is known as the father of Coordination Chemistry
a. **Werner** b. Hund c. Mullikan d. Columson
16. Primary Valency indicates----- of the metal ion
a. Coordination number **b. Oxidation state** c. both d. Neutral
Ligands
17. If the oxidation state of the complex increase then the Δ_0 value
a. Decreases **b. Increases** c. As such d. Moderate
18. An octahedral complex is formed when central metal atom undergoes
hybridization among theorbitals
a. sp^3 b. dsp^2 c. sp^3d **d. sp^3d^2**
19. How many unpaired electrons are there in a strong field iron(II)octahedral
complex?
a. **0** b. 1 c. 2 d. 4
20. Among the following ions which one has the highest paramagnetism
a. **$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$** b. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ c. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ d. $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
21. The splitting of degeneracy of d orbital due to ligands is known as
a. Octahedral splitting **b. Crystal field splitting**
c. tetrahedral splitting d. distorted Splitting

PART B (Each carries two marks)

1. Define crystal field splitting.
2. Define Crystal field field stabilization energy.
3. What is meant by Spectrochemical series?
4. What are the limitations of crystal field theory?
5. Calculate CFSE for d^4 high spin octahedral complex.
6. Calculate CFSE for d^9 tetra hedral complex.
7. Define Jan Teller Theorem.
8. Define MO theory.

PART C (Each carries Six marks)

1. Explain the postulates of Werner's Theory.
2. Describe CFSE and calculate its value for d^4 system in octahedral and tetrahedral fields of Ligands.
3. How does valence bond theory explain;
 - (i) $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic and squareplaner.
 - (ii) $[\text{Ni}(\text{Co})_4]$ is diamagnetic and tetrahedral.
4. Discuss the factors affecting the magnitude of crystal field splitting.
5. What are the postulates of Werner's coordination theory? How does it account for non- ionic nature of $\text{CoCl}_3.3\text{NH}_3$ complex.
6. Using valence bond theory explain the hybridization, geometry and magnetic properties of
 - (i) $[\text{Fe}(\text{CN})_6]^{3-}$ Complex and (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion.
7. Explain Jahn Teller Theorem.
8. How does valence bond theory explain the structures of $[\text{Co}(\text{NH}_3)]^{3+}$ and $[\text{CoF}_6]^{3-}$.
9. How does valence bond theory explain the structures of $[\text{Co}(\text{NH}_3)]^{3+}$ and $[\text{CoF}_6]^{3-}$.
10. Explain the features of crystal field theory.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY

INORGANIC CHEMISTRY-II (Coordination Chemistry)

Semester –III

Multiple Choice Questions for on line examination (Each question carry one mark)

UNIT-I

S. No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	Primary Valency indicates----- of the metal ion	Coordination number	Oxidation state	Neutral ligands	Negative ligands	Oxidation state
2	Primary valency of central metal ion is satisfied by	Positive ligands	Negative ligands	Neutral ligands	Bidentate ligands	Negative ligands
3	Secondary Valency of central metal ion is satisfied by	Either negative or neutral molecules	Bidentate ligands	Negative ligands only	neutral molecules only	Either negative or neutral molecules
4	Secondary valency is corresponds to ----- of metal atom	Oxidation state	Coordination number	Neutral ligands only	Neutral ligands	Coordination number
5	Werner's theory explain the	Colour of the complex	hybridisation	Magnetic property of the complex	Geometry of the complex	Geometry of the complex
6	$\Delta_{sp} =$	Δ_0	$1.3 \Delta_0$	$-1.3 \Delta_0$	$0.45 \Delta_0$	$1.3 \Delta_0$

7	Bonding and orbital arrangement is described by	CFT	LFT	VBT	MOT	LFT
8	$\Delta_0 =$	-6 Dq	-4	10 Dq	1 Dq	10 Dq
9	The axial Orbitals are known as	d- Orbitals	t_{2g} -Orbitals	e_g –Orbitals	none	e_g –Orbitals
10	The geometry of the complex having coordination number 5 is ---- ---	Trigonal bipyrimidal	Hexagonal	Tetrahedral	Trigonal pyramidal	Trigonal pyramidal
11	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
12	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
13	In the formation of σ - bonding in octahedral complexes , the non-bonding orbitals are	a_{1g}	t_{1u}	e_g	t_{2g}	e_g
13	Crystal field theory is also called as	Weak field theory	Strong field theory	ligand field theory	None	ligand field theory
14	In Crystal field theory ligands are consider as	Positive point charges	negative point charges	ligand field theory	None	negative point charges
15	In crystal field splitting of d orbitals d_{xy} , d_{yz} , d_{zx} orbitals are known as	a_{1g}	t_{1u}	e_g	t_{2g}	t_{2g}
16	Triply degenerate orbitals are	a_{1g}	e_u	e_g	t_{2g}	t_{2g}
17	Which theories are more	MO and LFT	MO and CFT	CFT and LFT	CFT and	MO and CFT

	complicated ?				Werner theory	
18	Valence bond theory was developed by	Linus Pauling	Werner	Mullikan	Hund	Linus Pauling
19	The LFT analysis is highly dependent on the geometry of the?	Bonds	Ligands	Electrons	Complex	Complex
20	The d orbitals of the ligands are usually?	Too high in energy	Low energy	High energy	Too low in energy	High energy
21	The s orbitals of the ligands are usually ?	Too high in energy	Low energy	High energy	Too low in energy	Too low in energy
22	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
23	If the oxidation state of the complex increase then the Δ_0 value	Decreases	Increases	As such	Moderate	Increases
24	The number of unpaired electrons in NiCl_4^{2-} (tetra hedral) are	two	zero	One	four	Two
25	Colour of the complex is satisfactorily explained by	Werner's theory	Valence bond theory	Crystal field theory	Ligand field theory	Crystal field theory
26	The CFSE for a high spin d^4 octahedral complex ion is	-14Dq	-6Dq	-12Dq	Zero	-6Dq
27	The largest crystal field splitting will be for the ligand (same metal ion)	Ox^{2-}	NO^{2-}	NH_3	CN^-	CN^-
28	Which of the following is a ligand which causes maximum crystal field splitting?	NH_3	CO	Ox^{2-}	F^-	CO

29	The order of splitting in cubic geometry is same as that in	tetrahedral	Square planar	Octahedral	tetragonally distorted octahedral	Tetrahedral
30	The number of unpaired electron in d^7 tetrahedral configuration is	3	2	1	7	3
31	Stability of a complex does not depend upon	nature of the central metal ion	Number of chelate rings	steric effects	mass of the complex	mass of the complex
32	Which of the following systems has maximum number of unpaired electrons?	d^6 (tetrahedral)	d^9 (octahedral)	d^7 (octahedral, high spin)	d^4 (octahedral, low spin)	d^6 (tetrahedral)
33	Which of the following has no CFSE in octahedral field?	Fe^{3+} (High spin)	Co^{2+} (low spin)	Fe^{3+} (low spin)	Cr^{3+} (high spin)	Fe^{3+} (low spin)
34	An octahedral complex is formed when central metal atom undergoes hybridization among the _____ orbitals	sp^3	dsp^2	sp^3d	sp^3d^2	sp^3d^2
35	In which one of the following species does the transition metal ion have d^3 electronic configuration?	$[Cr(NH_3)_6]^{3+}$	$[Co(OH_2)_6]^{2+}$	$[Fe(CN)_6]^{3-}$	$[CoF_6]^{3-}$	$[Fe(CN)_6]^{3-}$
36	(Crystal Field Theory) When the valence d orbitals of the central metal ion are split in energy in an octahedral ligand field, which orbitals are raised least in energy?	d_{xy} and $d_{x^2-y^2}$	d_{xy} , d_{xz} and d_{yz}	d_{xz} and d_{yz}	d_{xz} , d_{yz} and d_{z^2}	d_{xy} , d_{xz} and d_{yz}
37	(Crystal Field Theory) How many unpaired electrons are there in a strong field iron(II) octahedral complex?	0	1	2	4	2

38	Among the following ions which one has the highest paramagnetism	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
39	Which statement most <i>correctly</i> describes crystal field theory for a <i>d</i> block complex of unspecified geometry?	The theory considers covalent interactions between a metal centre and the surrounding ligands	The theory considers electrostatic interactions between a metal ion and the surrounding ligands which are taken to be point charges	The theory rationalizes the non-degeneracy of the metal <i>d</i> orbitals by considering the electrostatic repulsions between point charge ligands and electrons in the metal <i>d</i> orbitals	The theory rationalizes why the metal <i>d</i> orbitals are split into two levels	The theory rationalizes the non-degeneracy of the metal <i>d</i> orbitals by considering the electrostatic repulsions between point charge ligands and electrons in the metal <i>d</i> orbitals
40	Which of the following <i>correctly</i> places the ligands in their order in the spectrochemical series?	$\text{Br}^- < \text{Cl}^- < \text{NH}_3 < \text{H}_2\text{O}$	$\text{I}^- < \text{Br}^- < \text{H}_2\text{O} < [\text{OH}]^-$	$\text{F}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3$	$\text{I}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{en}$	$\text{I}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{en}$
41	Which of the following <i>correctly</i> places the metal centres in their order in the spectrochemical series?	$\text{Mn(II)} < \text{Fe(III)} < \text{Rh(III)}$	$\text{Co(III)} < \text{Co(II)} < \text{Rh(III)}$	$\text{Pt(IV)} < \text{Pd(II)} < \text{Ni(II)}$	$\text{Pd(II)} < \text{Ni(II)} < \text{Pt(IV)}$	$\text{Mn(II)} < \text{Fe(III)} < \text{Rh(III)}$
42	Which metal complex ion is expected to be subject to a Jahn-Teller distortion?	$[\text{Cr}(\text{OH}_2)_6]^{3+}$	$[\text{Cr}(\text{NH}_3)_6]^{2+}$	$[\text{Cr}(\text{CN})_6]^{3-}$	$[\text{Cr}(\text{bpy})_3]^{2+}$	$[\text{Cr}(\text{NH}_3)_6]^{2+}$
43	Which of the following complex ions is tetrahedral?	$[\text{PdCl}_4]^{2-}$	$[\text{PtCl}_4]^{2-}$	$[\text{NiCl}_4]^{2-}$	$[\text{AuCl}_4]^-$	$[\text{NiCl}_4]^{2-}$
44	Match up the correct formula and magnetic property. Which pair is <i>correct</i> ?	$[\text{Zn}(\text{OH}_2)_6]^{2+}$; paramagnetic	$[\text{Co}(\text{NH}_3)_6]^{3+}$; diamagnetic	$[\text{CoF}_6]^{3-}$; diamagnetic	$[\text{V}(\text{OH}_2)_6]^{2+}$; diamagnetic	$[\text{Co}(\text{NH}_3)_6]^{3+}$; diamagnetic

45	Which statement is <i>incorrect</i> about typical metal carbonyl complexes $M(CO)_n$?	They are likely to obey the 18-electron rule	They contain π -acceptor ligands	M is in a zero oxidation state	They are likely to be paramagnetic	They are likely to be paramagnetic
46	The splitting of degeneracy of d orbital due to ligands is known as	Octahedral splitting	Crystal field splitting	Degeneracy splitting	Splitting	Crystal field splitting
47	According to CFT, in the octahedral complexes the d orbital splits into	Lower t_{2g} and higher eg level	Lower t_{2g} and higher eg level	Higher t_{2g} and lower eg level	Lower d_{2g} and higher eg level	Lower t_{2g} and higher eg level
48	The degeneracy of d orbital is removed with the approach of the ligand due to	Ligand nucleus-metal nucleus repulsions	Ligand nucleus-metal electron attractions	Ligand electron-metal nucleus attractions	Ligand electron-metal electron repulsions	
49	The splitting of d orbital will be more in F^- as compared to Cl^- because	F^- is a strong field ligand than Cl^-	F^- is smaller in size than Cl^-	F^- is larger in size than Cl^-	F^- is a weak field ligand than Cl^-	F^- is a strong field ligand than Cl^-
50	According to CFT, as the ligand approaches towards d orbital it results into	Energy remains same	Splitting of d orbital	No effect	Degeneracy is maintained	Splitting of d orbital
51	Valence bond theory could explain the _____ of the complex	Stereochemistry	Geometry	Bonding	Stereochemistry and magnetic property	Stereochemistry and magnetic property
52	The number of unpaired electrons in $[Cr(NH_3)_6]^{3+}$ complex is	4	3	2	6	3
53	The oxidation state of central metal atom in $[Cr(NH_3)_6]^{3+}$ is	3+	2+	4+	6+	3+
54	Coordination sphere charge of $[Co(NH_3)_6]^{3+}$	+6	+9	+3	0	+3

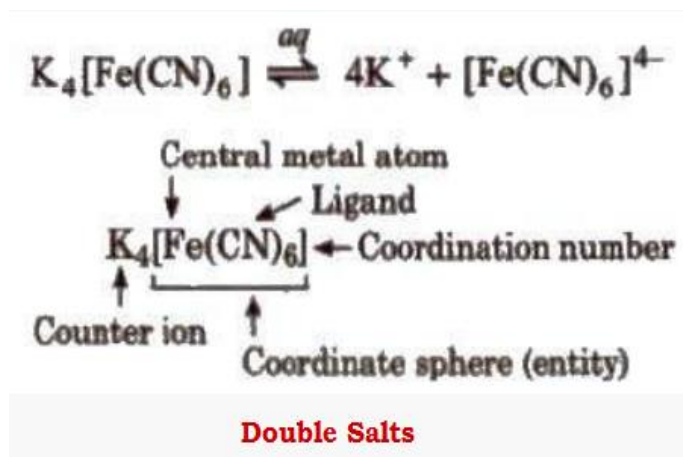
55	Coordination number of $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex	4	5	3	6	6
56	What is the outer most electronic configuration of cobalt in $[\text{CoF}_6]^{3-}$ complex ion is	$3d^6$	$3d^4$	$3d^3$	$3d^5$	$3d^6$
57	Which metal complex ion is expected to be subject to a Jahn-Teller distortion?	$[\text{Cr}(\text{OH}_2)_6]^{3+}$	$[\text{Cr}(\text{NH}_3)_6]^{2+}$	$[\text{Cr}(\text{CN})_6]^{3-}$	$[\text{Cr}(\text{bpy})_3]^{2+}$	$[\text{Cr}(\text{NH}_3)_6]^{2+}$
58	Ligand field theory describes the --- of coordination complexes	Bonding and orbital arrangement	Geometry	Magnetic property	d-orbital splitting	Bonding and orbital arrangement
59	In the complex formation, the central metal atom / ion acts as	Lewis base	Bronsted base	Lewis acid	Bronsted acid	Lewis acid
60	An octahedral complex is formed when central metal atom undergoes hybridization among the _____ orbitals	sp^3	dsp^2	sp^3d	sp^3d^2	sp^3d^2

UNIT-II

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coordination compounds

Coordination compounds are those addition molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds central metal atom or ion is linked by ions or molecules with coordinate bonds. E.g. Potassium ferrocyanide $K_4[Fe(CN)_6]$



These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution e.g. Mohr's salt. $FeSO_4 [NH_4] SO_4 \cdot 6H_2O$ get dissociated into Fe^{+2} , NH_4^+ , and SO_4^{2-} ions.

1. Complex ion or coordination Entity

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

(i) *Cationic complex entity*

It is the complex ion which carries positive charge e.g. $\text{Pt}(\text{NH}_3)_4]^{2+}$

(ii) Anionic complex entity

It is the complex ion which carries negative charge. E.g., $[\text{Fe}(\text{CN})_6]^{4-}$

2. Central atom or Ion

The atom or ion to which a fixed number of ions or groups are bound in central atom or ion.

It is also referred as Lewis acid. E.g., in $[\text{NiCl}_2(\text{H}_2\text{O})_4]$. Ni is central metal atom. It is generally transition elements.

3. Ligands

Ligands are electron donating species (ions or molecules) bound to the central atom in the coordination entity.

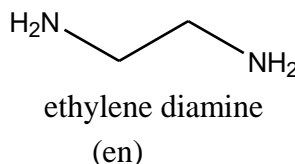
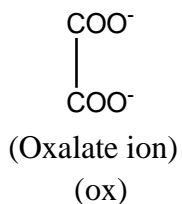
These may be charged or neutral. Ligands of the following types

(i) Unidentate

It is a ligand, which has one donor site, i.e., the ligand bound to a metal ion through a single donor site. E.g., H_2O , NH_3 , etc.

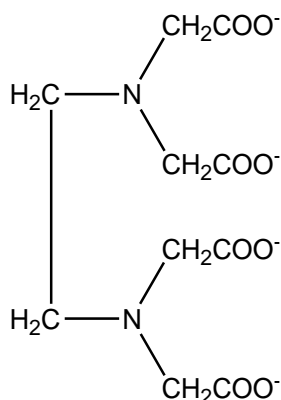
(ii) Didentate

It is the ligands which have two donor sites.



(iii) Polydentate

It is the ligands, which have several donor sites. E.g., $[\text{EDTA}]^{4-}$ is hexadentate ligand

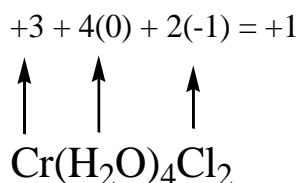


(iv) Ambidentate ligands

These are the monodentate ligands which can ligate through two different sites, e.g., NO_2 , SCN^- , etc.

Oxidation numbers

The oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.



Introduction

Complex compounds, metal complexes or just complexes are compounds which contain a central metal atom or ion closely surrounded by a cluster of ions or neutral molecules called *ligands*. The ligands are electron rich species and are usually bonded to the central nuclear atom by co-ordination bonds. Hence, these complexes are often referred to as *co-ordination bonds* and are represented by a square bracket- $[\text{Ni}(\text{CO})_4]$. In this example, nickel is the central metal atom and carbon monoxide is the ligand. The number of nearest ligands bonded to the central metal

atom is known as *co-ordination number* of that metal atom. Metal complexes with coordination number 2,4,5 and 6 are shown below:

Coordination number	Examples
2	$[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Ag}(\text{CN})_2]^-$
4	$[\text{Ni}(\text{CO})_4]$, $[\text{CuCl}_4]^{3-}$, $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$
5	$[\text{Fe}(\text{CO})_5]$
6	$[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$, $[\text{Co}(\text{NO}_2)_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$

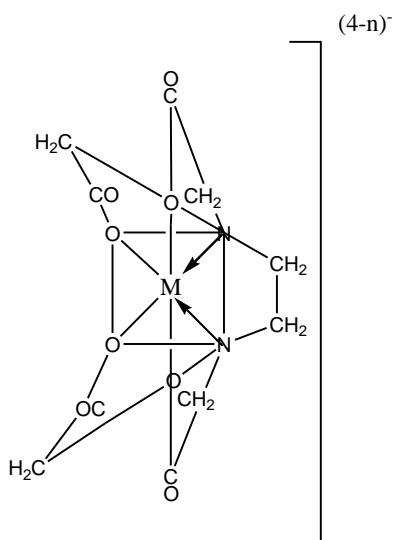
The coordination compounds differ largely from *double salts*. As the double salts tend to retain their identity even in solution, the properties of complexes are entirely different from those of the constituents.

A ligand that is capable of forming one coordinate covalent bond to the nuclear atom is called a *mono-or unidentate* ligand.

e.g.: F^- , Cl^- , CN^- , NO_2^- , H_2O , NH_3 , CO and NO .

When a ligand has two groups that are capable of bonding to the central atom, it is said to be a *bi-dentate*. Common examples are-oxalate, glycinate, acetylacetonate, dimethylglyoximate, 2,2' – dipyridyl, 1, 10-phenanthroline and ethylenediamine (en).

Further, if the two bonds from a ligand appear to enclose the metal atom in a pincer like structure, the resulting complex is known as a *chelate* (G.k, *chele* = *claw*). Chelate complexes are more stable than ordinary complexes in which the ligand is monodentate. Thus, $[\text{Cu}(\text{en})_2]^{2+}$ is more stable than $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Other ligands which have up to six co-ordinating groups are known. The most common example is *Ethylene Diamine Tetra-Acetic acid* (EDTA), Versene or complexone and its complexing behavior is shown in figure (n denotes the valance of the metal).



Depending on the number of metal atoms or ions present in the complexes, they are classified as *mononuclear* (if only one metal is present) and *polynuclear* (if more than one metal is present). For example, $[\text{Ni}(\text{CO})_4]$ is a mononuclear complex whereas $[\text{Fe}_5(\text{CO})_9]$ is a polynuclear complex.

Nomenclature of mono-nuclear complexes

The nomenclature system given below is the one recommended by the *Inorganic Nomenclature committee* of the *International Union of Pure and Applied Chemistry*.

- 1) Non ionic or molecular complexes are given one word name.
- 2) In ionic complexes, the cation is named first, then the anion separately.
- 3) The ligands with negative charge end in-O, Some example are-

O^{2-} (oxo)	Cl^- (chloro)	NH_2^- (amido)
OH^- (hydroxo)	Br^- (bromo)	NH^{2-} (imido)
$\text{C}_2\text{O}_4^{2-}$ (oxalato)	I^- (iodo)	NO_2^{2-} (nitro)
SO_4^{2-} (sulphato)	CN^- (cyano)	ONO^- (nitrito)

- 4) Neutral ligands are named as the molecule. Example are $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$ (ethylenediamine, en) $\text{C}_5\text{H}_5\text{N}$ (pyridine, py)

Exceptions to this rule are-

H₂O (*aquo*), NH₃ (*ammine*), CO (*carbonyl*), NO (*nitosyl*)

5) Positive ligands (rare) end in -ium

NH₂-NH₃⁺ (*hydrazinium*)

6) The ligands in a complex are named first and are given in the alphabetical order.

7) The number of identical ligands is given by the Greek prefixes di-, tri-, tetra-, penta-, hexa- and hepta- in the case of simple ligands.

8) The prefixes bis-, tris-, tetrakis-, pentakis-, etc. are used for complex ligands which themselves often contain the former prefixes:

e.g. triphenylphosphine, ethylenediamine. Usually these complex ligands have polysyllabic name and their name in the complex is enclosed in parenthesis.

9) The name of the central atom is given after the ligands together with its oxidation stage designated by a Roman numeral in brackets.

10) When the complex is a cation or a neutral molecule, the name of the metal atom is unchanged, but when it is an anion, the suffix- *ate* is added.

The above rules are illustrated in the following complexes:

Neutral Complexes

1)	[Fe(CO) ₅]	Pentacarbonyliron(0)
2)	[Pt(NH ₃) ₂ Cl ₂]	Diamminedichloroplatinum(II)
3)	[Cr(H ₂ O) ₃ Cl ₃]	Triaquatrichlorochromium(III)
4)	[PtNH ₃ (py)ClBr]	Amminebromochloropyridine platinum(II)
5)	[Co(NH ₃) ₃ NO ₂ (CN)Cl]	Triamminechlorocyanonitrocobalt(III)

Cationic complexes

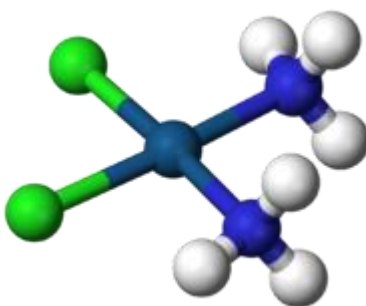
1)	[Pt(NH ₃) ₄ Cl ₂] Br ₂	Tetra-amminedichloroplatinum(IV) bromide
2)	[Pt(NH ₃) ₄ NO ₂ Cl] CO ₃	Tetra-amminechloronitroplatinum(IV) carbonate
3)	[Co(en) ₂ H ₂ O Cl] SO ₄	Aquochlorobis(ethylenediamine)cobalt (III) sulphate
4)	[Cr(H ₂ O) ₄ Cl ₂]Cl	Tetra-aquodichlorochromium(III)chloride
5)	[Co(NH ₃) ₄ Cl ₂]Cl	Tetra-amminedichlorocobalt(III)chloride
6)	[Ag(NH ₃) ₂]Cl	Diamminesilver(I) chloride

- | | | |
|----|---|---|
| 7) | $[\text{Rh}(\text{Ph}_3\text{P})_3]\text{Cl}$ | Tris(triphenylphosphine)rhodium(I) chloride |
| 8) | $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ | Tetra-aquocopper (II) ion. |

Anionic Complexes

- | | | |
|-----|--|---|
| 1) | $[\text{Fe}(\text{CN})_6]^{3-}$ | Hexacyanoferrate(III)ion |
| 2) | $[\text{Ni}(\text{CN})_4]^{2-}$ | Tetracyanonickelate(II)ion |
| 3) | $\text{NH}_4[\text{Co}(\text{H}_2\text{O})_2(\text{SCN})_4]$ | Ammoniumdiaquatetrakis(thiocyanato-S)
cobaltate(III) |
| 4) | $\text{K}_3[\text{FeF}_6]$ | Potassium hexafluoroferrate(III) |
| 5) | $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3]$ | Potassium amminetrichloro platinate(II) |
| 6) | $\text{K}_4[\text{Ni}(\text{CN})_4]$ | Potassium tetracyanonickelate (0) |
| 7) | $\text{Na}[\text{Al}(\text{OH})_4]$ | Sodium tetrahydroxoaluminate(III) |
| 8) | $\text{H}[\text{AuCl}_4]$ | Tetrachloroauric acid |
| 9) | $[\text{Ag}(\text{CN})_2]^-$ | Dicyanoargentate (I) ion |
| 10) | $\text{Na}[\text{Co}(\text{CO})_4]$ | Sodium tetracarbonylcobaltate(-I) |
| 11) | $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ | Potassium trioxalatoferrate(III) |

Coordination complex



Cisplatin, $\text{PtCl}_2(\text{NH}_3)_2$

A platinum atom with four ligands

In chemistry, a **coordination complex** or **metal complex**, is a structure consisting of a central atom or ion (usually metallic), bonded to a surrounding array of molecules or anions (ligands, complexing agents). The atom within a ligand that is directly bonded to the central

atom or ion is called the **donor atom**. Polydentate (multiple bonded) ligands can form a chelate complex. A ligand donates at least one pair of electrons to the central atom/ion.

Compounds that contain a coordination complex are called **coordination compounds**. The central atom or ion, together with all ligands forms the coordination sphere.

Coordination refers to the "coordinate covalent bonds" (dipolar bonds) between the ligands and the central atom. Originally, a complex implied a reversible association of molecules, atoms, or ions through such weak chemical bonds. As applied to coordination chemistry, this meaning has evolved. Some metal complexes are formed virtually irreversibly and many are bound together by bonds that are quite strong.

Structure of coordination complexes

The ions or molecules surrounding the central atom are called ligands. Ligands are generally bound to the central atom by a coordinate covalent bond (donating electrons from a lone electron pair into an empty metal orbital), and are said to be **coordinated** to the atom. There are also organic ligands such as alkenes whose pi bonds can coordinate to empty metal orbitals. An example is ethene in the complex known as Zeise's salt, $K^+[PtCl_3(C_2H_4)]^-$.

Geometry

In coordination chemistry, a structure is first described by its coordination number, the number of ligands attached to the metal (more specifically, the number of σ -type bonds between ligand(s) and the central atom). Usually one can count the ligands attached, but sometimes even the counting can become ambiguous. Coordination numbers are normally between two and nine, but large numbers of ligands are not uncommon for the lanthanides and actinides. The number of bonds depends on the size, charge, and electron configuration of the metal ion and the ligands. Metal ions may have more than one coordination number.

Typically the chemistry of complexes is dominated by interactions between s and p molecular orbital of the ligands and the d orbital of the metal ions. The s, p, and d orbitals of the metal can accommodate 18 electrons (see 18-Electron rule; for f-block elements, this extends to 32 electrons). The maximum coordination number for a certain metal is thus related to the electronic configuration of the metal ion (more specifically, the number of empty orbital) and to the ratio of

the size of the ligands and the metal ion. Large metals and small ligands lead to high coordination numbers, e.g. $[\text{Mo}(\text{CN})_8]^{4-}$. Small metals with large ligands lead to low coordination numbers, e.g. $\text{Pt}[\text{P}(\text{CMe}_3)]_2$. Due to their large size, lanthanides, actinides, and early transition metals tend to have high coordination numbers.

Different ligand structural arrangements result from the coordination number. Most structures follow the points-on-a-sphere pattern (or, as if the central atom were in the middle of a polyhedron where the corners of that shape are the locations of the ligands), where orbital overlap (between ligand and metal orbital) and ligand-ligand repulsions tend to lead to certain regular geometries. The most observed geometries are listed below, but there are many cases which deviate from a regular geometry, e.g. due to the use of ligands of different types (which results in irregular bond lengths; the coordination atoms do not follow a points-on-a-sphere pattern), due to the size of ligands, or due to electronic effects (see e.g. Jahn-Teller distortion):

- Linear for two-coordination,
- Trigonal planar for three-coordination,
- Tetrahedral or square planar for four-coordination
- Trigonal bipyramidal or square pyramidal for five-coordination,
- Octahedral (orthogonal) or trigonal prismatic for six-coordination,
- Pentagonal bipyramidal for seven-coordination,
- Square antiprismatic for eight-coordination, and
- Tri-capped trigonal prismatic (Triaugmented triangular prism) for nine coordination.

Some exceptions and provisions should be noted:

The idealized descriptions of 5-, 7-, 8-, and 9- coordination are often indistinct geometrically from alternative structures with slightly different L-M-L (ligand-metal-ligand) angles. The

classic example of this is the difference between square pyramidal and trigonal bipyramidal structures.

Due to special electronic effects such as (second-order) Jahn-Teller stabilization, certain geometries are stabilized relative to the other possibilities, e.g. for some compounds the trigonal prismatic geometry is stabilized relative to octahedral structures for six-coordination.

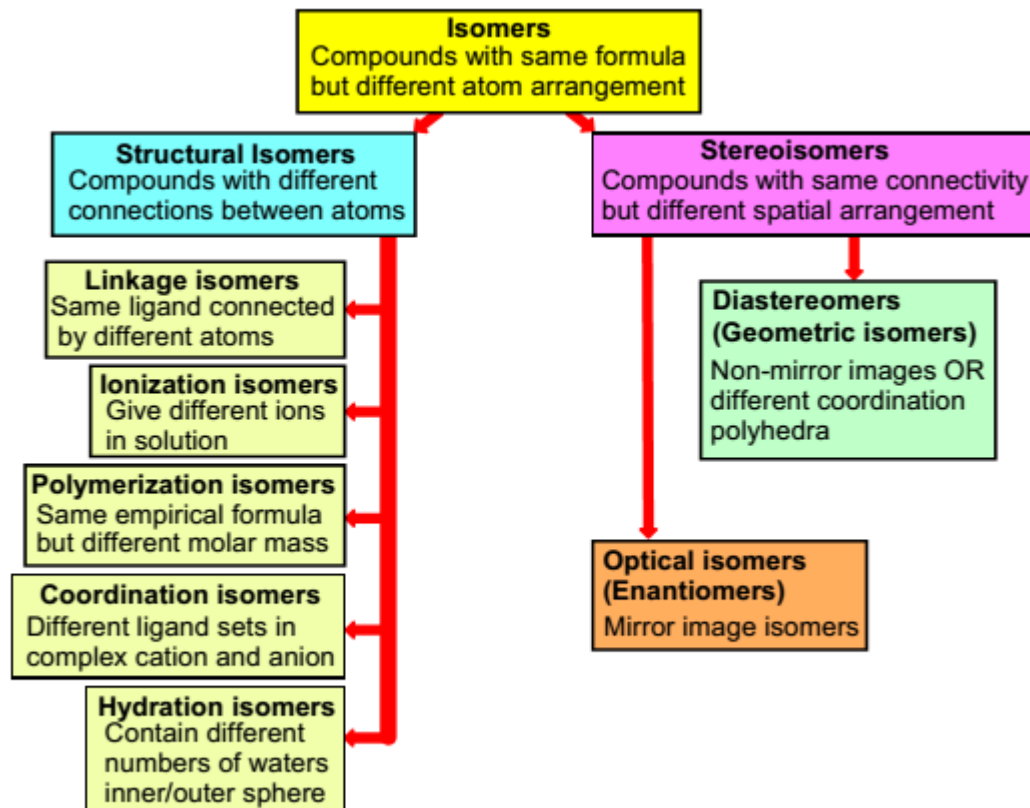
Isomerism

The arrangement of the ligands is fixed for a given complex, but in some cases it is mutable by a reaction that forms another stable isomer.

There exist many kinds of isomerism in coordination complexes, just as in many other compounds.

Isomerism in Coordination Chemistry

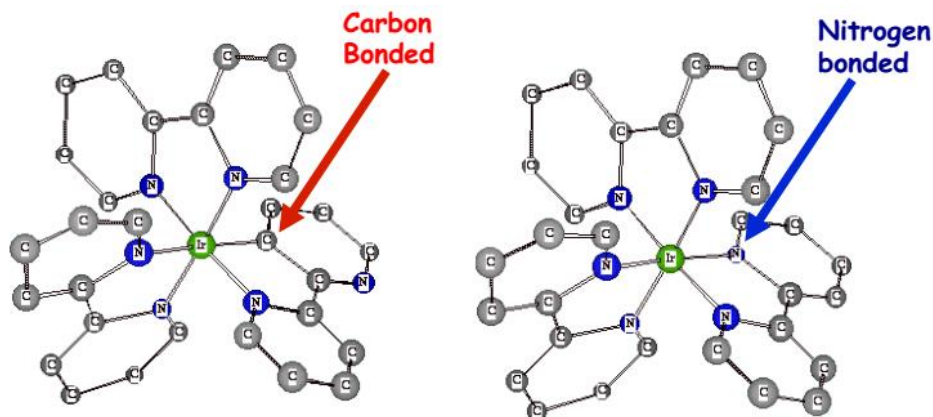
Two or more different compounds having the same formula are called isomers. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.



Structural Isomerism

(i) Linkage isomers:

Same ligand connected by different atoms. Two compounds formed by the linkage isomer of bpy are shown. Small changes in ligand bonding could result in dramatic chemical property change.



(ii) Ionization isomers:

Different ions when dissolved exchange of ions between inner and outer coordination sphere e.g. $[\text{Co}(\text{NH}_3)_5\text{Br}][\text{SO}_4]$ vs. $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$.

(iii) Coordination isomers:

Found in special cases where both the cation and anion are complexes

Examples: $\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ vs. $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$ vs. $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$

(iv) Hydration isomers:

Exchange of water and another ligand between inner and outer coordination sphere

eg. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (green crystals from c. HCl soln)

→ (dissolve H_2O) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (blue-green)

→ (heat) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet)

(v) Polymerization isomers:

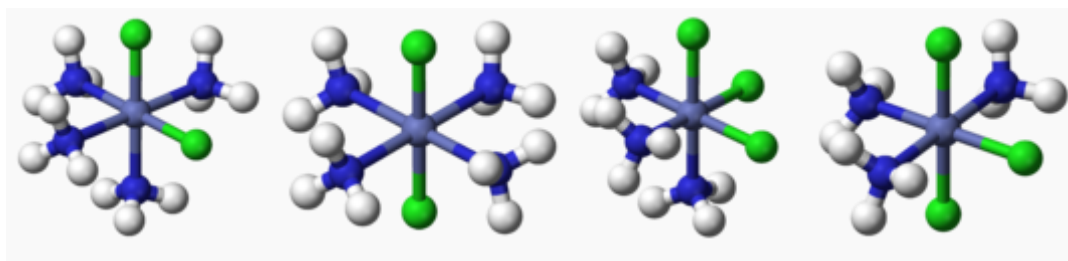
Identical empirical formulae but different molar masses (i.e. different degrees of aggregation)

Stereoisomerism

Stereoisomerism occurs with the same bonds in different orientations relative to one another. Stereoisomerism can be further classified into:

Cis-trans isomerism and facial-meridional isomerism

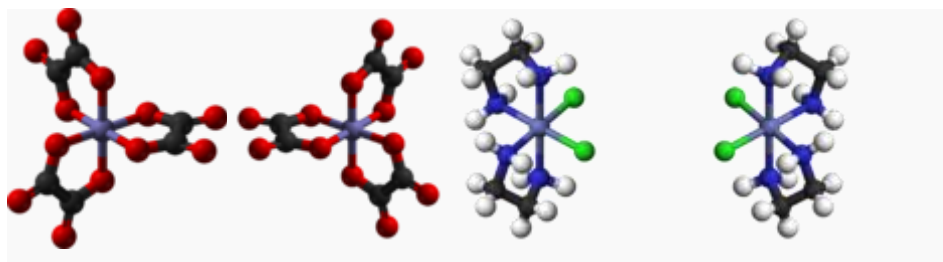
Cis-trans isomerism occurs in octahedral and square planar complexes (but not tetrahedral). When two ligands are mutually adjacent they are said to be **cis**, when opposite each other, **trans**. When three identical ligands occupy one face of an octahedron, the isomer is said to be facial, or **fac**. In a *fac* isomer, any two identical ligands are adjacent or *cis* to each other. If these three ligands and the metal ion are in one plane, the isomer is said to be meridional, or **mer**. A *mer* isomer can be considered as a combination of a *trans* and a *cis*, since it contains both trans and cis pairs of identical ligands.



cis-[CoCl₂(NH₃)₄]⁺ *trans*-[CoCl₂(NH₃)₄]⁺ *fac*-[CoCl₃(NH₃)₃] *mer*-[CoCl₃(NH₃)₃]

Optical isomerism

Optical isomerism occurs when the mirror image of a compound is not superimposable with the original compound. It is so called because such isomers are optically active, that is, they rotate the plane of polarized light. The symbol Λ (*lambda*) is used as a prefix to describe the left-handed propeller twist formed by three bidentate ligands, as shown. Similarly, the symbol Δ (*delta*) is used as a prefix for the right-handed propeller twist.



Λ -[Fe(ox)₃]³⁻ Δ -[Fe(ox)₃]³⁻ Λ -*cis*-[CoCl₂(en)₂]⁺ Δ -*cis*-[CoCl₂(en)₂]⁺

Structural isomerism

Structural isomerism occurs when the bonds are themselves different. Linkage isomerism is only one of several types of structural isomerism in coordination complexes (as well as other classes of chemical compounds). Linkage isomerism occurs with ambidentate ligands which can bind in more than one place. For example, NO₂ is an ambidentate ligand: it can bind to a metal at either the N atom or at an O atom.

Chelation and its industrial importance:

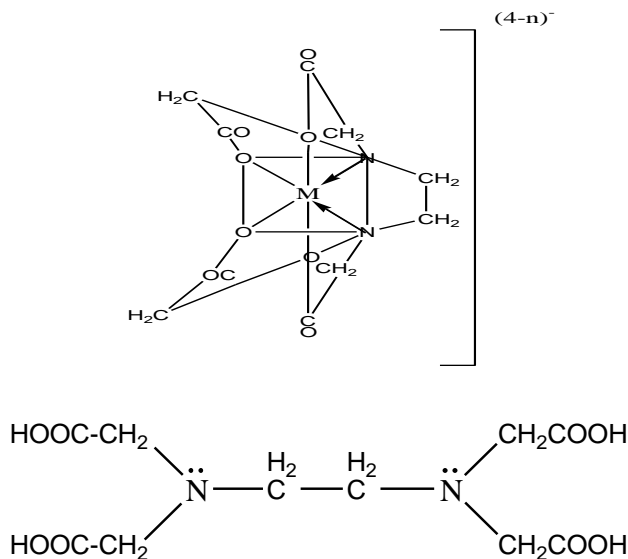
The presence of objectionable metal ions causes problems in many industries because of the adverse effects these can have on the quality of the product. These difficulties can be averted if the free metal ion concentration is considerably reduced. An effective way of achieving this is by the addition of suitable chelating agents which by complexing with the metal ion mask its characteristic reactions. The process by which a soluble complex of a metal is produced so that it is no longer precipitated by anions which form sparingly soluble salts with the free metal ion is known as *sequestration* (*Latin* sequester means to commit for safe keeping) and the reagents which bring this about are called *sequestering agents*.

Several tertiary amines that also contain carboxylic acid groups. i.e., the amino polycarboxylic acids (also known as complexones) form remarkably stable complexes with many metal ions. Their potential as sequestering agents was first recognised by *Schwarzenbach* in 1945, since that time they have been extensively investigated. The following are the name of few amino polycarboxylic acids:

- 1) Ethylene Diamine Tetra-Acetic acid (Abbreviated, EDTA)
- 2) Nitrilo Tri Acetic acid (abbreviated, NTA)
- 3) 1,2- diamino cyclohexane N,N',N' – tetra- acetic acid (DCTA)

Other related substances also have been investigated but have not been widely employed in industries. We shall confine our discussion to the application of EDTA.

Ethylenediaminetetra acetic acid (known by various trivial names as Trilon B, complexone II, versene, sequestrene and Chelaton -3) has the structure.



It has four acidic hydrogens and each nitrogen atom has an unshared pair of electrons. Thus, the molecule has six potential sites for bonding with a metal ion and may be considered to be a hexadentate ligand.

There is no doubt that EDTA has the widest general industrial application because of it's-

- (i) Relatively low price.
- (ii) High water solubility.
- (iii) Strain less five membered ring formations on Chelation.
- (iv) Hexadenticity, most frequently, matches with the coordination number of many metal ions.

The structure of metal-EDTA complex is given in the figure.

Some of their applications are given below:

- 1) One common application of EDTA is for the prevention or removal of scale in boilers.
- 2) Other uses of EDTA include-applications in laundry work, to eliminate harmful radio-active metals from the body, in medicine, dyeing etc.

- 3) Though EDTA is invariably a minor component of the detergent formulation, application of EDTA in the detergent industry include the following – liquid soap products, bar soaps, shampoos, wax removing floor cleaners and synthetic detergents.
- 4) *The very purpose of inverting EDTA is to shed more light on hardness in water.*

Limestone and other calcium minerals are among the most abundant minerals in the Earth's crust. Consequently, natural water invariably contains Ca^{2+} ions and frequently bicarbonate ions. Other ions often found in natural water include Mg^{2+} and Fe^{2+} . Natural water containing objectionable concentration of Ca^{2+} , Mg^{2+} and Fe^{2+} is called "HARD".

Two types of hardness are recognised: *Non carbonate, permanent hard water- Ca^{2+} , Mg^{2+} or Fe^{2+} ions as chlorides and sulphates. Water containing these metal ions and bicarbonates is called carbonate, temporary hard water.* Hardness is usually reported in parts per million (ppm) and is calculated as calcium carbonate.

Hard water is not suitable for drinking purposes, washing purposes and industrial purposes (in boilers).

Determination of hardness of water

The hardness of water can be determined in a number of ways: *Clark's method. Hehner's method and indicator method.*

The most recent indicator method makes use of titration of the water with EDTA and an indicator which changes colour when all the calcium and magnesium have reacted. The method is rapid convenient and accurate.

The usual procedure is to add 10 ml. of a buffer solution (pH 10), three drops of the indicator (Eriochrome Black T) to a 50 ml sample of water. Titration is carried out with the standard EDTA (1 ml = 1 mg CaCO_3). The end point is a colour change from wine red to blue.

The total hardness = ml. of reagent used x 20.

Illustration

50 ml. of hard water required 6.20 ml of EDTA which is equivalent to 6.20 mg of CaCO_3 .

$$1000 \text{ ml of water contains} = \frac{6.20 \times 1000}{50} = \mathbf{124 \text{ mg}}$$

Thus, the hardness is 124 ppm.

5) The analytical applications of EDTA are –

- (i) Use as a primary standard.
- (ii) The estimation of copper is steel.
- (iii) The determination of the number of anions.
- (iv) The extraction of beryllium free from aluminium.
- (v) The prevention of metal ions forming precipitation (*masking agent*).
- (vi) The estimation of (almost all) metal ions using complexometric titration.

Haemoglobin and Chlorophyll

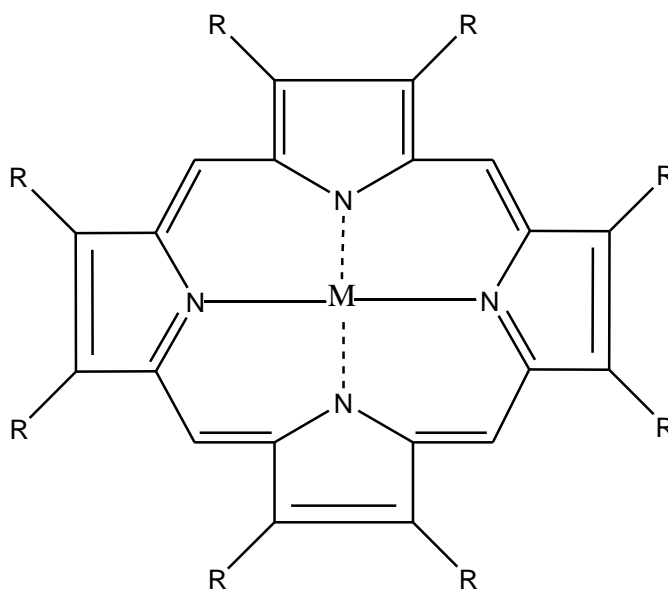
The inorganic constituents of biological system have been receiving increasing attention in recent years. The importance and the presence of metallic elements in living bodies (plants and animals) have been the keen interests to the chemists. It has been observed that the majority of the essential metallic elements are transition metals whose ability to form complexes is of the most characteristic aspects of their chemistry. Many metal complexes of biological macromolecules have been isolated *Haemoglobin*, *Chlorophyll*, *Myoglobin*, *haemocuprin*, *cyanocobalamin* (vitamin B_{12}) and *cytochrome-C*. We shall discuss haemoglobin and chlorophyll in detail.

Haemoglobin (also called Hemoglobin)

This is the most important agent for oxygen transport in living bodies. Though its primary function is to carry oxygen, it is also involved in the transport of CO_2 and with acid-base balance of the body. Hemoglobin takes up a large volume of oxygen in the lungs and carries it to the tissues.

Hemoglobin is the red matter that makes up about 95% of the dry weight of the red blood cell. Blood of a normal male contains about 15g, hemoglobin per 100 ml. of all of which is within the red blood cell. Haemoglobin contains 0.347% iron and its molecular weight is 64,458.

Hemoglobin is a *conjugated protein* whose prosthetic group is heme. Heme is associated with globin (a protein). Heme belongs to the class of metal-porphyrins. The basic frame work of all porphyrins is built of four pyrrole rings linked together in a larger ring like structure called *porphin*. By varying the substitution of eight hydrogen atom (shown by R on pyrrole rings) with different groups, the various porphyrins found in nature are produced. *Protoporphyrin IX* is found in heme.



Each hemoglobin molecule has four heme group bound to the globin on its surface. In each heme unit of hemoglobin, Fe (II) forms a four coordinated, square planar complex using four nitrogens of the protoporphyrin ring. The fifth coordination position of Fe (II) is occupied

by the imidazole nitrogen of histidine residue of the protein chain (globin) and the sixth position is occupied by a molecule of water (which is replaced by oxygen on oxygenation).

It has been investigated that hemoglobin can also form stable complexes with other ligands like NH_3 , amines, CN^- , CO, NO and in that these ligands compete with oxygen in *oxyhemoglobin*.

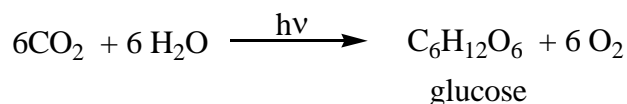
Hence, oxygenation is inhibited. The toxicity and highly poisonous character of these ligands have been thus explained.

CHLOROPHYLL

This is a green material found in plant and does not contain chlorine or any other halogen. The name derived, in part from its colour (Greek, chloros = light green), the remainder of the name is derived from a Greek term for leaf. Although we speak of chlorophyll in the singular, there are several different compounds called chlorophyll. Among them chlorophyll- α is the most abundant. This was first synthesized by Woodward in 1960.

Chlorophyll belongs to a class of compounds with power for transmission of energy. As heme serves the purpose of oxygen transport in the animal body, so does chlorophyll a porphyrin complex of Mg (II), perform the function of capturing light energy and transmitting it to a system for utilization in chemical reaction. This helps in the *photosynthesis*.

Photosynthesis is a complex sequence of processes in which solar energy is first absorbed and ultimately glucose is formed from carbon dioxide and water in the following way:



The characteristic property of chlorophyll, namely the capturing and transmitting light energy to system for chemical reaction may be attributed to the nature of Mg(II) complex. Evidently, magnesium ($1s^2, 2s^2, 2p^6, 3s^2$) is not a transition element and can form only stable sp^3 -hybridized tetrahedral complex. On the other hand, the porphyrin molecule by its rigid structure

holds the four donor nitrogen atoms in the same plane and thus forces any metal ion coordinating with it to assume a square planar structure (*Cf. hemoglobin*). Hence, the planar bonds to magnesium in chlorophyll must be in strained condition. The electrons constituting these bonds can therefore be readily excited by the absorption of light energy which may be re-emitted afterwards in the form of luminescence or transmitted to a system in a chemical reaction.

ANALYTICAL APPLICATION

I. Qualitative Analysis

- a) Ag(I) is separated from Hg_2Cl_2 and PbCl_2 in the qualitative analysis by dissolving it as $[\text{Ag}(\text{NH}_3)_2]^+$.
- b) Antimony, arsenic and tin sulphides are separated from the remaining II group sulphides since they dissolved in the presence of an excess sulphide ions as the complexes, SbS_4^{3-} , AsS_4^{3-} , SnS_3^{2-} .
- c) When in copper and cadmium salts solution, KCN is added in excess, both Cu and Cd form complexes- $\text{K}_3[\text{Cu}(\text{CN})_4]$ and $\text{K}_2[\text{Cd}(\text{CN})_4]$ respectively. These two complexes differ appreciably in their stability. When H_2S is passed in the aqueous solution of these two complexes, cadmium alone gets precipitated.
- d) Nickel, magnesium and aluminium ions are easily identified by the formation of highly coloured chelates in qualitative analysis.
- e) The most delicate reagent for the detection and estimation of nickel is dimethylglyoxime. This reagent reacts with nickel (II) ion in ammoniacal solution to yield a bright red, silky and bulky precipitate of the composition, $\text{Ni}(\text{dmg})_2$.

- f) Separation of zirconium and hafnium, which until recently was one of the most difficult analytical tasks, has been made simple by the use of chelates. The chelates of the two metals formed with theonyl trifluoroacetone possess different solubilities in benzene.

II. Quantitative Analysis

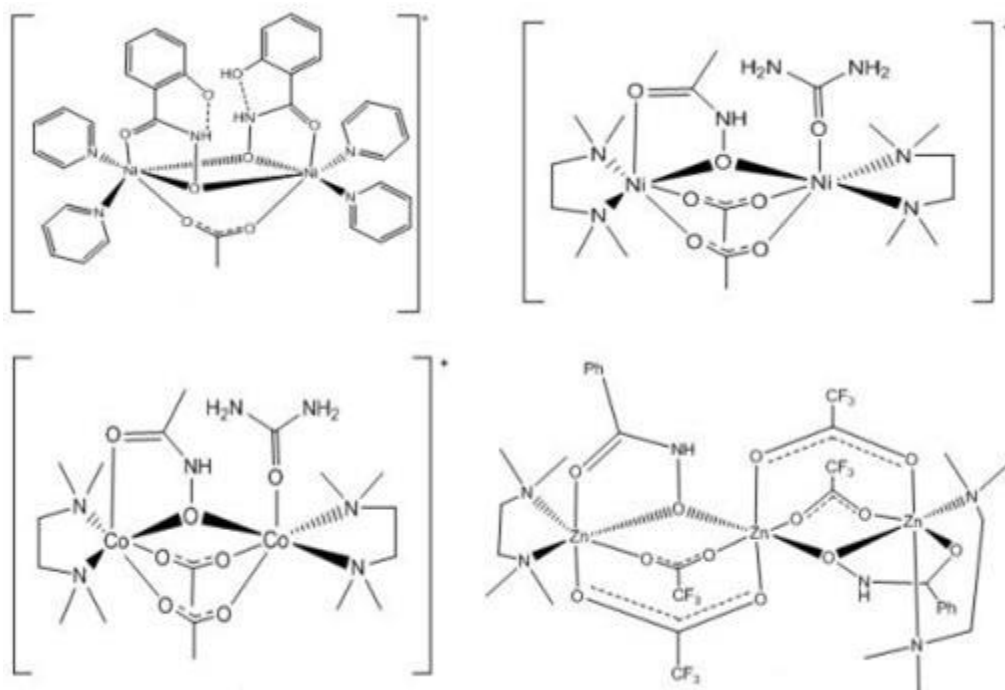
- a) Organic reagents which give insoluble complexes are widely used for the separation and determination of metals. The neutral complexes thus obtained can be used in gravimetric analysis to estimate metal ions. The high molecular weight of such complexes reduces the significance of weighing errors. By changing the conditions such as pH, the method can be used in the presence of other metal ions. One example is the red precipitate of $\text{Ni}(\text{dmg})_2$.
- b) Oxine (8- hydroxyquinoline) reacts with a large number of metal ions forming oxinates which are crystalline precipitates. Other notable example are cupferron, acetylacetone, 1,10-phenanthroline, α -benzoin oxime, dithiozone, anthranilic acid and thiourea.
- c) Many titration procedures now use EDTA in the determination of metals. These procedures usually involve competition for the metal between EDTA and a dye that can also serve as a ligand. Because EDTA tends to form chelates with most cations, it would appear at first glance to be totally lacking in specificity. In fact, however considerable control over the behavior of EDTA, as well as other chelating agents, can be achieved through pH regulation. Thus, for example, it is generally possible to determine trivalent cations without the interference from divalent species by performing the titration in a medium having a pH of about 1.
- d) One of the common reduction–oxidation (redox) indicators, ferroin, is a complex. It contains the $[\text{Fe}(\text{o-phen})_3]^{2+}$ ion, which is deep red, while Fe(III) compound is

pale blue. In a suitable oxidation-reduction titration, the removal of the colour of the ferroin is an indication that the end point has been reached. The ferroin is oxidized only after the reducing agent being titrated is completely oxidized.

Polynuclear complexes

Homometallic complexes:

There are two classes of homometallic dinuclear hydroxamate/imide complexes, one class features an O-hydroxamate/imide atom μ -bridging between the metal ions the other class includes dihydroxamic ligands which coordinate in an O,O'- bidentate fashion to isolated metal ions. For example, $[\text{Ni}_2(\text{shiH})(\text{shiH}_2)(\text{py})_4(\text{OAc})]$ belongs to the first class and comprises of two shiH₃- derived ligands that bridge the two Ni(II) ions via HN-O(1-) groups, this complex is extraordinarily similar to the structure of urease, which is a dinuclear Ni(II)- containing enzyme.

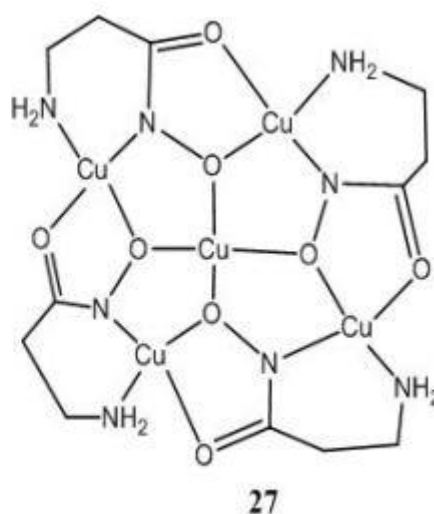
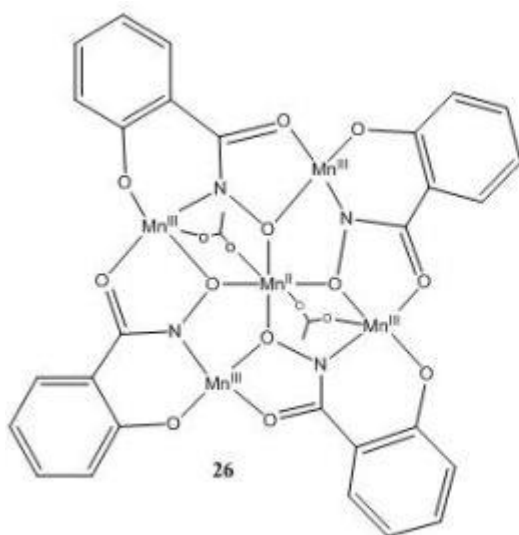


Two dinuclear Co(II) complexes have been reported with one or two bridging ahaH(1-) ligands. It was yielded by reacting the dinuclear complex $[\text{Co}_2(\mu\text{-H}_2\text{O})(\mu\text{-OAc})_2(\text{tmen})_2]$ and ahaH₂, when the starting material contained trifluoroacetic ligands rather than acetate ligands, the

reaction yielded a novel trinuclear complexes. For example, the trinuclear Zn(II) complex, $[\text{Zn}_3(\text{tfAcO})_4(\text{tmen})_2(\text{bhaH}_2)]$, which features two tmen ligands that cap the outer Zn(II) ions and two pairs of trifluoroacetic ligands that bridge the central Zn ion to the outer Zn ions. The two bhaH (1-) ligands form μ -O-bridging ligands between a pair of Zn(II) ions similar to that in dinuclear complexes.

Metallacrowns:

Hydroxamic acids can form polynuclear metal-ligand clusters, known as metallacrowns, which are analogues of crown ethers. Mn metallacrowns complexes formed with shiH₃, feature a 12-metallacrown -4 [12-MC-4] core structure and a central Mn(II) ion, which is situated above the metallacrowns plane (1.20Å) (Fig. 8, **26**). Each shiH₃ ligand is triply deprotonated with the hydroximato ligand chelating to one Mn(III) ion, as well as, the N atom and the phenolato O atom of the same shi(3-) ligand are coordinated to an adjacent Mn(III) ion.



The first Cu(II) [12-MC-4] complex characterised (**27**) shows β -alanine acting as a tridentate chelate, via the hydroximato group and the amine group. β -Aminohydroxamic acids form [12-MC-4] systems with fused 5- and 6- membered rings, whereas α -amino hydroxamic acid form 15-metallacrown-5 systems ([15-MC-5]), which creates a larger cavity size and are tuned towards the encapsulation of larger ions, for example, Gd(III) and Eu(III).

UNIT II

POSSIBLE QUESTIONS

PART A – Objective type questions (Each carry 1 mark)

- Among the following which is known as the chelating agent
a. NH_3 **b. DMG** c. Cl d. ONO
- Chelate effect is known as
a. Stability of complexes containing chelating ligands b. complexes containing chelate rings c. Size of the coordination complex d. Mass of the coordination complex
- Stability of the coordination complex is measured by the value of
a. $\text{Log } \beta$ b. $\text{Log } \alpha$ c. μ d. α
- Exchange of co-ordination group by a water molecule in complex molecule results in
a. Ionisation isomerism b. Ligand isomerism
c. Hydration isomerism d. Geometrical isomerism
- Haemoglobin is a
a. Cobalt complex b. Copper complex c. Iron complex **d. Porphyrin complex**
- The hybridization of Square planar symmetries is
a. sp b. sp^2 c. sp^3 **d. dsp^2**
- Chelation is defined as the process of formation of
a. Coordination complex b. Coordination compound c. Complex ion **d. Chelate**
- Which of the following exhibits Geometrical isomerism
a. $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ **b. $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$** c. $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^+$ d. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- What is the oxidation number of central metal atom in $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$

- a. **3** b. 2 c. 1 d. 4
10. What is the coordination number of platinum in $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
a. 3 b. 2 c. 1 **d. 4**
11. Charge of the coordination sphere in $\text{K}_4[\text{Cu}(\text{CN})_6]$ is
a. -4 b. -6 c. -3 d. -2
12. Among the following which is known as a neutral ligand
a. NH_3 b. ONO c. Cl d. CN
13. Which of the following exhibits Geometrical isomerism
a. $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ **b. $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$** c. $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^+$ d. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
14. The number of unpaired electrons in NiCl_4^{2-} is
a. two b. zero c. one d. four
15. Which of the following does not show optical isomerism?
 $[\text{Cr}(\text{ox})_3]^{3-}$ b. $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ **c. trans $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$** d. $[\text{Co}(\text{EDTA})]^-$
16. The IUPAC name of $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ is
a. Sodium trioxalatoferrate (III) b. Sodium trioxalatoiron(III)
c. Sodium tri(oxalate)ferrate (III) d. Sodium tri(oxalate)iron(III)
17. According to CFT, in the octahedral complexes the d orbital splits into
a. Lower t_{2g} and higher e_g level b. Lower t_{2g} and higher u_g level
c. Higher t_{2g} and lower e_g level d. Lower d_{2g} and higher e_g level
18. Which of the following complex ions is tetrahedral?
a. $[\text{PdCl}_4]^{2-}$ b. $[\text{PtCl}_4]^{2-}$ **c. $[\text{NiCl}_4]^{2-}$** d. $[\text{AuCl}_4]^-$
19. The s orbitals of the ligands are usually?
a. Too high in energy b. Low energy c. High energy **d. too low in energy**
20. The force of attraction between paramagnetic complexes and a magnetic field is proportional to the number of?
a. Paired electrons **b. unpaired electrons** c. Charged electrons d. uncharged electrons

PART B (Each carry 2 marks)

1. What are ligands? Give five examples of ligand.
2. Define coordination compound.
3. What are chelates? Give one example.
4. What are linkage isomers? Give one example.
5. Define labile complex. Give one example.
6. Define inert complex. Give one example.
7. What are the oxidation states and coordination numbers of the metal ions in the following.
(a) $K_4[Ni(CN)_4]$ (b) $[Co(en)_3]_2(SO_4)_3$
8. Write the formula of the following complex.
(a) Sodium dicyanoaurate (I)
(b) Pentaammine nitro cobalt (II) chloride
9. Write the names of the following.
(a) $K_4[Ni(CO)_4]$ (b) $K [BF_4]$
10. Define polynuclear complexes. Give an example.

PART C (Each carry 6 marks)

1. Write the Formula of the following
 - (i) Bis(Acetylacetonate) copper(II)
 - (ii) Sodium dicyanoaurate (I)
 - (iii) Hexaquaairon(II)sulphate
 - (iv) Potassium tetracyanonickelate(0)
 - (v) Tris(ethylenediamine)cobalt(III) sulphate
 - (vi) Tetraammineaquabromo cobalt(III) nitrate
2. Name the different kinds of structural isomers in coordination compounds.

3. Discuss the geometrical isomerism in compound with coordination number 4.
4. Write the rules for naming the coordination compound.
5. Describe labile and inert complexes. Explain the factors affecting the inertness of complexes.
6. Discuss the geometrical isomerism in compound with coordination number 6.
7. Write the IUPAC names, Coordination number, Oxidation state and geometry of the following.
 - (a) $[\text{Pt}(\text{NH}_3)][\text{CoCl}_4]$
 - (b) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
 - (c) $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{SO}_4$

[16CHU302]

Batch: 2016-2019

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY

INORGANIC CHEMISTRY-II (Coordination Chemistry)

Semester –III

Multiple Choice Questions for on line examination (Each question carry one mark)
UNIT II

S. No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	Stability of a complex does not depend upon	nature of the central metal ion	Number of chelate rings	steric effects	mass of the complex	mass of the complex
2	Maximum value of $\log \beta$ is that of	AgI	AgCl	AgBr	AgF	AgI
3	What is the coordination number of platinum in $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	3	2	1	4	4
4	What is the oxidation number of central metal atom in $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$	3	2	1	4	3
5	Among the following which is known as a neutral ligand	NH_3	ONO	Cl	CN	NH_3
6	Among the following which is known as	NH_3	H_2O	CO	CN	CN

	negative ligand					
7	Which of the following exhibits Geometrical isomerism	$[\text{Cr}(\text{en})_2\text{Cl}_2]^+$	$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^+$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
8	Which of the following does not show optical isomerism?	$[\text{Cr}(\text{ox})_3]^{3-}$	$[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$	trans $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	$[\text{Co}(\text{EDTA})]^-$	trans $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
9	The IUPAC name of $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ is	Sodium trioxalatoferrate (III)	Sodium trioxalatoiron(III)	Sodium tri(oxalate)ferrate (III)	Sodium tri(oxalate)iron(II)	Sodium trioxalatoferrate (III)
10	Which of the following ligand is bidentate?	EDTA	Ethylenediamine	Acetato	Pyridine	Ethylenediamine
11	The number of ions per mole of the complex $\text{CoCl}_3 \cdot 5\text{NH}_3$ in aqueous solution will be	Three	Four	Nine	Two	Three
12	Which factor does not affect the labile and inertness of the complex	Size of the central metal ion	Charge on the central metal ion	d-electron configuration	Geometry of the complex	Geometry of the complex
13	Which of the following has lowest oxidation state of central atom?	$\text{Na}_3[\text{Fe}(\text{CN})_6]$	$\text{Na}[\text{Co}(\text{CO})_4]$	$\text{Fe}(\text{CO})_5$	$[\text{Co}(\text{en})_3]\text{Cl}_3$	$\text{Na}[\text{Co}(\text{CO})_4]$
14	The complexes $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ are examples of	Geometrical isomerism	Coordination isomerism	Linkage isomerism	Position isomerism	Linkage isomerism
15	The formula of the complex tris(ethylene diamine)cobalt (III) sulphate is	$[\text{Co}(\text{en})_3]\text{SO}_4$	$[\text{Co}(\text{en})_3]_2\text{SO}_4$	$[\text{Co}(\text{en})_3\text{SO}_4]$	$[\text{Co}(\text{en})_3]_2(\text{SO}_4)_2$	$[\text{Co}(\text{en})_3]_2(\text{SO}_4)_2$
16	The IUPAC name of $\text{K}_4[\text{Ni}(\text{CN})_4]$ is	Potassium tetracyanonickel (III)	Potassium tetracyanonickel(II)	Potassium tetracyanonickelate(0)	Potassium tetracyanonickelate(IV)	Potassium tetracyanonickelate(0)
17	The IUPAC name of $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ is	Hexaammine platinum(IV)	Hexaammine platinum(II)	Hexaammine platinate(IV)	Hexaammine platinate(0)	Hexaammine platinum(IV)

		Chloride	Chloride	Chloride	Chloride	Chloride
18	The IUPAC name of $K_4[Fe(CN)_6]$ is	Potassium hexacyanoferrate (III)	Potassium ferrocyanide	Potassium hexacyanoiron(III)	Potassium hexacyanoferrate (II)	Potassium hexacyanoferrate (II)
19	If a ligand is attached to the central metal atom only by one coordination bond then the ligand is called as	Monodentate ligand	Bidentate ligand	Tridentate ligand	Tetra dentate ligand	Monodentate ligand
20	If a ligand is attached to the central metal atom by two coordination bond then the ligand is called as	Monodentate ligand	Bidentate ligand	Tridentate ligand	Tetra dentate ligand	Bidentate ligand
21	If a ligand is attached to the central metal atom by three coordination bond then the ligand is called as	Monodentate ligand	Bidentate ligand	Tridentate ligand	Tetra dentate ligand	Tridentate ligand
22	Chelation is defined as the process of formation of	Coordination complex	Coordination compound	Complex ion	Chelate	Chelate
23	Among the following which is known as the chelating agent	NH_3	CN	Cl	ONO	DMG
24	Chelate effect is known as	Stability of complexes containing chelating ligands	complexes containing chelate rings	Size of the coordination complex	Mass of the coordination complex	Stability of complexes containing chelating ligands
25	Stability of the coordination complex is measured by the value of	$\log \beta$	$\log \alpha$	μ	α	$\log \beta$
26	Vitamin B_{12} chelate is a	Cobalt complex	Copper complex	Iron complex	Porphyrin complex	Cobalt complex
27	Haemoglobin is a	Cobalt complex	Copper complex	Iron complex	Porphyrin complex	Porphyrin complex
28	Chlorophyll is a	Cobalt	Copper complex	Iron complex	Magnesium	Magnesium

		complex			Porphyrin complex	Porphyrin complex
29	Among the following which ligand is used in the determination of hardness of water	EDTA	Acetato	Carbanato	Sulphato	EDTA
30	What is the coordination number of the Au atom in $K[Au(CN)_2(SCN)_2]$?	5	4	3	6	4
31	The hybridization of Square planar symmetries is -----	sp	sp^2	sp^3	dsp^2	dsp^2
32	Potash Alum is an example for	Simple Salt	Ligand	Co ordination compounds	Lattice Compounds	Lattice Compounds
33	Polydentate ligands in which two are more donar atoms are attached with the same metal ion and produce rings are called -----	Briged ligand	Chelating ligand	Flexidentate ligand	Ambidentate ligand	Chelating ligand
34	The number of ions per mole of the complex $CoCl_3.6NH_3$ in aqueous solution will be	9	2	4	3	4
35	The number of ions per mole of the complex $CoCl_3.4NH_3$ in aqueous solution will be	7	3	2	1	2
36	The number of ions per mole of the complex $CoCl_3.3NH_3$ in aqueous solution will be	6	0	4	2	0
37	IUPAC name of $[Co(en)_2Br_2]Cl$ is	Dibromo bis(ethylenedia mine cobalt(III) chloride	Bis(ethylenedia mine dibromo cobalt(III) chloride	Dibromo bis(ethylenediami ne cobalt(II) chloride	Bis(ethylenedia mine dibromo cobalt(II) chloride	Dibromo bis(ethylenedia mine cobalt(III) chloride
38	Oxidation state of $K_4[Cu(CN)_6]$	4	3	2	1	2

39	Among the following which one is a positive ligand	imido	pyridine	nitronium	thio	nitronium
40	Charge of the coordination sphere in $K_4[Cu(CN)_6]$ is	-4	-6	-3	-2	-4
41	Coordination number of copper in $K_4[Cu(CN)_6]$ is	5	3	4	6	6
42	Coordination number of cobalt in $[Co(NH_3)_5(ONO)]Cl_2$ is	5	3	6	4	6
43	Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is	1	2	3	4	4
44	Which compound is zero valent metal complex?	$[Cu(NH_3)_4]SO_4$	$[Pt(NH_3)_2Cl_2]$	$[Ni(CO)_4]$	$K_3[Fe(CN)_6]$	$[Ni(CO)_4]$
45	Which complex can not ionize in solution?	$[Pt(NH_3)_6]Cl_4$	$K_2[Pt(F_6)]$	$K_4[Fe(CN)_6]$	$[CoCl_3(NH_3)_3]$	$[CoCl_3(NH_3)_3]$
46	The pair of compounds having metals in their highest oxidation state is	MnO_2 , $FeCl_3$	$[MnO_4]^-$, CrO_2Cl_2	$[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$	$[NiCl_4]^{2-}$, $[CoCl_4]^-$	$[MnO_4]^-$, CrO_2Cl_2
47	Which one of the following is the correct electron configuration for the Fe^{3+} ion?	$[Ar] 4s^1 3d^5$	$[Ar] 3d^5$	$[Ar] 4s^2 3d^3$	$[Ar] 3d^6$	$[Ar] 3d^5$
48	Exchange of co-ordination group by a water molecule in complex molecule results in	Ionisation isomerism	Ligand isomerism	Hydration isomerism	Geometrical isomerism	Hydration isomerism
49	Which of the following compounds can exhibit cis-trans isomerism?	$[Fe(CO)_5NO_2]^{2+}$	$[Cu(CO)_5Cl]^{+D}$	$[MnClBr_3]^{2-}$	$[Ni(CO)_2(NH_3)_2]^{2+}$	$[Ni(CO)_2(NH_3)_2]^{2+}$
50	Which of the following square planar complex ions can have cis-trans isomers?	$[Pt(NH_3)_4]^{2+}$	$[Ni(NH_3)_4]^{2+}$	$[Pt(NH_3)_2Cl_2]$	$[Pt(NH_3)Cl_3]^-$	$[Pt(NH_3)_2Cl_2]$
51	Which one of the following has an optical isomer? (en = ethylenediamine)	$[Zn(en)(NH_3)_2]^{2+}$	$[Co(en)_3]^{3+}$	$[Co(H_2O)_4(en)]^{3+}$	$[Zn(en)_2]^{2+}$	$[Co(en)_3]^{3+}$
52	Which one of the following compounds will exhibit linkage isomerism	$[Pt(NH_3)_2Cl_2]$	$[Co(NH_3)_5NO_2]Cl_2$	$[Co(NH_3)_4Cl_2]NO_2$	$[Ag(NH_3)_2]NO_2$	$[Co(NH_3)_5NO_2]Cl_2$

53	The IUPAC name for the complex $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ is	nitrito-N-pentaamminecobalt (III) chloride	nitrito-N-pentaamminecobalt (II) chloride	pentaamminenitrito-N-cobalt (II) chloride	pentaamminenitrito-N-cobalt (III) chloride	pentaamminenitrito-N-cobalt (III) chloride
54	Oxidation state of cobalt in $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ is	2	4	3	1	3
55	Coordination number of cobalt in $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ is	5	6	7	4	6
56	If the complex having the 6 coordination number, its geometry is	Octahedral	Square planar	Tetrahedral	Tetragonal	Octahedral
57	If the complex having d-block as the central atom and the 4 coordination number, its geometry is	Octahedral	Square planar	Tetrahedral	Tetragonal	Square planar
58	Write the formula for the coordination compound, Potassium hexacyanoferrate (III)	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{K}_4[\text{Fe}(\text{CN})_5\text{Cl}]$	$\text{K}[\text{Fe}(\text{CN})_5\text{Cl}]$	$\text{K}[\text{Fe}(\text{CN})_6]$	$\text{K}_3[\text{Fe}(\text{CN})_6]$
59	Charge of the sphere in $\text{K}_3[\text{Fe}(\text{CN})_6]$ is	-2	-3	-4	-6	-3
60	Coordination number of Iron in $\text{K}_3[\text{Fe}(\text{CN})_6]$ is	5	4	6	3	6

UNIT-III

Transition Elements

General group trends with special reference to electronic configuration, colour, variable valency, magnetic and catalytic properties, ability to form complexes. Stability of various oxidation states and e.m.f. (Latimer diagrams) Different between the first, second and third transition series. Chemistry of Cr, Mn, Fe and Co in various oxidation states with special reference to the following compounds: peroxo compounds of chromium, potassium dichromate, potassium permanganate, potassium ferrocyanide, potassium ferricyanide, sodium nitroprusside and sodium cobalt nitrite.

Introduction

The elements belonging to 3 to 12 group, present in the center of the periodic table are called transition metals. These are actually d- block metals and form a bridge in between the s and p block elements, the metals and non metals. The transition metals are unique among the chemical elements. The elements in which the last electron enters the d- sub shell of their penultimate shell (n-1 shell) are known as d- block elements.

Thus, transition metals can be broadly defined as those which either as elements or as ions have partially filled d-sub shell. Since d-sub shell is partially filled, the elements are called as d- block elements.

The transition metals are classified into four transition series. Each series (Except 6d) consists of 10 elements. (This is because the d- sub-shell can occupy only 10 electrons and they get filled up when we move along a period in a series.)

First Transition Series

It is a part of the fourth period and consists of 10 elements from Scandium (At no: 21) to zinc (at no 30) in which 3d - sub-shells are progressively filled. This is also called as 3d series which corresponds to the filling of the 3d orbital.

Element	Atomic number	Symbol	Electronic configuration
Scandium	21	Sc	[Ar] 3d ¹ 4s ²
Titanium	22	Ti	[Ar] 3d ² 4s ²
Vanadium	23	V	[Ar] 3d ³ 4s ²
Chromium	24	Cr	[Ar] 3d ⁵ 4s ¹
Manganese	25	Mn	[Ar] 3d ⁵ 4s ²
Iron	26	Fe	[Ar] 3d ⁶ 4s ²
Cobalt	27	Co	[Ar] 3d ⁷ 4s ²
Nickel	28	Ni	[Ar] 3d ⁸ 4s ²
Copper	29	Cu	[Ar] 3d ¹⁰ 4s ¹
Zinc	30	Zn	[Ar] 3d ¹⁰ 4s ²

Second Transition Series

Second transition series is a part of the fifth period and consists of 10 elements from Yttrium (At no: 39) to cadmium (At no: 48) in which 4d- sub-shells are being progressively filled. This is also called 4d series which corresponds to the filling of the 4d orbital.

Element	Atomic Number	Symbol	Electronic configuration
Yttrium	39	Y	[Kr] 4d ¹ 5s ²
Zirconium	40	Zr	[Kr] 4d ² 5s ²
Niobium	41	Nb	[Kr] 4d ⁴ 5s ¹
Molybdenum	42	Mo	[Kr] 4d ⁵ 5s ¹
Technetium	43	Tc	[Kr] 4d ⁵ 5s ²
Ruthenium	44	Ru	[Kr] 4d ⁷ 5s ¹
Rhodium	45	Rh	[Kr] 4d ⁸ 5s ¹
Palladium	46	Pd	[Kr] 4d ¹⁰ 5s ⁰
Silver	47	Ag	[Kr] 4d ¹⁰ 5s ¹
Cadmium	48	Cd	[Kr] 4d ¹⁰ 5s ²

Third Transition Series

It is a part of the sixth period and consists of 10 elements from Lanthanum (At no: 57) and Hafnium (At no: 72) to Mercury (At no: 80) in which the 5d sub-shell is progressively filled. This is also called as 5d series which corresponds with the filling of 5d orbital.

Element	Atomic number	Symbol	Electronic configuration
Lanthanum	57	La	[Xe] 5d ¹ 6s ²
Hafnium	72	Hf	[Xe] 4f ¹⁴ 5d ² 6s ²
Tantalum	73	Ta	[Xe] 4f ¹⁴ 5d ³ 6s ²
Tungsten	74	W	[Xe] 4f ¹⁴ 5d ⁴ 6s ²
Rhenium	75	Re	[Xe] 4f ¹⁴ 5d ⁵ 6s ²
Osmium	76	Os	[Xe] 4f ¹⁴ 5d ⁶ 6s ²
Iridium	77	Ir	[Xe] 4f ¹⁴ 5d ⁷ 6s ²
Platinum	78	Pt	[Xe] 4f ¹⁴ 5d ⁹ 6s ¹
Gold	79	Au	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
Mercury	80	Hg	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²

Fourth Transition Series

It is a part of the seventh period and is an incomplete series starting from actinium (At no: 89) in which 6d sub-shell is being progressively filled. This is also called as 6d series which corresponds with the filling of 6d orbitals. This series contains only 3 elements. They are actinium with atomic number 89 followed by two elements with atomic numbers 104 and 105.

Element	Atomic No	Symbol	Electronic configuration
Actinium	89	Ac	[Rn] 6d ¹ 7s ²

Transition metal charges

The valence electrons of transition metals are responsible for the charges that these metals carry or show and has been explained below. **The valence or the electrons in the**

ultimate shell enter the 'd' orbital. The first element in each series starts with one valence electron or 'd' electron and the last element will have 10 'd' electrons. Variable oxidation state or variable valency is one of the most striking features of the transition elements. All transition elements, except the first and last member of each series exhibit variable valency, related to its electronic structure. These elements lose both the 's' and the 'd' electrons and thus have a lot of valencies. Consequently, all transition elements in general exhibit variable valencies. Valencies of first transition series are

Element	Oxidation state/valency
Sc	+2, +3
Ti	+2, +3, +4
V	+2, +3, +4, +5
Cr	+1 to +6 (+4 and +5 are unstable)
Mn	+2 to +6 (+4, +5 and +6 are unstable)
Fe	+2 to +6 (+4, +5 and +6 are unstable)
Co	+2 to +6 (+4 is unstable)
Ni	+2, +3, +4
Cu	+1, +2
Zn	+2

Characteristics of Transition Metals

The transition metals properties are described as follows. Transition elements have partly filled d- orbitals. These elements show several interesting properties like variable oxidation state or variable valency, formation of colored complexes and paramagnetic behavior. These metals and their compounds also exhibit catalytic properties.

Some of the important properties of transition metals are

1. Electronic Configuration

The electronic configuration of transition elements may in general be represented as

(n-1) d¹⁻¹⁰ ns^{1 or 2}

The (n-1) means penultimate or next to the outermost shell and d- orbital may have 1 to 10 electrons and the s- orbital of the outermost shell (n) may have 1 or 2 electrons. The electronic configurations of all the four series of elements are given in a table above.

2. Atomic and ionic radii

The atomic and ionic radii of the elements of a particular transition series decreases from left to right. In the first series, the atomic radii become almost constant for chromium, because of two factors-Increase in nuclear charge and increase in the screening effect which just balance each other.

Atomic radii of Chromium is - 117pm. Mn, the next element has an atomic radii of 117 pm. The next three elements, Co, Ni and Cu has 116. 115 and 117 respectively. To summarize, atomic and ionic radii decrease with increase in atomic number, due to increase in nuclear charge.

3. Magnetic Properties

Magnetic character is of two types.

- Paramagnetic
- Diamagnetic

Those which are attracted by the magnetic field are termed as paramagnetic and those repelled by the magnetic field are diamagnetic. Transition elements and their compounds are paramagnetic in nature, they conduct electricity.

Paramagnetism is due to the presence of **unpaired electrons** in the d- orbitals of the transition metal atoms, ions or molecules. The greater the number of unpaired electrons, the greater will be its magnetic behavior. So, all transition metals with at least one unpaired electron are paramagnetic.

4. Color

Most d- block compounds are colored in the solid or in solution states. The color of the transition metal ions is due to the presence of unpaired or incomplete (n-1) d orbitals and the ability to promote an electron from one energy level to another. In these ions d- electrons are promoted to the higher energy levels within the same d- sub-shell. The color exhibited depends upon the complementary color of light observed by these ions.

Colors of some transition metals are

Ions	Color observed
Fe^{2+}	Green
Ni^{2+}	Green
Cu^{2+}	Blue
Fe^{3+}	Yellow
Mn^{2+}	Pink

5. Complex formation

Complex formation or complexation is a typical behavior of transition metals. In these complex compounds, the transition metal ions form co-ordinate bonds with a number of neutral or negatively charged ions which are capable of donating electrons to the metal atom.

A few examples are $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, etc.

6. Catalytic behavior

Most of the transition elements and their compounds are good catalysts. Platinum, cobalt, nickel, chromium, manganese, vanadium pent-oxide, etc are good examples. They are used as catalysts since they have incomplete d- orbitals and can form unstable intermediates which can then change into products.

Transition Metals

- Inner transition elements are also called as f- block elements. The elements in these group are present below the main table and contains two series.
- The first series is called as Lanthanoid series and starts from Cerium (Ce atomic number - 58) to Lutetium (Lu atomic number- 71). There are totally 14 elements in this series.
- The second series is called the actinoid series. This series also contains 14 elements from Thorium (Th - 90) to Lawrencium (Lr- 103).
- Most of the actinoids are radioactive isotopes, and do not occur in nature. They are the result of a radioactive decay and thus are not stable.

THE COLOURS OF COMPLEX METAL IONS

This page is going to take a simple look at the origin of colour in complex ions - in particular, why so many transition metal ions are coloured. Be aware that this is only an introduction to what can grow into an extremely complicated topic.

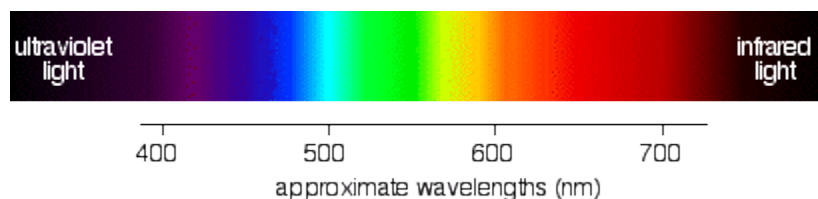
Why do we see some compounds as being coloured?

White light

You will know, of course, that if you pass white light through a prism it splits into all the colours of the rainbow. Visible light is simply a small part of an electromagnetic spectrum most of which we can't see - gamma rays, X-rays, infra-red, radio waves and so on.

Each of these has a particular wavelength, ranging from 10^{-16} metres for gamma rays to several hundred metres for radio waves. Visible light has wavelengths from about 400 to 750 nm. (1 nanometre = 10^{-9} metres.)

The diagram shows an approximation to the spectrum of visible light.



Zinc with the electronic structure $[\text{Ar}] 3d^{10}4s^2$ doesn't count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level.

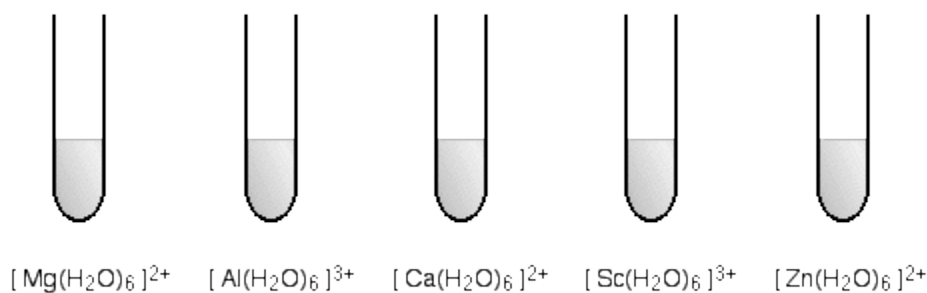
At the other end of the row, scandium ($[\text{Ar}] 3d^14s^2$) doesn't really count as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons.

The Sc^{3+} ion doesn't count as a transition metal ion because its 3d level is empty.

Some sample colours

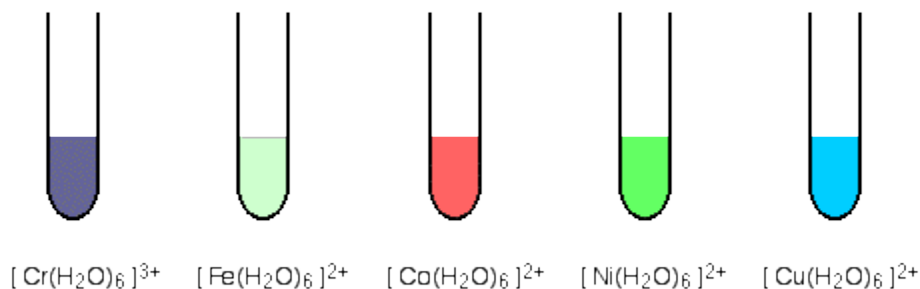
The diagrams show the approximate colours of some typical hexaaqua metal ions, with the formula $[\text{M}(\text{H}_2\text{O})_6]^{n+}$. The charge on these ions is typically 2+ or 3+.

Non-transition metal ions



These ions are all colourless. (Sorry, I can't do genuinely colourless!)

Transition metal ions



The corresponding transition metal ions are coloured. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly coloured - but they *are* coloured.

So . . . what causes transition metal ions to absorb wavelengths from visible light (causing colour) whereas non-transition metal ions don't? And why does the colour vary so much from ion to ion?

The origin of colour in complex ions containing transition metals

Complex ions containing transition metals are usually coloured, whereas the similar ions from non-transition metals aren't. That suggests that the partly filled d orbitals must be involved in generating the colour in some way. Remember that transition metals are defined as having partly filled d orbitals.

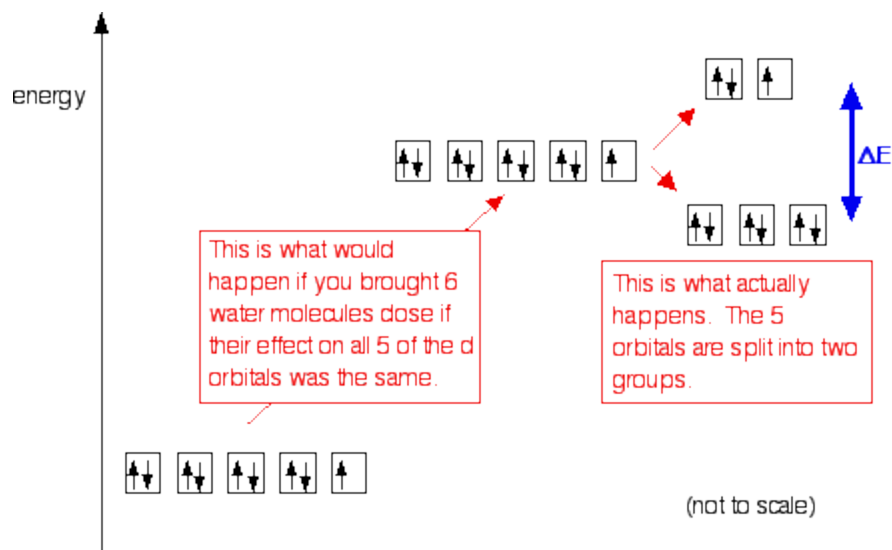
Octahedral complexes

For simplicity we are going to look at the octahedral complexes which have six simple ligands arranged around the central metal ion. The argument isn't really any different if you have multidentate ligands - it's just slightly more difficult to imagine!

When the ligands bond with the transition metal ion, there is repulsion between the electrons in the ligands and the electrons in the d orbitals of the metal ion. That raises the energy of the d orbitals.

However, because of the way the d orbitals are arranged in space, it doesn't raise all their energies by the same amount. Instead, it splits them into two groups.

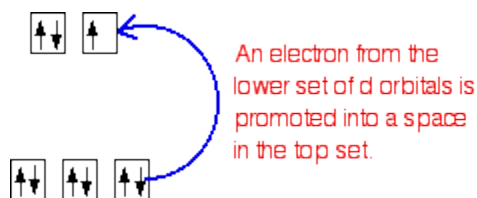
The diagram shows the arrangement of the d electrons in a Cu^{2+} ion before and after six water molecules bond with it.



Whenever 6 ligands are arranged around a transition metal ion, the d orbitals are always split into 2 groups in this way - 2 with a higher energy than the other 3.

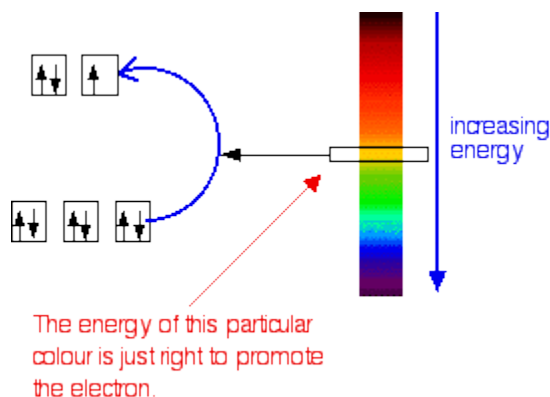
The size of the energy gap between them (shown by the blue arrows on the diagram) varies with the nature of the transition metal ion, its oxidation state (whether it is 3+ or 2+, for example), and the nature of the ligands.

When white light is passed through a solution of this ion, some of the energy in the light is used to promote an electron from the lower set of orbitals into a space in the upper set.



Each wavelength of light has a particular energy associated with it. Red light has the lowest energy in the visible region. Violet light has the greatest energy.

Suppose that the energy gap in the d orbitals of the complex ion corresponded to the energy of yellow light.



The yellow light would be absorbed because its energy would be used in promoting the electron. That leaves the other colours.

Your eye would see the light passing through as a dark blue, because blue is the complementary colour of yellow.

What about non-transition metal complex ions?

Non-transition metals don't have partly filled d orbitals. Visible light is only absorbed if some energy from the light is used to promote an electron over exactly the right energy gap. Non-transition metals don't have any electron transitions which can absorb wavelengths from visible light.

For example, although scandium is a member of the d block, its ion (Sc^{3+}) hasn't got any d electrons left to move around. This is no different from an ion based on Mg^{2+} or Al^{3+} . Scandium(III) complexes are colourless because no visible light is absorbed.

In the zinc case, the 3d level is completely full - there aren't any gaps to promote an electron in to. Zinc complexes are also colourless.

Tetrahedral complexes

Simple tetrahedral complexes have four ligands arranged around the central metal ion. Again the ligands have an effect on the energy of the d electrons in the metal ion. This time, of course, the ligands are arranged differently in space relative to the shapes of the d orbitals.

The net effect is that when the d orbitals split into two groups, three of them have a greater

energy, and the other two a lesser energy (the opposite of the arrangement in an octahedral complex).

Apart from this difference of detail, the explanation for the origin of colour in terms of the absorption of particular wavelengths of light is exactly the same as for octahedral complexes.

The factors affecting the colour of a transition metal complex ion

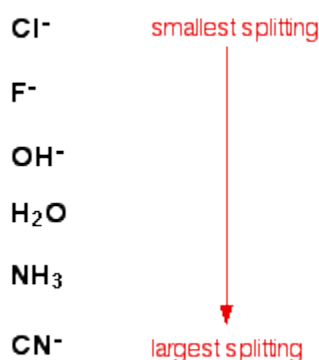
In each case we are going to choose a particular metal ion for the centre of the complex, and change other factors. Colour changes in a fairly haphazard way from metal to metal across a transition series.

The nature of the ligand

Different ligands have different effects on the energies of the d orbitals of the central ion. Some ligands have strong electrical fields which cause a large energy gap when the d orbitals split into two groups. Others have much weaker fields producing much smaller gaps.

Remember that the size of the gap determines what wavelength of light is going to get absorbed.

The list shows some common ligands. Those at the top produce the smallest splitting; those at the bottom the largest splitting.



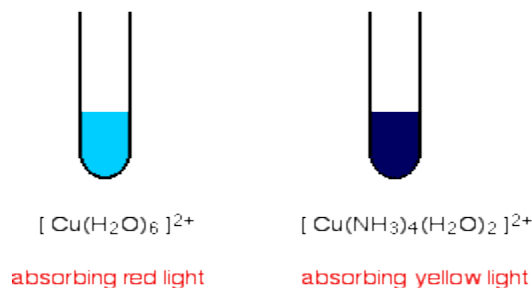
The greater the splitting, the more energy is needed to promote an electron from the lower group of orbitals to the higher ones. In terms of the colour of the light absorbed, greater energy corresponds to shorter wavelengths.

That means that as the splitting increases, the light absorbed will tend to shift away from the red

end of the spectrum towards orange, yellow and so on.

There is a fairly clear-cut case in copper(II) chemistry.

If you add an excess of ammonia solution to hexaaquacopper(II) ions in solution, the pale blue (cyan) colour is replaced by a dark inky blue as some of the water molecules in the complex ion are replaced by ammonia.

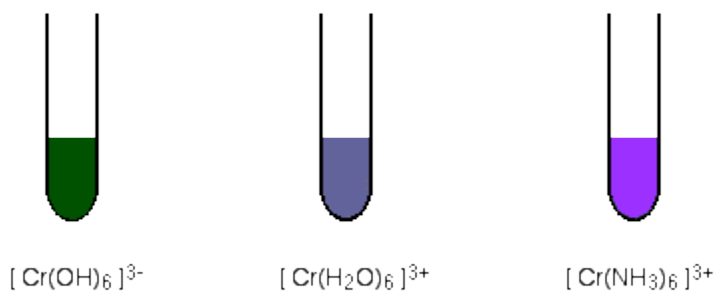


The first complex must be absorbing red light in order to give the complementary colour cyan. The second one must be absorbing in the yellow region in order to give the complementary colour dark blue.

Yellow light has a higher energy than red light. You need that higher energy because ammonia causes more splitting of the d orbitals than water does.

It isn't often as simple to see as this, though! Trying to sort out what is being absorbed when you have murky colours not on the simple colour wheel further up the page is much more of a problem.

The diagrams show some approximate colours of some ions based on chromium(III).



It is obvious that changing the ligand is changing the colour, but trying to explain the colours in

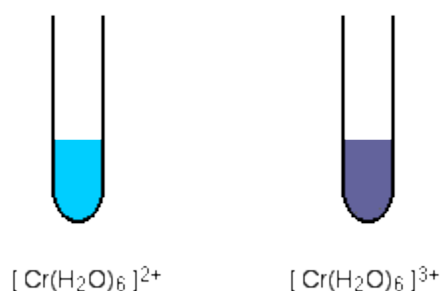
terms of our simple theory isn't easy.

The oxidation state of the metal

As the oxidation state of the metal increases, so also does the amount of splitting of the d orbitals.

Changes of oxidation state therefore change the colour of the light absorbed, and so the colour of the light you see.

Taking another example from chromium chemistry involving only a change of oxidation state (from +2 to +3):



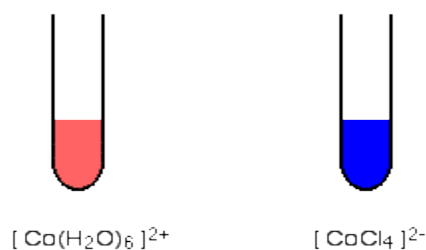
The 2+ ion is almost the same colour as the hexaaquacopper(II) ion, and the 3+ ion is the hard-to-describe violet-blue-gey colour.

The co-ordination of the ion

Splitting is greater if the ion is octahedral than if it is tetrahedral, and therefore the colour will change with a change of co-ordination. Unfortunately, I can't think of a single simple example to illustrate this with!

The problem is that an ion will normally only change co-ordination if you change the ligand - and changing the ligand will change the colour as well. You can't isolate out the effect of the co-ordination change.

For example, a commonly quoted case comes from cobalt(II) chemistry, with the ions $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$.



The difference in the colours is going to be a combination of the effect of the change of ligand, and the change of the number of ligands.

There are various substances which show magnetic behavior. We have substances that are attracted by the magnetic field and are called paramagnetic. This phenomenon is called paramagnetism. Paramagnetic property is only shown when the substance contains one or more unpaired electrons. When a substance acquires a permanent magnetic moment, it is known as ferromagnetic and the phenomenon is called ferromagnetism. On the other hand we also have substances which are repelled by magnetic field and are called as diamagnetic substances. A substance shows diamagnetism when it contains only paired electrons.

Most of the transition elements show paramagnetic behavior. The unpaired electrons in (n-1) d orbitals are responsible for the magnetic properties. The paramagnetic character of the transition metals increases on moving from left to right as the number of unpaired electron increases from one to five. The middle elements are found to possess the maximum paramagnetic property. The magnetic properties decrease with the decrease in the number of unpaired electrons. The transition metals which contain paired electrons depict diamagnetic behavior.

Explanation for magnetic properties

An electron is a charged particle (negatively charged) which revolves around the nucleus and spins on its own axis. A [magnetic](#) field is generated due to the orbital motion and spin of the electron. The spinning of an electron in an orbit is very much similar to flow of electric current in a closed circuit. Therefore an unpaired electron is regarded as a micro magnet which has a definite magnetic moment. A substance which contains an unpaired electron when placed in a magnetic field interacts with the applied field. Consequently, an attractive force is exerted and paramagnetic property is shown. The number of unpaired electrons determines the magnitude of

magnetic moment. Higher the number of unpaired electrons more is the magnetic moment and greater will be the paramagnetic behavior of the substance.

In the case of paired electrons, the electrons in each pair will have opposite spin. The magnetic field created by the electrons of same pair is equal and opposite in nature. Hence the magnetic field which is created by one [electron](#) is canceled by the other. So the net effect of the magnetic moment is zero. These kind of substances show diamagnetic property and are repelled by the applied magnetic field.

Catalytic properties

Most of the transition metals and their compounds particularly oxides have good catalytic properties. Platinum, iron, vanadium pentoxide, nickel, etc., are important catalysts. Platinum is a general catalyst. Nickel powder is a good catalyst for hydrogenation of unsaturated organic compound such as, hydrogenation of oils some typical industrial catalysts are,

- (i) Vanadium pentoxide (V_2O_5) is used in the Contact process for the manufacture of sulphuric acid,
- (ii) Finely divided iron is used in the Haber's process for the synthesis of ammonia.

Explanation : Most transition elements act as good catalyst because of,

- (i) The presence of vacant d-orbitals.
- (ii) The tendency to exhibit variable oxidation states.
- (iii) The tendency to form reaction intermediates with reactants.
- (iv) The presence of defects in their crystal lattices.

Alloy formation : Transition metals form alloys among themselves. The alloys of transition metals are hard and high melting as compared to the host metal. Various steels are alloys of iron with metals such as chromium, vanadium, molybdenum, tungsten, manganese etc.

Explanation : The atomic radii of the transition elements in any series are not much different from each other. As a result, they can very easily replace each other in the lattice and form solid solutions over an appreciable composition range. Such solid solutions are called alloys.

Chemical reactivity : The d-block elements (transition elements) have lesser tendency to react, i.e., these are less reactive as compared to s-block elements.

Explanation : Low reactivity of transition elements is due to,

- (i) Their high ionisation energies.
- (ii) Low heats of hydration of their ions.
- (iii) Their high heats of sublimation.

Oxidation state

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the transition metals have multiple potential oxidation states.

Introduction

Oxidation results in an increase in the oxidation state. Reduction results in a decrease in the oxidation state. If an atom is reduced, it has a higher number of valence shell electrons, and therefore a higher oxidation state, and is a strong oxidant. For example, oxygen (O) and fluorine (F) are very strong oxidants. On the other hand, lithium (Li) and sodium (Na) are incredibly strong reducing agents (likes to be oxidized), meaning that they easily lose electrons. In this module, we will precisely go over the oxidation states of transition metals.

Unpaired Electrons of d-orbitals

To fully understand the phenomena of oxidation states of transition metals, we have to understand how the unpaired d-orbital electrons bond. There are five orbitals in the d subshell manifold. As the number of unpaired valence electrons increases, the d-orbital increases, the highest oxidation state increases. This is because unpaired valence electrons are unstable and eager to bond with other chemical species. This means that the oxidation states would be the highest in the very middle of the transition metal periods due to the presence of the highest number of unpaired valence electrons. To determine the oxidation state, unpaired d-orbital

electrons are added to the 2s orbital electrons since the 3d orbital is located before the 4s orbital in the periodic table.

For example: Scandium has one unpaired electron in the d-orbital. It is added to the 2 electrons of the s-orbital and therefore the oxidation state is +3. So that would mathematically look like: 1s electron + 1s electron + 1d electron = 3 total electrons = oxidation state of +3. The formula for determining oxidation states would be (**with the exception of copper and chromium**):

Highest Oxidation State for a Transition metal = Number of Unpaired d-electrons + Two s-orbital electrons

The number of d-electrons range from 1 (in Sc) to 10 (in Cu and Zn) below:

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

It was mentioned previously that both copper and chromium do not follow the general formula for transition metal oxidation states. This is because copper has 9 d-electrons, which would produce 4 paired d-electrons and 1 unpaired d-electron. Since copper is just 1 electron short of having a completely full d-orbital, it steals an electron from the s-orbital, allowing it to have 10 d-electrons. Likewise, chromium has 4 d-electrons, only 1 short of having a half-filled d-orbital, so it steals an electron from the s-orbital, allowing chromium to have 5 d-electrons.

Rules about Transition Metals

Free elements (elements that are not combined with other elements) have an oxidation state of zero, e.g., the oxidation state of Cr (chromium) is 0.

For ions, the oxidation state is equal to the charge of the ion, e.g., the ion Fe^{3+} (ferric ion) has an oxidation state of +3.

The oxidation state of a neutral compound is zero, e.g., What is the oxidation state of Fe in FeCl_3 ?

Answer: Cl has an oxidation state of -1. Since there are 3 Cl atoms the negative charge is -3. Since FeCl_3 has no overall charge, the compound has a neutral charge, and therefore the oxidation state of Fe is +3.

In other words, it is: Fe^{3+} and 3Cl^- , which makes up FeCl_3 with a neutral charge.

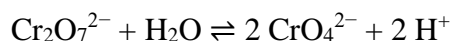
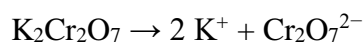
Multiple Oxidation States

As stated above, most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and therefore their oxidation state is almost always +1 (from losing it) and alkaline earth metals have two electrons in their valence s-orbital, resulting with an oxidation state of +2 (from losing both). This is not the case for transition metals since transition metals have 5 d-orbitals. The d-orbital has a variety of oxidation states. The s-orbital also contributes to determining the oxidation states.

Potassium dichromate

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is a common inorganic chemical reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications. As with all hexavalent chromium compounds, it is acutely and chronically harmful to health. It is a crystalline ionic solid with a very bright, red-orange color. The salt is popular in the laboratory because it is not deliquescent, in contrast to the more industrially relevant salt sodium dichromate.

Potassium dichromate is usually prepared by the reaction of potassium chloride on sodium dichromate. Alternatively, it can be obtained from potassium chromate by roasting chrome ore with potassium hydroxide. It is soluble in water and in the dissolution process it ionizes:



Reactions

Potassium dichromate is an oxidising agent in organic chemistry, and is milder than potassium permanganate. It is used to oxidize alcohols. It converts primary alcohols into aldehydes and,

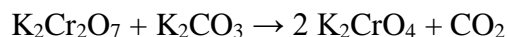
under more forcing conditions, into carboxylic acids. In contrast, potassium permanganate tends to give carboxylic acids as the sole products. Secondary alcohols are converted into ketones. For example, menthone may be prepared by oxidation of menthol with acidified dichromate. Tertiary alcohols cannot be oxidized.

In an aqueous solution the color change exhibited can be used to test for distinguishing aldehydes from ketones. Aldehydes reduce dichromate from the +6 to the +3 oxidation state, changing color from orange to green. This color change arises because the aldehyde can be oxidized to the corresponding carboxylic acid. A ketone will show no such change because it cannot be oxidized further, and so the solution will remain orange.

When heated strongly, it decomposes with the evolution of oxygen.



When an alkali is added to an orange red solution containing dichromate ions, a yellow solution is obtained due to the formation of chromate ions. For example, potassium chromate is produced industrially using potash:



The reaction is reversible.

Treatment with cold sulphuric acid gives red crystals of chromic anhydride (CrO_3):



On heating with concentrated acid, oxygen is evolved:



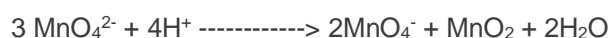
Uses

Potassium dichromate has few major applications, as the sodium salt is dominant industrially.

The main use is as a precursor to [potassium chrome alum](#), used in [leather tanning](#).[†]

Pottassium Permanganate (KMnO₄)

Pottassium Permanganate (KMnO₄) is prepared from Pyrolusite ore (MnO₂). The finely powdered Pyrolusite ore (MnO₂) is fused with an alkali metal hydroxide like KOH in the presence of air or an oxidizing agent like KNO₃ to give the dark green potassium Manganate (K₂MnO₄). Potassium manganate disproportionate in a neutral or acidic solution to give potassium permanganate.



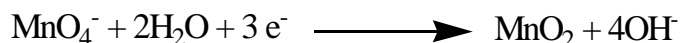
Commercially potassium permanganate is prepared by the alkaline oxidative fusion of Pyrolusite ore (MnO₂) followed by the electrolytic oxidation of manganate (4) ion.

**Properties of Potassium permanganate (KMnO₄)****1. Potassium permanganate (KMnO₄): Action of Heat**

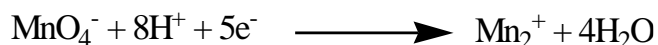
Potassium permanganate on strong heating gives potassium manganate, manganese dioxide and oxygen.

**2. Oxidising properties of Potassium permanganate (KMnO₄)**

Potassium permanganate is a powerful oxidizing agent in alkaline or acidic solution. The relevant half reactions are:

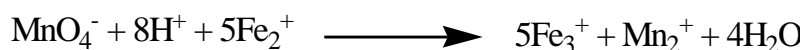
1. Alkaline medium (pH > 7)

2. Acidic medium (pH <7)

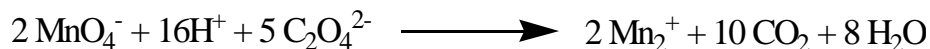


A few important oxidizing reactions of Potassium permanganate (KMnO₄)

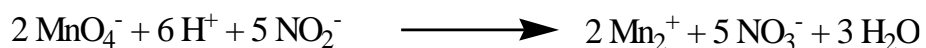
1. In acidic medium potassium permanganate oxidizes green ferrous salts to yellow ferric salts



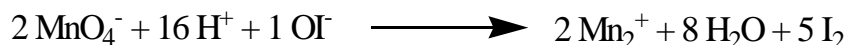
2. in acidic medium potassium permanganate oxidizes oxalic acid or oxalate salts to CO₂ and water



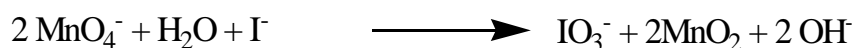
3. In acidic medium potassium permanganate oxidizes nitrites to nitrate.



4. In acidic medium potassium permanganate oxidises iodides to iodine.



5. In alkaline medium potassium permanganate oxidizes iodides to iodates .



Potassium ferrocyanide

Potassium ferrocyanide is the inorganic compound with formula $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. It is the potassium salt of the coordination complex $[\text{Fe}(\text{CN})_6]^{4-}$. This salt forms lemon-yellow monoclinic crystals.

Synthesis

Modern production

Potassium ferrocyanide is produced industrially from hydrogen cyanide, ferrous chloride, and calcium hydroxide, the combination of which affords $\text{Ca}_2[\text{Fe}(\text{CN})_6] \cdot 11\text{H}_2\text{O}$. This solution is then treated with potassium salts to precipitate the mixed calcium-potassium salt $\text{CaK}_2[\text{Fe}(\text{CN})_6]$, which in turn is treated with potassium carbonate to give the tetrapotassium salt.

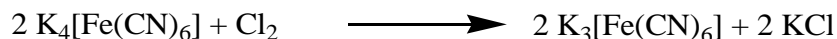
Historical production

Historically, the compound was manufactured from organically derived nitrogenous carbon sources, iron filings, and potassium carbonate. Common nitrogen and carbon sources were torrefied horn, leather scrap, offal, or dried blood.

Chemical reactions

Treatment of potassium ferrocyanide with nitric acid gives $\text{H}_2[\text{Fe}(\text{NO})(\text{CN})_5]$. After neutralization of this intermediate with sodium carbonate, red crystals of sodium nitroprusside can be selectively crystallized.

Upon treatment with chlorine gas, potassium ferrocyanide converts to potassium ferricyanide:



This reaction can be used to remove potassium ferrocyanide from a solution.

A famous reaction involves treatment with ferric salts to give Prussian blue. With the approximate composition $\text{K}[\text{Fe}_2(\text{CN})_6]$, this insoluble but deeply colored material is the blue of blueprinting.

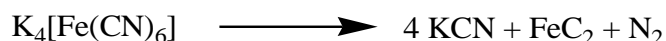
Applications

Potassium ferrocyanide finds many niche applications in industry. It and the related sodium salt are widely used as anticaking agents for both road salt and table salt. The potassium and sodium ferrocyanides are also used in the purification of tin and the separation of copper from molybdenum ores. Potassium ferrocyanide is used in the production of wine and citric acid.

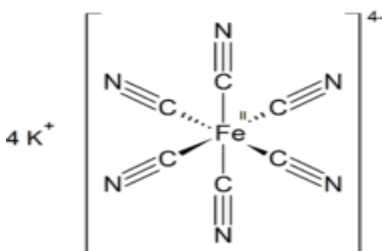
In the laboratory, potassium ferrocyanide is used to determine the concentration of potassium permanganate, a compound often used in titrations based on redox reactions. Potassium ferrocyanide is used in a mixture with potassium ferricyanide and phosphate buffered solution to provide a buffer for beta-galactosidase, which is used to cleave X-Gal, giving a bright blue visualization where an antibody (or other molecule), conjugated to Beta-gal, has bonded to its target. On reacting with Fe(3) it gives a Prussian blue colour. Thus it is used as an identifying reagent for iron in labs.

Potassium ferrocyanide can be used as a fertilizer for plants.

Prior to 1900 AD, before the invention of the Castner process, potassium ferrocyanide was the most important source of alkali metal cyanides. In this historical process, potassium cyanide was produced by decomposing potassium ferrocyanide:



Structure



Like other metal cyanides, solid potassium ferrocyanide, both as the hydrate and anhydrous salts, has a complicated polymeric structure. The polymer consists of octahedral $[\text{Fe}(\text{CN})_6]^{4-}$ centers crosslinked with K^+ ions that are bound to the CN ligands. The $\text{K}^+ \cdots \text{NC}$ linkages break when the solid is dissolved in water.

Toxicity

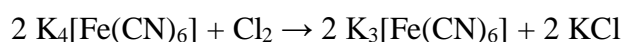
Potassium ferrocyanide is nontoxic, and is not decomposed to cyanide in the body. The toxicity in rate is low, with lethal dose (LD50) at 6400 mg/kg.

Potassium ferricyanide

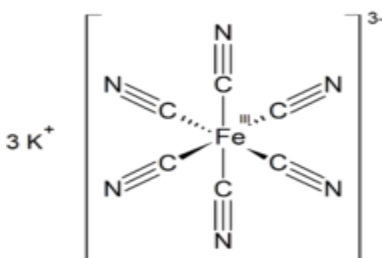
Potassium ferricyanide is the chemical compound with the formula $K_3[Fe(CN)_6]$. This bright red salt contains the octahedrally coordinated $[Fe(CN)_6]^{3-}$ ion. It is soluble in water and its solution shows some green-yellow fluorescence. It was discovered in 1822 by Leopold Gmelin and was initially used in the production of ultramarine dyes.

Preparation

Potassium ferricyanide is manufactured by passing chlorine through a solution of potassium ferrocyanide. Potassium ferricyanide separates from the solution:



Structure



Like other metal cyanides, solid potassium ferricyanide has a complicated polymeric structure. The polymer consists of octahedral $[Fe(CN)_6]^{3-}$ centers crosslinked with K^+ ions that are bound to the CN ligands. The $K^+ \cdots NCFe$ linkages break when the solid is dissolved in water.

Applications

In the 19th century, it was used for reading palimpsests and old manuscripts.

The compound has widespread use in blueprint drawing and in photography (Cyanotype process). Several photographic print toning processes involve the use of potassium ferricyanide. Potassium ferricyanide is used as an oxidizing agent to remove silver from negatives and positives, a process called dot etching. In color photography, potassium ferricyanide is used to reduce the size of color dots without reducing their number, as a kind of manual color correction.

It is also used in black-and-white photography with sodium thiosulfate (hypo) to reduce the density of a negative or gelatin silver print where the mixture is known as Farmer's reducer; this can help offset problems from overexposure of the negative, or brighten the highlights in the print.

The compound is also used to harden iron and steel, in electroplating, dyeing wool, as a laboratory reagent, and as a mild oxidizing agent in organic chemistry.

Potassium ferricyanide is also one of two compounds present in ferroxyl indicator solution (along with phenolphthalein) which turns blue (Prussian blue) in the presence of Fe^{2+} ions, and which can therefore be used to detect metal oxidation that will lead to rust. It is possible to calculate the number of moles of Fe^{2+} ions by using a colorimeter, because of the very intense color of Prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

Potassium ferricyanide is often used in physiology experiments as a means of increasing a solution's redox potential ($E^\circ \sim 436 \text{ mV}$ at pH 7). As such, it can oxidize reduced cytochrome c ($E^\circ \sim 247 \text{ mV}$ at pH 7) in intact isolated mitochondria. Sodium dithionite is usually used as a reducing chemical in such experiments ($E^\circ \sim -420 \text{ mV}$ at pH 7).

Potassium ferricyanide is used in many amperometric biosensors as an electron transfer agent replacing an enzyme's natural electron transfer agent such as oxygen as with the enzyme glucose oxidase. It is used as this ingredient in many commercially available blood glucose meters for use by diabetics.

Potassium ferricyanide is combined with potassium hydroxide (or sodium hydroxide as a substitute) and water to formulate Murakami's etchant. This etchant is used by metallographers to provide contrast between binder and carbide phases in cemented carbides.

Prussian blue

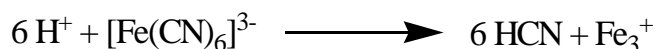
Prussian blue, the deep blue pigment in blue printing, is generated by the reaction of $\text{K}_3[\text{Fe}(\text{CN})_6]$ with ferrous (Fe^{2+}) ions as well as $\text{K}_4[\text{Fe}(\text{CN})_6]$ with ferric salts.

In histology, potassium ferricyanide is used to detect ferrous iron in biological tissue. Potassium ferricyanide reacts with ferrous iron in acidic solution to produce the insoluble blue pigment, commonly referred to as Turnbull's blue or Prussian blue. To detect ferric (Fe^{3+}) iron,

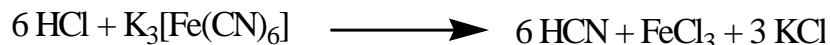
potassium *ferrocyanide* is used instead in the Perls' Prussian blue staining method. The material formed in the Turnbull's blue reaction and the compound formed in the Prussian blue reaction are the same.

Safety

Potassium ferricyanide has low toxicity, its main hazard being that it is a mild irritant to the eyes and skin. However, under very strongly acidic conditions, highly toxic hydrogen cyanide gas is evolved, according to the equation:



The reaction with hydrochloric acid is as follows:

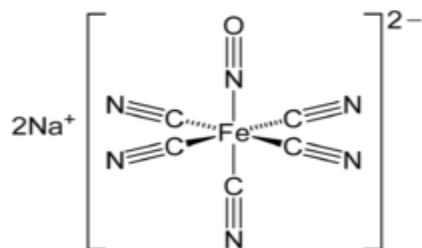


Sodium nitroprusside

Sodium nitroprusside (SNP), sold under the brand name Nitropress among others, is a medication used to lower blood pressure. This may be done if the blood pressure is very high and resulting in symptoms, in certain types of heart failure, and during surgery to decrease bleeding. It is used by continuous injection into a vein. Onset is typically immediate and effects last for up to ten minutes.

Common side effects include low blood pressure and cyanide toxicity. Other serious side effects include methemoglobinemia. It is not generally recommended during pregnancy due to concerns of side effects. High doses are not recommended for more than ten minutes. It works by causing the dilation of blood vessels.

Sodium nitroprusside was discovered as early as 1850 and found to be useful in medicine in 1928. It is on the World Health Organization's List of Essential Medicines, the most effective and safe medicines needed in a health system. In the United States a course of treatment costs less than 25 USD.



Medical use

Sodium nitroprusside is intravenously infused in cases of acute hypertensive crises. Its effects are usually seen within a few minutes.

Nitric oxide reduces both total peripheral resistance and venous return, thus decreasing both preload and afterload. So, it can be used in severe congestive heart failure where this combination of effects can act to increase cardiac output. In situations where cardiac output is normal, the effect is to reduce blood pressure. It is sometimes also used to induce hypotension (to reduce bleeding) for surgical procedures (for which it is also FDA, TGA, and MHRA labelled).

This compound has also been used as a treatment for aortic valve stenosis, oesophageal varices, myocardial infarction, pulmonary hypertension, respiratory distress syndrome in the newborn, shock, and ergot toxicity.

Adverse effects by incidence and severity

- Bradyarrhythmia (low heart rate)
- Hypotension (low blood pressure)
- Palpitations
- Tachyarrhythmia (high heart rate)
- Apprehension
- Restlessness
- Confusion
- Dizziness
- Headache
- Somnolence

- Rash
- Sweating
- Thyroid suppression
- Muscle twitch
- Oliguria
- Renal azotemia

Sodium cobaltinitrite

Sodium cobalt nitrite is a coordination compound with the formula $\text{Na}_3\text{Co}(\text{NO}_2)_6$. The anion of this yellow-colored salt consists of a cobalt(III) center *N*-bonded to six nitrito ligands. It is a reagent for the qualitative test for potassium and ammonium ions.

Synthesis and reactions

The compound is prepared by oxidation of cobalt(II) salts in the presence of sodium nitrite:



Application for analysis of potassium

Although the sodium cobaltinitrite is soluble in water, it forms the basis of a quantitative determination of potassium, thallium, and ammonium ions. Under the recommended reaction conditions the insoluble double salt, $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6] \cdot \text{H}_2\text{O}$ is precipitated and weighed. In geochemical analysis, sodium cobaltinitrite is used to distinguish alkali feldspars from plagioclase feldspars in thin section.

UNIT III**POSSIBLE QUESTIONS****PART A – Objective type questions (Each carry 1 mark)**

- The general electronic configuration of d-block elements is
a. $(n-1)d^{1-10} ns^{0-2}$ b. $(n-1) d^{1-5} ns^2$ c. $(n-1)d^0 ns^1$ d. None of these
- Formation of colored ions is possible when compounds contains
 a. paired electrons **b. unpaired electrons** c. lone pairs of electrons d. none of the above
- Paramagnetism is common in
 a. p-block elements **b. d-block elements** c. s-block elements d. f-block elements
- The colour of $Ti(H_2O)_6^{3+}$ ion is due
a. d-d transition b. Presence of water molecules
 c. Inter atomic transfer of electrons d. None of the above
- the correct electronic configuration of copper atom is
a. $3d^{10} 4s^1$ b. $3d^{10} 4s^2$ c. $3d^9 4s^2$ d. $3d^9 4s^1$
- Silver salt used in photography is
 a. AgCl **b. AgBr** c. AgF d. AgNO₃
- Which of the ions will give colourless aqueous solution?
 a. Ni²⁺ b. Fe²⁺ c. Cu²⁺ **d. Cu⁺**
- The most common oxidation state for d-block elements are
 a. +1 **b. +2** c. +3 d. +4
- Which of the following has the maximum number of unpaired electrons
 a. Ti³⁺ **b. Mn²⁺** c. V³⁺ d. Fe²⁺
- The transition element with lowest atomic number
 a. Ti **b. Sc** c. Cr d. Zn
- Which transition element show maximum oxidation state
 a. Scandium **b. Osmium** c. Vanadium d. Yttrium
- All the transition elements show Character
a. Metallic b. insulating c. super conducting d. semi conducting
- V³⁺ ion shows
 a. pink color **b. green color** c. red color d. colorless

14. In the manufacture of ammonia we are using As a catalyst
a. Iron b. Palladium c. platinum d. vanadium
15. The magnetic property is termed as
 a. Ergg b. Pascal **c. Bohr magneton** d. joules
16. Zr and Hf have almost equal radii because of
 a. Shielding effect b. pairing effect c. trans effect **d. lanthanide contraction**
17. The common oxidation state for transition elements
 a. +1 **b. +2** c. +3 d. +4
18. Catalytic properties of the d-block elements are due to its Electrons
 a. Paired electrons **b. unpaired electrons** c. Charged electrons d. uncharged electrons
19. In contact process is used as a catalyst
 a. Pt **b. V₂O₅** c. Fe d. Ni
20. The outermost electronic configuration of Ti³⁺ ion
 a. 3d¹ **b. 3d²** c. 3d³ d. 3d⁰

PART B (Each carry 2 marks)

- What is the justification for classifying Zn, Cd and Hg as transition elements?
- Write the electronic configuration of W (Z=74) and Mo (Z=42).
- Write the oxidation states of Cu, Ni, Co and Zn.
- How do you explain the anomalous electronic configurations of Cr and Cu?
- Calculate the magnetic moment (Spin only) for the complex K₄[Mn(NCS)₆]
- Name four elements belonging to the group of copper.
- Name two elements belonging to second and third transition series which are used as catalysts.
- Write the uses of Potassium dichromate.
- Write the preparation and uses of potassium permanganate.
- Write the preparation and uses of potassium ferricyanide.

PART C (Each carry 6 marks)

1. Discuss the variation of oxidation states among the elements of first, second and third transition series.
2. Write the preparation, properties and uses of Potassium dichromate.
3. Give a brief account on magnetic property of first, second and third transition series.
4. Discuss the colour of first, second and third transition elements with an example.
5. Discuss the stability of various oxidation states and e.m.f. of transition elements.
6. Write the preparation, properties and uses of potassium ferricyanide.
7. Write the uses of Potassium permanganate and potassium ferrocyanide.
8. Discuss the electronic configurations among the elements of first, second and third transition series.
9. Explain the difference between the first, second and third transition series.

[16CHU302]

Batch: 2016-2019

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY

INORGANIC CHEMISTRY-II (Coordination Chemistry)

Semester –III

Multiple Choice Questions for on line examination (Each question carry one mark)

UNIT-III

S. No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	Which of the following is expected to be diamagnetic?	CrCl_3	CuCl_2	ZnCl_2	CuSO_4	ZnCl_2
2	The expected magnetic moment of Ti^{3+} ion is	4.90	2.84	1.73	0	1.73
3	Which of the following is expected to have the highest Magnetic moment?	Co^{2+}	Cu^{2+}	Ni^{2+}	Mn^{2+}	Mn^{2+}
4	Which of the following is used as calibrant in magnetic measurements?	CoCl_4^{2-}	$\text{KCu}(\text{CN})_2$	$\text{CoHg}(\text{CNS})_4$	Fe_3O_4	$\text{CoHg}(\text{CNS})_4$
5	The most familiar example of ferromagnetic substance is	Copper	Iron	Manganese	Zinc	Iron

6	Among the following which one is known as ferromagnetic substance	Cobalt	Copper	Zinc	Manganese	Cobalt
7	Among the following which one is known as ferromagnetic substance	Nickel	Copper	Zinc	Manganese	Nickel
8	The magnetic moment of the coordination compound is associated with the	Number of unpaired electrons	Charge of complex	Oxidation state of complex	Ligands of the complex	Number of unpaired electrons
9	The relationship between the number the number of unpaired electrons of an ion and its magnetic moment is represented by the symbol	β	μ	Σ	π	μ
10	The unit of μ is	BM	AM	M	UM	BM
11	The unpaired electrons are arises due to the----- of electrons	Charge	Size	Spin and orbital motion	mass	Spin and Orbital motion
12	The magnetic moment is calculated by	Plank's constant	Spin only formula	Orbital angular quantum number	emf	Spin only formula
13	As the oxidation state increases, the metal ions become more	basic	stable	hard	acidic	acidic
14	The relative stability of oxidation states of transition metals can be predicted on the basis of	Ionic strength	Volume	Electrode potential	Density	Electrode potential
15	The relative stability of oxidation states of transition metals can be predicted on the basis of	Ionic strength	Ionization energy	Volume	Density	Ionization energy
16	Among the following which is used in the manufacture of vanaspati	Finely divided Nickel and palladium	Iron powder	Molybdenum	Zinc chromite	Finely divided Nickel and palladium
17	Among the following which is used in the manufacture of ammonia	Finely divided iron and	Zinc chromite	Platinum pentaoxide	Vanadium pentaoxide	Finely divided iron and

		molybdenum				molybdenum
18	Zinc chromite is used in the synthesis of	polythene	Ammonia	Methyl alcohol	Ethanol	Methyl alcohol
19	Which is used in the oxidation of alcohols to aldehydes	Tallen's reagent	Grignard reagent	Fenton's reagent	Bayer's reagent	Fenton's reagent
20	Fenton's reagent is known as the mixture of	$\text{TiCl}_4 + \text{H}_2\text{O}$	$\text{FeSO}_4 + \text{H}_2\text{O}_2$	$\text{CuSO}_4 + \text{H}_2\text{O}_2$	$\text{FeSO}_4 + \text{H}_2\text{O}$	$\text{FeSO}_4 + \text{H}_2\text{O}_2$
21	The mixture of $\text{FeSO}_4 + \text{H}_2\text{O}_2$ is known as	Tallen's reagent	Grignard reagent	Fenton's reagent	Bayer's reagent	Fenton's reagent
22	Ziegler –Natta catalyst is used for the manufacture of	Vanaspati	Ammonia	polythene	Methyl alcohol	Polythene
23	TiCl_4 is known as	Fenton's reagent	Ziegler-Natta catalyst	Grignard reagent	Fenton's reagent	Ziegler-Natta catalyst
24	Which is known as Ziegler –Natta catalyst	$\text{TiCl}_4 + \text{H}_2\text{O}$	$\text{FeSO}_4 + \text{H}_2\text{O}_2$	TiCl_4	$\text{FeSO}_4 + \text{H}_2\text{O}_2$	TiCl_4
25	What is the colour of Sc^{3+}	Purple	pink	Colourless	Green	Colourless
26	What is the colour of Cu^{2+}	pink	Blue	Pink	Yellow	Blue
27	The coordination number of Third transition series is	6	4	8	5	8
28	The Maximum oxidation state of Fe is	+3	+2	+6	+4	+6
29	The maximum oxidation state of Ru and Os is	+5	+8	+6	+7	+8
30	Which is used in the manufacture of ammonia	Fe	Pt/Rh	Ni/Ru	Co	Pt/Rh
31	Which is known as Adam's catalyst	Fe/FeO	Pt	Pt/PtO	Fe	Pt/PtO
32	Which is used for the hydrogenation reactions in organic chemistry	Pd	Pt	Fe	Ni	Pd
33	Which is used in tracker in process for converting C_2H_4 to CH_3CHO	Pd	PdCl_2	NiCl_2	Ni	PdCl_2
34	Re(IV) has the electronic configuration of	d^2	d^3	d^4	d^5	d^3

35	The metal which is used as Adam's catalyst	Pd	Pt	Co	Ni	Pt
36	The highest oxidation state shown by rhenium is	+5	+8	+6	+7	+7
37	The common oxidation state for transition elements	+1	+2	+3	+4	+2
38	Catalytic properties of the d-block elements are due to its Electrons	Paired electrons	unpaired electrons	Charged electrons	uncharged electrons	unpaired electrons
39	The outermost electronic configuration of Ti^{3+} ion	$3d^1$	$3d^2$	$3d^3$	$3d^0$	$3d^1$
40	In contact process is used as a catalyst	Pt	V_2O_5	Fe	Ni	V_2O_5
41	V^{3+} ion shows Colour	Pink	Green	Red	colourless	Green
42	In the manufacture of ammonia which is used as a catalyst	Palladium	Iron	platinum	vanadium	Iron
43	The magnetic property is termed as	Ergg	Pascal	Bohr Magnetron	joules	Bohr Magnetron
44	The general electronic configuration of d-block elements is	$(n-1)d^{1-10} ns^{0-2}$	$(n-1) d^{1-5} ns^2$	$(n-1)d^0 ns^1$	$(n-1)f^{1-14} ns^1$	$(n-1)d^{1-10} ns^{0-2}$
45	Formation of coloured ions is possible when compounds contains	paired electrons	unpaired electrons	lone pairs of electrons	Electrons in f-orbitals	unpaired electrons
46	Paramagnetism is common in	p-block elements	d-block elements	s-block elements	f-block elements	d-block elements
47	The colour of $[Ti(H_2O)_6]^{3+}$ ion is due	d-d transition	Presence of water molecules	Inter atomic transfer of electrons	Oxidation state of central metal ion	d-d transition
48	the correct electronic configuration of copper atom is	$3d^{10} 4s^1$	$3d^{10} 4s^2$	$3d^9 4s^2$	$3d^9 4s^1$	$3d^{10} 4s^1$
49	Silver salt used in photography is	AgCl	AgBr	AgF	$AgNO_3$	AgBr
50	The first transition series comprises of	Scandium to	Lanthanum to	Yttrium to	Lithium to Neon	Scandium to

	elements from	Zinc	hafnium	cadmium		Zinc
51	The number of unpaired electrons in Fe^{3+} (Z=26) is	4	6	5	2	5
52	In first transition series, the divalent compound having maximum magnetic moment is of:	Mn	Fe	Cu	Cr	Mn
53	d-block elements show all the following properties expect:	Variable oxidation states	Catalytic properties	Natural radioactivity	Colour of the compounds	Natural radioactivity
54	Which of the following does not belong to first transition series?	Silver	Cobalt	Chromium	Vanadium	Silver
55	The second transition series comprises of elements from	Scandium to Zinc	Lanthanum to hafnium	Yttrium to Cadmium	Lithium to Neon	Yttrium to Cadmium
56	The third transition series comprises of elements from	Scandium to Zinc	Lanthanum to hafnium	Yttrium to Cadmium	Lanthanum to mercury	Lanthanum to mercury
57	Which of the ions will give colourless aqueous solution?	Ni^{2+}	Fe^{2+}	Cu^{2+}	Cu^{+}	Cu^{+}
58	The most common oxidation state for d-block elements are	+1	+2	+3	+4	+2
59	Which of the following has the maximum number of unpaired electrons	Ti^{3+}	Mn^{2+}	V^{3+}	Fe^{2+}	Mn^{2+}
60	The transition element with lowest atomic number	Ti	Sc	Cr	Zn	Sc
61	Which is used in calico printing	Sodium dichromate	Potassium dichromate	Chromic acid	Potassium chromate	Potassium dichromate
62	The mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Con.H}_2\text{SO}_4$ is known as	Chromic acid	Potassium dichromate	Chromic acid	Potassium chromate	Chromic acid
63	Chromic acid is the mixture of -----	$\text{K}_2\text{Cr}_2\text{O}_7 + \text{Con.H}_2\text{SO}_4$	$\text{K}_2\text{Cr}_2\text{O}_7 + \text{Con.HNO}_3$	$\text{K}_2\text{Cr}_2\text{O}_7 + \text{Con.HCl}$	$\text{K}_2\text{Cr}_2\text{O}_7 + \text{CH}_3\text{COOH}$	$\text{K}_2\text{Cr}_2\text{O}_7 + \text{Con.H}_2\text{SO}_4$
64	Potassium permanganate is used as an	Cleaning agent	Reducing agent	Catalyst	Oxidising agent	Oxidizing agent
65	Baeyer's Reagent is	Alkaline Potassium permanganate	Alkaline Sodium permanganate	Potassium chromate	Potassium dichromate	Alkaline Potassium permanganate

66	Which is obtained from coal gas	Potassium chromate	Potassium dichromate	Potassium ferrocyanide	Potassium ferricyanide	Potassium ferrocyanide
67	$\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ is known as	Potassium nitroprusside	Pentacyano Nitro iron sodium dihydrate	Sodium nitroprusside	Sodium hexa cyanate	Sodium nitroprusside
68	Write the correct IUPAC name for $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ is	Sodium hexanitritocobalt(III)	Hexanitritocobalt (III) Sodium	Sodium hexanitritocobalt(III)	Sodium hexanitrocobalt(I II)	Sodium hexanitritocobalt(III)

UNIT IV

Lanthanoids and Actinoids:

Electronic configuration, oxidation states, colour, spectral and magnetic properties, lanthanide contraction, separation of lanthanides (ion-exchange method only).

Lanthanides (5f- Block elements)

Introduction

Lanthanides (also called lanthanoids) are called first inner transition series or third transition and come immediately after lanthanum. They are classified as f block elements along with the actinides. They are commonly called the rare earths. They are characterized by the filling up of the 4f energy levels which are not usually involved in bonding. These highly electropositive elements have a common oxidation state of +3 and generally resemble each other in their chemical and physical properties. They have a generic symbol “Ln”.

DISCOVERY AND OCCURRENCE

In 1794, Swedish chemist, Gadolin, discovered an oxide called yttria. Yttria was broken down to— yttria, erbia and terbia. Over the years, more separation was achieved, and more oxide discovered e.g. lutetia. The names were later obtained by changing the ending –a to -um. Major sources of lanthanides are Monazite sand—composed of phosphates of thorium, cerium, neodymium and lanthanum; the phosphate portion of monazite contains small traces of other lanthanide ions and the only lanthanide that does not occur naturally is promethium, which is made artificially by nuclear reaction. Bastnaesite, found in USA and Madagascar is a mixed fluorocarbonate $M^{III}CO_3F$ where M is La or the lanthanide metals. It provides 20% total supply of lanthanides. An also very small amount of xenotime mineral is mined.

Electronic configuration

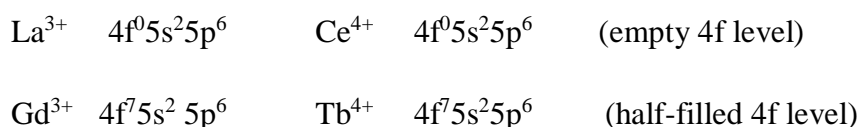
- ❖ The general electronic configuration of these elements is $ns^2(n-1)d^{0-1}(n-2)f^{1-14}$
- ❖ They resemble each other very closely as they have same electronic configuration in nth and (n -1) valency shell. Their most common oxidation state is +3 involving only 5d¹ and 6s² electrons. An alternate electronic configuration is also suggested that after Ce, the d electron also shifts to 4f orbital, except for those elements where it will disturb f¹ or f¹⁴ configuration.

Element	Symbol	Atomic number	Electronic Configuration
Lanthanum	La	57	[Xe] 4f ⁰ 5d ¹ 6s ²
Cerium	Ce	58	[Xe] 4f ¹ 5d ¹ 6s ²
Praseodymium	Pr	59	[Xe] 4f ³ 6s ²
Neodymium	Nd	60	[Xe] 4f ⁴ 6s ²
Promethium	Pm	61	[Xe] 4f ⁵ 6s ²
Samarium	Sm	62	[Xe] 4f ⁶ 6s ²
Europium	Eu	63	[Xe] 4f ⁷ 6s ²
Gadolinium	Gd	64	[Xe] 4f ⁷ 5d ¹ 6s ²
Terbium	Tb	65	[Xe] 4f ⁹ 6s ²
Dysprosium	Dy	66	[Xe] 4f ¹⁰ 6s ²
Holmium	Ho	67	[Xe] 4f ¹¹ 6s ²
Erbium	Er	68	[Xe] 4f ¹² 6s ²
Thulium	Tm	69	[Xe] 4f ¹³ 6s ²
Ytterbium	Yb	70	[Xe] 4f ¹⁴ 6s ²
Lutetium	Lu	71	[Xe] 4f ¹⁴ 5d ¹ 6s ²

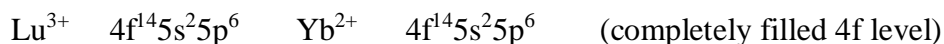
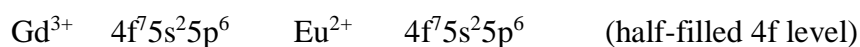
Table. Ground electronic configurations of the lanthanides

Oxidation States

Lanthanides exhibit a principal oxidation state of +3 which contain an outer shell containing 8 electrons and an underlying layer containing up to 14 electrons. The +3 ions of La, Gd and Lu which contain respectively an empty, a half-filled, and a completely filled 4f level are especially stable. Ce can exhibit an oxidation state of +4 in which it has the same electronic structure with La⁺³, an empty 4f level-noble gas configuration). Also, Tb⁴⁺ exists which has the same electronic structure as Gd³⁺ i.e. a half-filled 4f level. An empty, a half filled and a completely filled 4f shell confers some extra stability on a particular oxidation state.

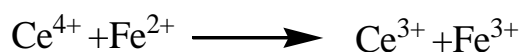


Also, Eu^{+2} is isoelectronic with Gd^{+3} *i.e.* half-filled 4f level and Yb^{+2} is isoelectronic with Lu^{+3}



In addition, +2 and +4 states exist for elements that are close to these states. For example, Sm^{2+} and Tm^{2+} occur with f^6 and f^{13} arrangements and Pr^{4+} and Nd^{4+} have f^1 and f^2 arrangements.

The most stable oxidation state is Ln^{3+} and Ln^{2+} and Ln^{4+} are less stable. Ce^{4+} is strongly oxidizing and Sm^{2+} is strongly reducing:



{ Ce^{4+} and Sm^{2+} are converted to +3 state, showing that it is the most stable oxidation state}

Colour:

The colours are due to Laporte forbidden f-f transitions. The absorption bands of Ln^{+3} ions (except Ce^{+3} and Yb^{+3} ions) are very weak but sharp when compared to those of d – block elements. Many of these bands are line-like and become even narrower as the temperature is lowered. These narrow bands appear due to f-f transition and are independent of the nature of the anion present. As 4f electrons lie deep inside the atom, the colours of Ln^{+3} ions are not affected by changing the anion.

Spectral properties of Lanthanoid complexes

Lanthanide ions are weakly coloured. The spectra of their complexes show much narrower and more distinct absorption bands which is associated with weak f-f transition. The 4f orbitals are deeply embedded inside the atom and well shielded by 5s and 5p electrons. The f electrons are practically unaffected by complex formation; hence colour remains almost constant for a particular ion regardless of the ligands shown in table. The bands due to f-f transition are sharp compared to the broad bands for d-d transition. Absorption bands due to 4f-5d transitions are broad and are affected by ligand environment.

All lanthanoid ions (except $\text{La}^{3+}(f^0)$ and $\text{Lu}^{3+}(f^{14})$) show luminescence $\text{Eu}^{3+}(f^6)$ and $\text{Tb}^{3+}(f^8)$ showing particularly strong emissions. This has been attributed to the large number of excited states that exist which decays to the ground state with either emission of energy (fluorescence) or non-radiative pathways. The origin of this is f-f transition. The luminescence of lanthanoid complexes is the reason they are used as phosphors on TV screens and fluorescent lighting.

The Colours Of Some Aqueous Lanthanides

Ions	No of 4f e's	Colour	Ions	No of 4f e's	Colour	Ions	No of 4f e's	Colour	Isoelectronic Ln^{3+}
La^{3+}	$4f^0$	Colourless	Lu^{3+}	$4f^{14}$	Colourless	Ce^{4+}	$4f^0$	Orange-red	La^{3+} Colourless
Ce^{3+}	$4f^1$	Colourless	Yb^{3+}	$4f^{13}$	Colourless	Sm^{2+}	$4f^6$	Yellow	Eu^{3+} Pale pink
Pr^{3+}	$4f^2$	Green	Tm^{3+}	$4f^{12}$	Green	Eu^{2+}	$4f^7$	Pale greenish yellow	Gd^{3+} Colourless
Nd^{3+}	$4f^3$	Lilac	Er^{3+}	$4f^{11}$	Lilac	Yb^{2+}	$4f^{14}$	Colourless	Lu^{3+} Colourless
Pm^{3+}	$4f^4$	pink	Ho^{3+}	$4f^{10}$	Pink				
Sm^{3+}	$4f^5$	Yellow	Dy^{3+}	$4f^9$	Yellow				
Eu^{3+}	$4f^6$	Pale pink	Tb^{3+}	$4f^8$	Pale pink				
Gd^{3+}	$4f^7$	Colourless							

Magnetic properties

The 4f electrons are responsible for the strong magnetism exhibited by the metals and compounds of the lanthanides. In the incomplete 4f sub shell the magnetic effects of the different electrons do not cancel out each other as they do in a completed sub shell, and this factor gives rise to the interesting magnetic behaviour of these elements. At higher temperatures, all the lanthanides except lutetium are paramagnetic (weakly magnetic), and this paramagnetism frequently shows a strong anisotropy. As the temperature is lowered, many of the metals exhibit a point below which they become antiferromagnetism (i.e., magnetic moments of the ions are aligned but some are opposed to others), and, as the temperatures are lowered still further, many of them go through a series of spin rearrangements, which may or may not be in conformity with the regular crystal lattice. Finally, at still lower temperatures, a number of these elements become ferromagnetic (i.e., strongly magnetic, like iron). Some of the metals have saturation moments (magnetism

observed when all the magnetic moments of the ions are aligned) greater than iron, cobalt, or nickel. They also show a strong anisotropy in their magnetic behaviour depending on the crystal direction. Study of the magnetism of rare-earth elements has had great influence on present-day theories of magnetism.

Lanthanide Contraction (or Atomic and ionic radii):

The energies of 4f and 5d -orbitals are nearly same, beginning near to atomic number 57 La. Similar behavior is also observed for 5f and 6d - orbitals at atomic number 89 Ac.

The shielding of one f- electron by another from the effect of nuclear charge is quite weak due to shape of f-orbitals and hence with increasing atomic number the effective nuclear charge experienced by each 4f e increases, because of this there is contraction of atomic or ionic - radii proceeding from La to Lu. This decrease in atomic or ionic radii is called Lanthanide Contraction. Due to Lanthanide contraction the chemical properties of Lanthanides are almost similar.

Case of Lanthanide Contraction:

In Lanthanides the additional electrons enters 4f-sub shell but not in the valence shell namely sixth shell. The shielding effect of one electron in 4f- sub shell by another in the same sub-shell (i.e. mutual shielding effect of 4f- electrons) is being even smaller than that of d-electrons, because the shape of f sub-shell is very much diffused. The nuclear charge (i.e. atomic number) increases by unity at each step. Thus the nuclear charge increases at each step, while there is no comparable increase in the mutual shielding effect of 4f-electron. This results in that electrons in the outermost shell experience increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic- radii go on decreasing as we move from La₅₇ to Lu₇₁.

Consequences of lanthanide contraction:

Some important consequences of lanthanides contraction are as under:

(i) *High density of post lanthanide elements:*

Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. The arrangement of atoms in metallic lattice is much compact that the densities are very high. The density of 2nd transition series is slightly higher than 1st

transition series, while the densities of 3rd transition series is almost double than 2nd transition series.

(ii) *Basic character of oxides, Ln_2O_3 and hydroxides, $\text{Ln}(\text{OH})_3$:*

There is decrease in basic strength of oxides and hydroxides of lanthanides with increase in atomic number. The basicity decreases as ionic radii decreases. The basicity of Ln^{+3} ions may be expected to decrease in the order, $\text{La}^{+3} > \text{Ce}^{+3} > \text{Pr}^{+3} \dots > \text{Lu}^{+3}$. These differences in basicity are reflected in (a) thermal decomposition of oxy-salts. *i.e.* more basic oxy-salts decompose less easily (b) hydrolysis of ions—more basic ions hydrolyse less readily (c) solubilities of salts (d) formation of complexes and (e) decreasing ease of oxidation of the metals with increasing atomic number—oxidation potential for the couple $\text{Ln} \rightarrow \text{Ln}^{+3} + 3\text{e}^-$ regularly goes on decreasing.

Due to lanthanide contraction the decrease in size of Ln^{+3} ions from La^{+3} to Lu^{+3} increases the covalent character (*i.e.* decreases the ionic character) between Ln^{+3} and OH ions in $\text{Ln}(\text{III})$ hydroxides. Thus $\text{La}(\text{OH})_3$ is the most basic while $\text{Lu}(\text{OH})_3$ is the least basic.

Similarly there is a decrease in the basic strength of the oxides, Ln_2O_3 with the increase of atomic number of Ln-atom.

(iii) Small variation in the properties on account of Lanthanide contraction allows the separation of Lanthanides by the methods based on fractional crystallization and basicity differences.

(iv) The pair of elements *i.e.* Zr-Hf, Nb-Ta, have almost similar size and they are much closer to one another in properties than the pairs of elements of 1st and 2nd transition series, *e.g.* solubilities of their salts are very much similar to one another.

(v) *Occurrence of Y with heavy Lanthanides:*

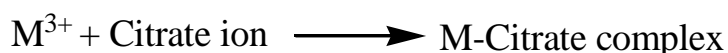
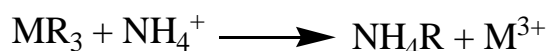
The crystal radii of Y^{+3} and Er^{+3} are equal ($\text{Y}^{+3}=0.93 \text{ \AA}$ and $\text{Er}^{+3}=0.96 \text{ \AA}$). This similarities in atomic size of these two cations coupled with the equality in ionic charge (= +3 in both the ions) accounts for the invariable occurrence of Y with heavier Lanthanides.

Separation of Lanthanides - Ion exchange method:

A synthetic ion-exchange resin with functional groups like --COOH and $\text{--SO}_3\text{H}$ is packed in a long column fixed in a vertical position. The steady decrease in size and consequent decrease in basicity causes the steady increase the complexing ability with increasing atomic number of lanthanides. When an aqueous solution containing the mixture of trivalent lanthanide ion $\text{M}^{+3}(\text{aq})$ is passed through a column having synthetic cation-exchange resin $(\text{HR})_{\text{solid}}$, the M^{+3} ions replace H^+ ion of the resin and thus get fixed on that



Small Lu^{3+} gets more hydrated than La^{3+} and is bigger in size. So $\text{La}^{3+}(\text{aq})$ gets strongly bound to the resin column than others. In order to recover M^{3+} ions fixed on the resin, the column is eluted with a citric acid–ammonium citrate solution (eluant). During elution process NH_4^+ ions replace M^{3+} ion and M-citrate complexes are formed.



A citrate buffer (citric acid/ammonium citrate) solution (which complexes with the lanthanide ions) is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution. Since the smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column. By the correct choice of conditions the lutetium ion, $\text{Lu}^{+3}(\text{aq})$, emerges first from the column, followed by the cations ytterbium, thulium, erbium, etc, in order of increasing ionic radius. By using a long ion-exchange column, the elements may be obtained at 99.9% with one pass. The bigger aquated ion is least strongly held and comes out first. Other ions remain on the column and can be separated by repeated elution.

Applications of lanthanides

1. Use as catalysts: Lanthanide catalysts have been repeatedly recommended for use in numerous organic reactions, including the hydrogenation of ketones to form secondary alcohols, the hydrogenation of olefins to form alkanes, the dehydrogenation of alcohols and butanes, and the formation of polyesters.

2. Use in the glasses industry: Cerium oxides has been found to be a more rapid polishing agent for glass than rouge, and are used in the polishing of lenses for cameras, binoculars, and eyeglasses, as well as in polishing mirrors and television faceplates. Neodymium is added to some glasses to counteract the yellowish tint caused by iron impurities. Very pure neodymium oxide, when added in sufficient quantities (1–5 percent), gives a beautiful purple glass.
3. Use in the metallurgical industry: Small amounts of misch metal and cerium have long been added to other metals or alloys to remove their nonmetallic impurities. Misch metal added to cast iron makes a more malleable nodular iron. Added to some steels, it makes them less brittle. The addition of misch metal to certain alloys has been reported to increase the tensile strength and improve the hot workability and the high-temperature oxidation resistance.
4. Use in the television industry: It has been found that if a small amount of europium oxide (Eu_2O_3) is added to yttrium oxide (Y_2O_3), it gives a brilliant-red phosphor. Colour television screens utilize red, green, and blue phosphors. Some television companies have substituted gadolinium oxide for the yttrium oxide. Considerable amounts of mixed rare-earth fluorides are used to make cored carbon rods, which are used as arcs in searchlights and in some of the lights used by the motion-picture industry.
5. Other applications: Another significant industrial application of rare earths is in the manufacture of strong permanent magnets. Alloys of cobalt with rare earths, such as cobalt–samarium, produce permanent magnets that are far superior to most of the varieties now on the market. Another relatively recent development is the use of a barium phosphate-europium phosphor in a sensitive X-ray film that forms satisfactory images with only half the exposure.

Actinides (5f- Block elements)

Introduction

The elements in which the extra electron enters 5f- orbitals of $(n-2)^{\text{th}}$ main shall are known as 5f-block elements, actinides or actinones. Thus, according to the definition of actinides only thirteen elements from Th_{90} ($5f^0 6d^2 7s^2$) to No_{102} ($5f^{14} 6d^0 7s^2$) should be the members of actinide series. However, all the fifteen elements from Ac_{89} ($5f^0 6d^1 7s^2$) to Lw_{103} ($5f^{14} 6d^1 7s^2$) are considered as the members of actinide series, since all these fifteen elements

have same physical and chemical properties. In fact actinium is prototype of actinides as lanthanum is the prototype of lanthanides.

Electronic configuration of actinides:

General electronic configuration of actinides is $2, 8, 18, 32, 5s^2, p^6 d^{10} f^{0-14}, 6s^2 p^6 d^{0-2}, 7s^2$

Nos.	Name	At. No. and symbol	Electronic configuration
1	Actinium	Ac ₈₉	[Rn] $5f^0 6d^1 7s^2$
2	Thorium	Th ₉₀	[Rn] $5f^0 6d^2 7s^2$
3	Protactinium	Pa ₉₁	[Rn] $5f^2 6d^1 7s^2$
4	Uranium	U ₉₂	[Rn] $5f^3 6d^1 7s^2$
5	Neptunium	Np ₉₃	[Rn] $5f^4 6d^1 7s^2$
6	Plutonium	Pu ₉₄	[Rn] $5f^6 6d^0 7s^2$
7	Americium	Am ₉₅	[Rn] $5f^7 6d^0 7s^2$
8	Curium	Cm ₉₆	[Rn] $5f^7 6d^1 7s^2$
9	Berkelium	Bk ₉₇	[Rn] $5f^9 6d^0 7s^2$
10	Californium	Cf ₉₈	[Rn] $5f^{10} 6d^0 7s^2$
11	Einsteinium	Es ₉₉	[Rn] $5f^{11} 6d^0 7s^2$
12	Fermium	Fm ₁₀₀	[Rn] $5f^{12} 6d^0 7s^2$
13	Mendelevium	Md ₁₀₁	[Rn] $5f^{13} 6d^0 7s^2$
14	Nobelium	No ₁₀₂	[Rn] $5f^{14} 6d^0 7s^2$
15	Lawrencium	Lw ₁₀₃	[Rn] $5f^{14} 6d^1 7s^2$

Oxidation states of actinide elements

Composition of the oxidation states of lanthanides with those of actinides indicates that +3 oxidation state is most common for both the series of elements. The oxidation state of actinide element is given below:

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
						+2								
+3	-	-	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4	+4						
		+5	+5	+5	+5	+5								
			+6	+6	+6	+6								
				+7	+7									

This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series. The increasing stability of +3 oxidation state is illustrated by the increasing difficulty of oxidation above +3 oxidation state. Actinides show a greater multiplicity of oxidation states. Since in the first half of the actinide series (i.e. lower

actinides) the energy required for the conversion $5f \rightarrow 6d$ is less than that required for the conversion $4f \rightarrow 5d$, the lower actinides should show higher oxidation state such as +4, +5, +6 and +7. Correspondingly, since in the second half of the actinide series (i.e. higher actinides), the energy required for the conversion $5f \rightarrow 6d$ is more than that required for the conversion $4f \rightarrow 5d$, and the higher actinides should show more lower oxidation states such as +2. The tripositive oxidation state occurs widely in each series. The two groups of elements are not entirely comparable in this respect. The +3 state characteristic of lanthanides does not appear in aqueous solution of Th and Pa and this oxidation state becomes the predominantly stable oxidation state in aqueous solution of the actinides only when we reach Am. For Th & Pa the +4 & +5 oxidation states are important respectively. From Uranium onward there is very closely related groups U, Np, Pu & Am in which the stability of higher oxidation state takes place.

Magnetic properties of Actinide elements

In the 5f-series, Pu^{+3} and Am^{+3} ions show analogous behavior as noted for Sm^{+3} and Eu^{+3} ions in 4f-series. The magnetic properties of the actinides ions are considerably more difficult to explain than those of the lanthanide ions. The values of magnetic moments found experimentally are usually lower than those calculated using Russell-Saunders coupling scheme. This is due perhaps to the inadequacy of the Russell-Saunders coupling scheme for 5f ions and also to more soluble ligand field effects which involve 5f-orbitals to a greater extent than the 4f-orbitals are involved in bonding in the lanthanide complexes.

An equation used for the calculation of molar susceptibility X_M is given by,

$$X_M = \frac{Ng^2\beta^2 J(J+1)}{3KT} + N\alpha$$

Where N = Avogadro's number, g = Lande splitting factor

Which is given by:

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

$$\begin{aligned}\beta &= \text{Bohr magneton} = \frac{eh}{2\pi mc} \\ &= 9.27 \times 10^{-21} \text{ erg/gauss}\end{aligned}$$

J = Total angular momentums of atom = $|L+S|$ K = Boltzmann constant, T = absolute temperature and α = small temperature independent term due to second order Zeeman effect. Strictly speaking the above equation can be applied only to gaseous ions in which the multiplet intervals are larger compound to KT and value of J to be used in it is taken from the ground state symbols of ions.

Uses of actinides

- Plutonium is used in the manufacture of nuclear weapons and as the power source in nuclear power plants.
- On a smaller scale, Plutonium is also used as a power source in smaller devices such as the heart pacemaker.
- Californium is used in smoke detectors,
- Curium is a power source in space vehicles,
- Americium is utilized in the treatment of cancer.

UNIT IV

POSSIBLE QUESTIONS**PART A – Objective type questions (Each carry 1 mark)**

1. The colour of $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ion is due
 - a. **d-d transition**
 - b. Presence of water molecules
 - c. Inter atomic transfer of electrons
 - d. None of the above
2. The electronic configuration of Lanthanides is filled in
 - a. **f block**
 - b. p block
 - c. d block
 - d. s block
3. The electronic configuration of Actinides is
 - a. 4f orbitals
 - b. **5f orbitals**
 - c. 6f orbitals
 - d. 7f orbitals
4. The lanthanide contraction will affect the
 - a. acidity
 - b. **basicity**
 - c. conductivity
 - d. neutrality
5. the most common oxidation state of lanthanides is
 - a. +2
 - b. +1
 - c. **+3**
 - d. +4
6. The most common oxidation state for d-block elements are
 - a. +1
 - b. **+2**
 - c. +3
 - d. +4
7. Lanthanides are extracted from
 - a. Limonite
 - b. **Monazite**
 - c. Magnetite
 - d. Cassiterite
8. The elements in which the extra electron enters (n-2)f orbitals are called
 - a. s block elements
 - b. p block elements
 - c. d block elements
 - d. **f block elements**
9. The Lanthanides contraction is due to
 - a. Perfect shielding of 4f electron
 - b. **imperfect shielding of 4f electron**
 - c. Perfect shielding of 3d electron
 - d. imperfect shielding of 3d electron
10. Ceria is used in
 - a. toys
 - b. Tracer bullets
 - c. **gas lamp materials**
 - d. none of the above
11. All the transition elements show Character
 - a. **Metallic**
 - b. insulating
 - c. super conducting
 - d. semi conducting
12. Lanthanides are separated by
 - a. Steam distillation
 - b. **Fractional crystallization**
 - c. Fractional distillation
 - d. Sublimation
13. Which of the following forms oxocations
 - a. Alkalis
 - b. lanthanides
 - c. **actinides**
 - d. inert gases

14. Maximum oxidation states for lanthanides are
a. +3 **b. +4** c. +5 d. +8
15. Alloys of lanthanides are called
a. Misch metals b. pyroboric alloy c. brassd. nichrome
16. Lanthanides are also called
a. alkali metals b. alkaline earth metals **c. rare earth metals** d. inert metals
17. Common oxidation state for lanthanides is
a. +1 b. +2 **c. +3** d. +4
18. The main ore of uranium is
a. carnotite b. bauxite c. carnolite d. zincite
19. Actinide contraction is caused by due to
a. 6d orbital **b. 5f orbital** c. 5d orbital d. 4f orbital
20. The only radioactive element in lanthanides
a. La b. Hf **c. Pm** d. Os

PART B (Each carry 2 marks)

1. Why lanthanoids are paramagnetic in nature?
2. Why maximum numbers of actinides are radio active in nature?
3. Write any two uses of lanthanides.
4. Why do actinides show higher oxidation states than lanthanides?
5. What are lanthanides? Give the variations in oxidation number.
6. Write any two uses of actinides.
7. What is meant by lanthanide contraction?

PART C (Each carry 6 marks)

1. What are lanthanides? Describe ion exchange method for the separation of lanthanides
2. Write a note on lanthanide contraction.
3. Write the differences between lanthanides and actinides
4. Explain the electronic configuration, colour, oxidation states of f-block elements in the periodic table

5. Write a note on contraction and electronic configuration of actinides.
6. Explain one method for extract the lanthanides.
7. Explain the magnetic properties of Lanthanides.
8. Discuss the differences between lanthanides and actinides

[16CHU302]

Batch: 2016-2019

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY

INORGANIC CHEMISTRY-II (Coordination Chemistry)

Semester –III

Multiple Choice Questions for on line examination (Each question carry one mark)

UNIT-IV

S. No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	The electronic configuration of Lanthanides is filled in	f block	p block	d block	s block	f block
2	The electronic configuration of Actinides is	4f orbitals	5f orbitals	6f orbitals	7f orbitals	5f orbitals
3	The lanthanide contraction will affect the	acidity	basicity	conductivity	neutrality	basicity
4	the most common oxidation state of lanthanides is	1	2	3	4	3
5	Lanthanides are extracted from	Limonite	Monazite	Magnetite	Cassiterite	Monazite
6	The elements in which the extra electron enters (n-2)f orbitals are called	s block elements	p block elements	d block elements	f block elements	f block elements
7	The Lanthanides contraction is due to	Perfect shielding of 3d electron	imperfect shielding of 4f electron	Perfect shielding of 4f electron	imperfect shielding of 3d electron	imperfect shielding of 4f electron
8	Ceria is used in	toys	Tracer bullets	gas lamp	none of the	gas lamp

				materials	above	materials
9	Lanthanides are separated by	Steam distillation	Fractional crystallization	Fractional distillation	Sublimation	Fractional crystallization
10	Which of the following forms oxocations	Alkalis	lanthanides	actinides	inert gases	actinides
11	Maximum oxidation states foe lanthanides are	3	4	6	8	4
12	Alloys of lanthanides are called	Mish metals	pyroboric alloy	brass	nichrome	Mish metals
13	Lanthanides are also called	alkali metals	alkaline earth metals	rare earth metals	inert metals	rare earth metals
14	Common oxidation state for lanthanides is	1	2	3	4	3
15	The main ore of uranium is	bauxite	carnitite	carnolite	zincite	carnitite
16	Actinide contraction is caused by due to	6d orbital	5f orbital	5d orbital	4f orbital	5f orbital
17	The only radioactive element in lanthanides	Hf	La	Pm	Os	Pm
18	Thorium was first discovered by	Chadwick	Newland	Goldstein	Berzelius	Berzelius
19	The oxides of lanthanide is called	Cerite	araldite	cuprite	zincite	Cerite
20	The maximum oxidation state for actinides is	4	5	6	7	7
21	the color of transition in lanthanides is due to	d-d transition	s-s transition	f-f transition	f-d transition	f-f transition
22	the color region for lanthanides	2000-5000	2000-10000	5000-10000	0-2000	2000-10000
23	on moving Ce to Lu in the radii is	increases	decreases	no change	zero	decreases
24	compare lanthanides, actinides are in nature	colored	non colored	diamagnetic	ferromagnetic	colored
25	lanthanides and actinides are enter into Shell	(n-2)d	(n-2)f	(n-1)f	(n-1)d	(n-2)f
26	Among all the lanthanides Is the most abundant element	lanthanum	cerium	lutetium	gadolinium	cerium
27 is the less abundant element is lanthanides	lanthanum	thallium	lutetium	gadolinium	thallium
28	In aqueous solutions lanthanides exhibit	2	3	4	5	3

 oxidation state					
29	Which state is stable for lanthanides	monopositive	dipositive	tripositive	zero state	v
30 has maximum magnetic property in lanthanides	lanthanum	cerium	holmium	erbium	holmium
31	Pr ³⁺ exhibit color	pink	green	yellow	red	pink
32	the color of the La ³⁺ is	red	colorless	pink	yellow	colorless
33	the color of the lanthanides was explained by	smith	tanabe	bailey	rossey	smith
34	Due to the lanthanide contraction ionic radii is	increases	decreases	zero	non zero	decreases
35	Based on lanthanide contraction of their salts are closed to each other	conductivity	solubility	color	magnetism	solubility
36 is the f-block element but it is belongs to d-block	Thorium	cerium	samarium	yttrium	yttrium
37	the formation of bond which affect the complex formation of f orbitals	ionic	hydrogen	covalent	coordination	covalent
38	lanthanides are highly dense metals and they possess high	boiling point	melting point	ionization energy	electrode potential	melting point
39	The percentage of cerium in pyrophoric alloys	40.5	45.5	50.5	35.5	40.5
40	the important use of pyrophoric alloy is making	toys	gun	tracer bullets	box	tracer bullets
41	lanthanides are easily react with to liberate	oxygen	ammonia	nitrogen	hydrogen	hydrogen
42	In actinides has +2 oxidation state	curium	actinium	americium	fermium	americium
43	All the actinides in nature	conductive	radioactive	nonmetallic	inert	radioactive
44	actinides are basic than actinides	high	low	zero	no	high
45	Misch metal is used to making parts of	gun	toys	jet engine	aero plane	jet engine
46 Salts are used in medicine	cerium	thallium	thorium	samarium	cerium
47	In petroleum industry is used as a catalyst	Nd ₂ O ₄	Ce ₂ O ₃	La(OH) ₃	Pr ₂ O ₃	Ce ₂ O ₃
48 is used in glass industry	Nd ₂ O ₄	Ce ₂ O ₃	La(OH) ₃	PrO	Nd ₂ O ₄

49	In the treatment of cancer is used as a medicine	cerium	thallium	thorium	lanthanum	thorium
50	uranium and plutonium are used as for nuclear reactors	moderators	fuel	desiccator	control rods	fuel
51	In the making of incandescent lights Are used	ceria	thoria	alumina	magnesia	thoria
52	When ionic radii is increased, the stability of the complexes are	a. increased	b. decreased	c. no change	d. maintained	b. decreased
53	The electronic configuration of Lanthanides is filled in	f block	p block	d block	s block	f block
54	The electronic configuration of Actinides is	4f orbitals	5f orbitals	6f orbitals	7f orbitals	5f orbitals
55	The lanthanide contraction will affect the	acidity	basicity	conductivity	neutrality	basicity
56	the most common oxidation state of lanthanides is	1	2	3	4	3
57	Lanthanides are extracted from	Limonite	Monazite	Magnetite	Cassiterite	Monazite
58	The elements in which the extra electron enters (n-2)f orbitals are called	s block elements	p block elements	d block elements	f block elements	f block elements
59	The Lanthanides contraction is due to	Perfect shielding of 3d electron	imperfect shielding of 4f electron	Perfect shielding of 4f electron	imperfect shielding of 3d electron	imperfect shielding of 4f electron
60	Ceria is used in	toys	Tracer bullets	gas lamp materials	none of the above	gas lamp materials

UNIT V

Inorganic Reaction Mechanism

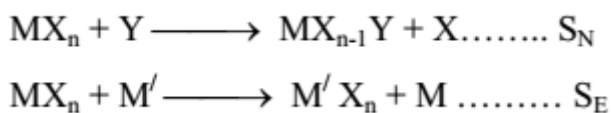
Introduction to inorganic reaction mechanisms. Substitution reactions in square planar complexes, Trans- effect, theories of trans effect. Thermodynamic and Kinetic stability.

Introduction to inorganic reaction mechanisms

Ligand substitution reactions of coordination complexes can be illustrated by the general equation,



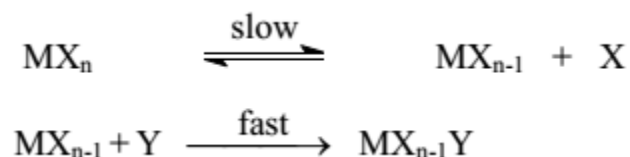
where 'M' is a metal atom or ion and 'X', 'Y' are any two ligands. For simplicity the charges have been ignored. In keeping with organic chemistry terminology, substitution reactions have been conveniently divided into nucleophilic (S_N) and electrophilic (S_E) substitutions:



Electrophilic substitution mechanisms will not be considered further. For a ligand substitution process, S_N mechanisms are relevant and can be further subdivided into two paths like:

(i) S_N1 dissociation (substitution, nucleophilic, unimolecular):

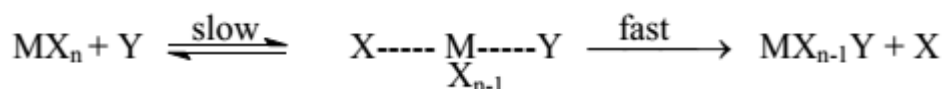
This type of reaction can be illustrated as:



Such reactions are insensitive to the nature of the incoming nucleophile, 'Y', but sensitive to the leaving group 'X' and reach the transition state principally by the internal accumulation of the energy to break the bond to the leaving group. The detection of an intermediate of reduced coordination number is the best diagnosis of the S_N1 mechanism.

(ii) S_N2 displacement (substitution, nucleophilic, bimolecular):

This type of reaction involves a bimolecular rate determining step followed by a rapid cleavage of 'X'



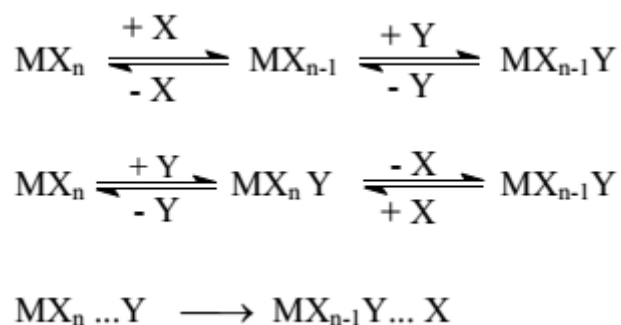
These reactions are affected by the nature of the entering group. Stereospecificity *i.e.* retention of configuration suggests an $\text{S}_{\text{N}}2$ reaction.

One of the great complicating factors in assigning mechanism of substitution reactions is the existence of borderline mechanism or intermediate mechanism between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$. Depending upon the nature of participation of entering ligand in the transition state, it has been suggested to classify ligand substitution reactions into four categories:

- (a) $\text{S}_{\text{N}}1$ (lim), where the rate determining step involves only bond breaking and definite evidence for intermediate with reduced coordination number exists;
- (b) $\text{S}_{\text{N}}1$, in which bond breaking is important in the rate determining step but no evidence for the existence of intermediate of reduced coordination can be presented;
- (c) $\text{S}_{\text{N}}2$ (lim), in which the rate determining step involves only ligand-substrate bond making and definite evidence for intermediate of increased coordination number exists;
- (d) $\text{S}_{\text{N}}2$, in which the rate determining step involves about equal bond making and bond breaking in the transition state.

An alternative classification has been proposed by Langford and Stengle. According to them the ligand substitution processes can be classified in terms of stoichiometric and intimate mechanism. Stoichiometric mechanism relates to the identification of the sequence of elementary steps involved in a complicated overall reaction. Intimate mechanism is the understanding of the magnitude of the rate constants for the individual steps in terms of rearrangements of atoms and bonds.

Stoichiometric Mechanism: Three paths for ligand substitutions are illustrated below:



In dissociative path (D), the leaving ligand is lost in the first step, producing an intermediate of reduced coordination number. In associative (A) path the entering ligand adds to the complex in the first step, producing an intermediate of increased coordination number. In the concerted path termed interchange (I), the leaving group is moving from the inner to outer sphere while the entering group is moving from outer to inner sphere.

Intimate mechanism: Two categories of intimate mechanism may be distinguished operationally.

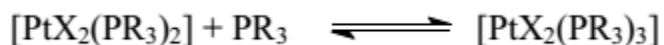
1. Associative activation (a): The reaction rate is approximately as sensitive to variation of the entering group as to variation of the leaving group.
2. Dissociative activation (d): The reaction rate is much more sensitive to variation of the leaving group than to the variation of the entering group.

D mechanism must be dissociative. A mechanism must be associative. 'I' reaction may have a variety of transition states, but two well-defined types will be those resembling the transition state of A and D reactions. The A-like transition in an 'I' process will display substantial bonding to both the entering and leaving groups, and the entering group will display an important part in determining its energy. Such a transition state in an I path will be indicated by adding a notation 'a'. The D-like transition state of I reaction is one with only weak bonding to both the entering and leaving groups (the bonding may be very weak indeed). The entering group effect on the reaction rate will be small. Such an 'I' process will be denoted with an added d. However, the effect of charge and size of the central metal ion influences the mechanism of a reaction.

6 Assessment of the mechanism for square planar substitutions

It is now established beyond doubt that the intimate mechanism of square planar substitution is a type i.e. the energy of the transition state is profoundly affected by the nature of the entering group. The theoretical considerations lead to the conclusion that planar d^8 substitutions are ideal cases for an associative mechanism involving a five coordinated intermediate or transition state. Isolation of such intermediate depends on the presence of deep potential wells along the reaction profile. The presence of such minima depends on a number of factors, which are difficult to understand and cannot be easily predicted. For example, there is good evidence that all the reactions of tertiary phosphines with bis- β -diketonato complexes of Pt(II) and Pd(II) proceed *via* five coordinated species. Though some can be isolated, others can only be detected spectroscopically and many cannot be observed at all.

A necessary consequence of assigning these five coordinated species as intermediate or transition state is that the five coordinated d^8 molecules show a tendency to lose a ligand. For example, NMR spectroscopic measurements show that five coordinated $[\text{PdBr}_2(\text{PMe}_3)_3]$ and $[\text{PdBr}(\text{PMe}_3)_4]^{4+}$ readily lose Br^- and PMe_3 respectively in CD_2Cl_2 solution. Several examples of four and five coordination equilibrium of the type (1.40) have been detected by variable temperature NMR spectroscopy.



For the five coordinated species there are two possibilities, depending on whether the detailed mechanism is A or I_a . In the A process, there is a minimum in the plot of free energy versus reaction coordinate, corresponding to a symmetrical (D_{3h}) trigonalbipyramidal structure. In the I_a process, the symmetric trigonal bipyramid is the highest energy structure and is the transition state. The validity of the A mechanism is certainly strongly suggested by the impressive correlation of a wide variety of substituent effects based on a process that proceed through an approximately trigonal bipyramidal transition state and a trigonal bipyramidal intermediate. Intimate analysis of the five coordinate transition state shows that the three ligands, that occupy the trigonal plane in the trigonal bipyramidal, may take advantage of certain σ - and π -bonding possibilities which are substantially changed from the ground state square planar complex. On the other hand, the bonding situation of the apical ligands is not appreciably different from the ground state complex. Thus, the assumption of an approximately trigonal bipyramidal geometry

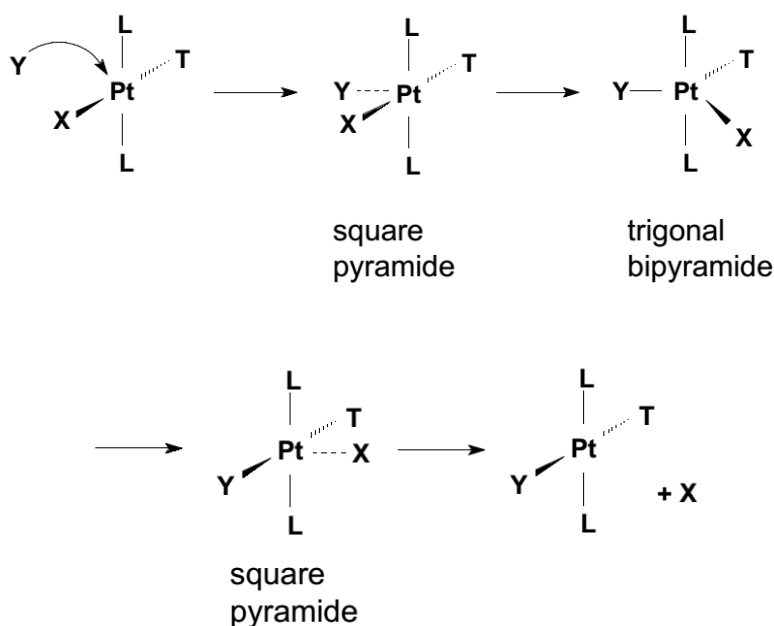
for the transition state correctly predicts relatively large substituent effects for the ligands in the trigonal plane (the *trans*, entering, and leaving groups) and relatively small effects for the apical ligands (the *cis* groups).

Substitution in Square Planar Metal Complexes

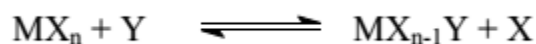
Extensively studied for square planar Ni^{2+} , Pd^{2+} and Pt^{2+} (d^8) substitutions in water and non-polar solvents:



- Almost all examples of square planar geometry are d^8 electron counts so electron counts are not a factor.
- However, ΔCFSE going from square planar to TBP geometry is still unfavourable by $0.242\Delta_{\text{oct}}$ so this adds to the barrier for square planar substitution and this is one of the main reasons why square planar substitution is slower for 2nd and 3rd row metals.
- Metal ions with d^8 configuration (Rh^{I} , Ir^{I} , Pt^{II} , Pd^{II} , Au^{III}).
- Best studied: $\text{Pt}(\text{II})$ complexes rate of ligand substitution relatively slow and it convenient to measure.
- Nucleophilic substitution reactions in square planar $\text{Pt}(\text{II})$ complexes usually proceed by an associative mechanism.
- Substitution at square planar $\text{Pt}(\text{II})$ is stereoretentive.

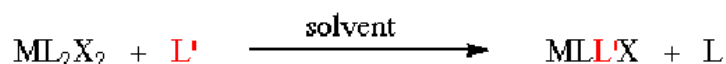


The most fundamental reaction a complex can undergo is ligand substitution reaction, a reaction in which one Lewis base displaces another from a Lewis acid:



This class of reaction includes complex formation, in which the leaving group, the displaced base X and the entering group, the displacing base Y, is some other ligand (one of the ligands involved is often also the solvent species). The rates of such reactions vary widely, ranging from completion within the time for reactant mixing to years. H. Taube called complexes having substitution half life $t_{1/2} < 30$ sec as labile and called those with longer $t_{1/2}$ as inert. Studying reactions of labile complexes require techniques such as stopped-flow, P-jump, or T-jump (in which system at equilibrium is perturbed by a sudden change in pressure or temperature and its relaxation to a new equilibrium monitored).

Factors are affecting the substitution reactions in square planar complexes



The following factors are affecting the substitution reaction in square planar complexes

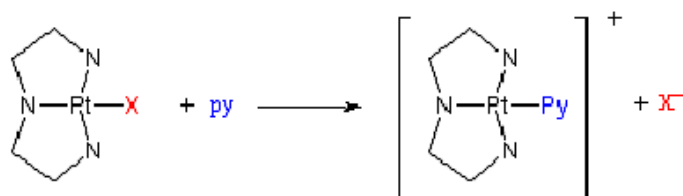
- i). Role of the Entering Group
- ii). The Role of The Leaving Group
- iii). The Nature of the Other Ligands in the Complex
- iv). Effect of the Metal Centre
- i). Role of the Entering Group*

„ The rate of substitution is proportional to the nucleophilicity of entering group i.e. for most reactions of Pt(II). The rate constant increases in the order: $\text{H}_2\text{O} < \text{NH}_3 = \text{py} < \text{Br}^- < \text{I}^- < \text{CN}^-$. The ordering is consistent with Pt(II) being a soft metal centre.

- ii). The Role Of The Leaving Group*



For the reaction in H_2O at 250 C the sequence of lability is; $\text{H}_2\text{O} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{N}_3^- > \text{SCN}^- > \text{NO}_2^- > \text{CN}^-$ with a spread of over 10^6 in rate across series.



The leaving group does not affect the nucleophilic discrimination factors only the intrinsic reactivity. The series tend to parallel the strength of the Metal-L bond

iii). *The nature of other ligands in the complex*

Nature of the ligands present in the complex also affects the substitution reactions.

Trans effect

Definition

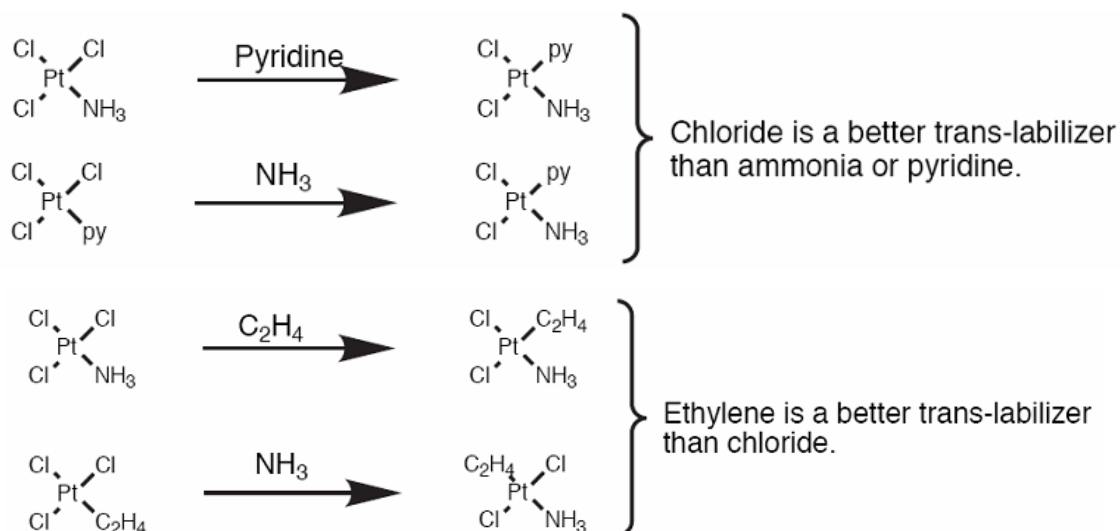
“The trans effect is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.”

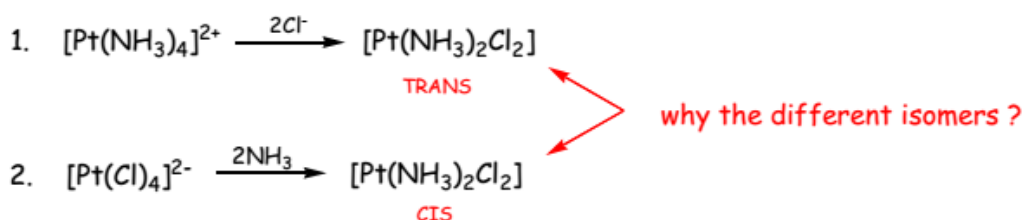
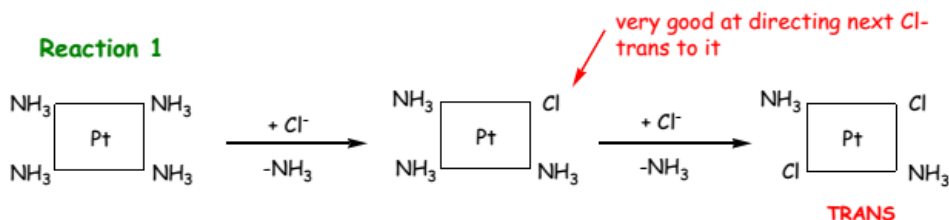
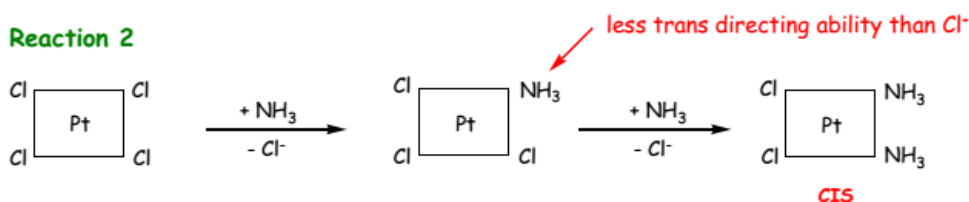
OR

“The ability of a ligand in a square planar complex to direct the replacement if the ligand trans to it.”

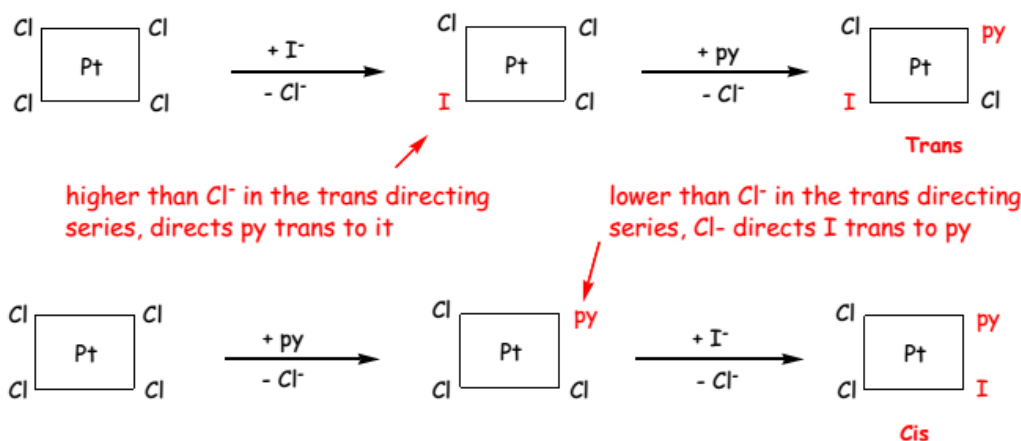
The trans effect is given as the following series:

$\text{CN}^- > \text{NO}_2^- > \text{I}^- = \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{NH}_3 > \text{H}_2\text{O}$



**Reaction 1****Reaction 2****Conclusion:**

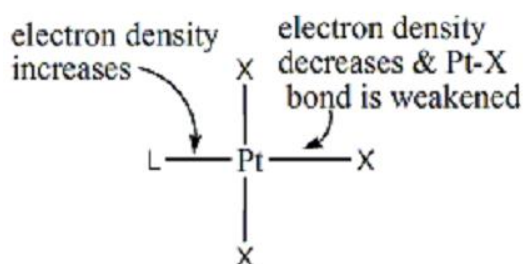
- Cl^- has a greater *trans* directing effect than NH_3 . Trans directing series $\text{Cl}^- > \text{NH}_3$.
- Depends on order in which the reagents are added as to which geometric isomer is formed so has uses for devising synthesis of Pt(II) complexes.
- e.g. consider the preparation of *cis* and *trans* $\text{PtCl}_2\text{I}(\text{py})$ from $[\text{PtCl}_4]^{2-}$, I^- and py.

 **π -bonding theory**

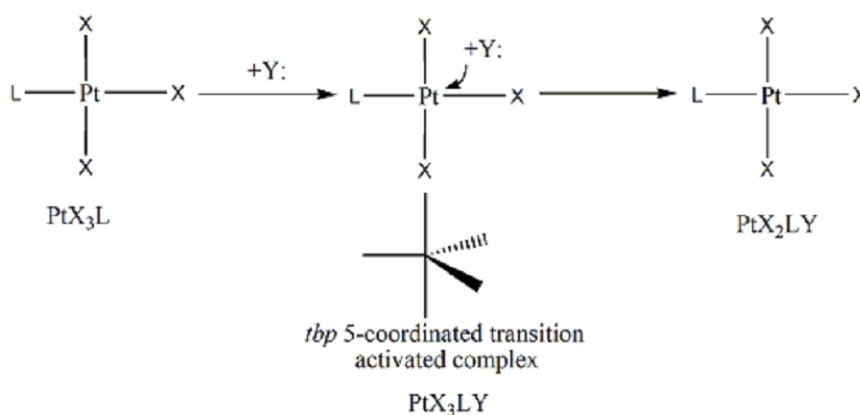
The Chatt (1955) and Orgel (1956) explained the high trans effect of the π -bonding ligands like PR_3 , NO, CO, C_2H_4 , CN and given π -bonding theory of trans effect.

According to this theory the vacant π and π^* orbitals of the π -bonding ligands accept a pair of electrons from the filled d-orbitals of the metal (d_{xz} and d_{yz} orbital) to form metal ligand π -bond ($d\pi - d\pi$ or $d\pi - p\pi$ bond).

In case of Pt(II) square-planar complexes, PtX_2L (L is the π -bonding ligand) the d_{yz} orbital of Pt(II) with a pair of electrons overlaps with the empty p_z orbital of the π -bonding ligand, L to form the $d\pi-p\pi$ bond between Pt(II) and L. The formation of π -bond in the complex increases the electron density in the direction of L and diminishes it in the direction of the ligand, X trans to L. Thus Pt-X bond trans to L is weakened.



The weakening of Pt-X bond trans to L facilitates the approach of the entering ligand, say Y: with its lone pair in the direction of diminished electron density to form the five coordinated transition state complex, PtLX_3Y , which on losing X yields PtLX_2Y . In the formation of PtLX_3Y the ligand trans to L is replaced by the incoming group, Y. The transition state complex has distorted *trigonal-bipyramidal* (*tbp*) structure in which two X's groups which are cis to L both in the initial and final states form the apexes.



The formation of $d\pi-p\pi$ bond between Pt(II) and π -bonding ligand, L in the 5-coordinated transition activated complex as in the below cited **Figure 1** Smaller d-orbital lobes adjacent to the group X which is to be replaced by Y may be marked in the figure.

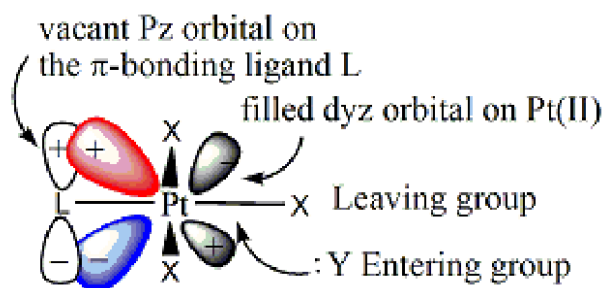


Figure 1: Formation of $d\pi$ - $d\pi$ bond in the 5-coordinated activated complex formed during the substitution reaction in Pt(II) square planar complex $PtLX_3$



A Schematic representation of double bond in $Pt-PR_3$ is shown in **Figure 2**. π -bond is formed by the donation of a pair of electrons from the phosphorous to platinum and the π -bond by the overlap of filled d-orbital of platinum and a vacant d-orbital of phosphorous atom. If the ligand PR_3 and X are in the xy plane, the d-orbital shown in either d_{xz} or d_{yz} .

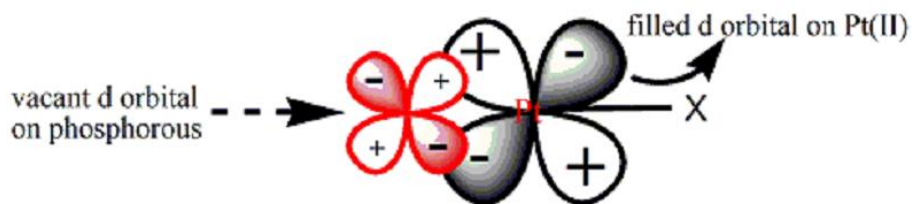


Figure 2: Schematic representation of R_3P-Pt double bond

Chatt *et al* emphasises that the removal of charge from Pt(II) by π -bonding of L enhances the addition of the entering group, Y and favours a more rapid reaction. According to Orgel the formation of π -bond between Pt(II) and π -bonding ligand L enhances the stability of the 5-coordinated transition state complex, thus lowering the activation energy for its formation and speeding up the reaction.

The formation of π -bond weakens the metal-ligand bond trans to a π -bonding ligand is evident from the fact that in the square-planar complex anion, $[(C_2H_4)PtCl_3]^-$, the Pt-Cl bond trans to C_2H_4 is slightly larger than those cis to C_2H_4 . Pt-trans-Cl stretching frequency is lower than the average of the two Pt cis-Cl frequencies. Lower the frequency, the weaker (i.e. longer) the bond.

STABILITY OF THE CPMPLEXES

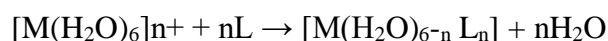
The use of the term stability is without any qualification means that complex is existent under suitable condition and it is possible to store complex for appreciable time.

The use of term stability is general because the coordination compounds are stable in one reagent but dissociate or decompose in presence of another reagent. It is also possible that term stability can be referred as an action of heat or light or compound. The stability of complex is expressed qualitatively in terms of

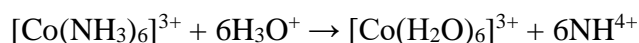
- (i) Thermodynamic stability (ii) Kinetic stability

THERMODYNAMIC STABILITY:

It is the measure of extent of formation or transformation of complex under given set of condition at equilibrium. Thermodynamic stability depends on the strength of bond between metal ligand. The most of complexes are highly stable but they are dissociated in aqueous solution to some extent. The strength of bond between metal and ligand varies widely. For example the complexes like $[\text{Co}(\text{SCN})_4]^{2+}$ ion the bond is very weak and on dilution, it breaks immediately and forms another compound.



On the other hand, the complex of $[\text{Fe}(\text{CN})_6]^{3-}$ the bond is stronger in aqueous solution and in this complex Fe^{3+} cannot be detected by any sensitive reagent. So it is indicated that thermodynamic stability deals with metal-ligand bond energy, stability constant and other thermodynamic parameters. In terms of thermodynamic stability, the complexes are referred as stable and unstable. The thermodynamic stability of the species is the measure of extent to which species will be formed or transformed into other species under certain condition when system attained equilibrium. The tetra cyano nickelate ion is a good example of thermodynamically stable complex that is kinetically labile. The classic example of the opposite case. i.e. a kinetically inert complex and thermodynamically unstable is the Hexa amine cobalt(III) cation in acid solution. It is expected to decompose:



The tremendous thermodynamic driving force of six basic ammonia molecules combining with six protons results in an equilibrium constant for the above reaction of value 10^{25} . Nevertheless acidification of a solution of Hexamine cobalt(III) results in on immediate

change and several days are required (at room temperature) for degradation of the complex despite the favourable thermodynamics. The inertness of the complex results from the absence of a suitable low-energy pathway for the acidolysis reaction. The difference between stability and inertness can be expressed thermodynamically; a stable complex has large positive free energies of reaction ΔG^0 . The standard enthalpy change, ΔH^0 for this reaction is related to the equilibrium constant, β_n by the well thermodynamic equation.

$$\Delta G^0 = -RT \ln \beta$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

For similar complexes of various ions of the same charge of a particular transition series and particular ligand, ΔS^0 values would not differ substantially and hence a change in ΔH^0 value be related to change in β_n values. So order of values of ΔH^0 is also the order of the β_n value.

KINETIC STABILITY:

It is referred to rate or speed at which a complex formation or transformation reaction proceeds at equilibrium. Time factors play an important role in deciding the kinetic stability of the complex. The kinetic stability deals with the rate and mechanism of a chemical reaction. In kinetic stability, hence the complexes are referred as “inert” or “labile”. Tabe had used term “Inert” for thermodynamically stable complexes and “labile” for reactive complexes. The exceptions are complexes of some Polydentate ligands like the naturally occurring chlorophyll which is extremely inert to exchange with Mg^{2+} ion in solution, the extended conjugation helps making the ring rigid. The effect of EDTA addition upon homeostatic equilibrium of some trace elements, including copper has been evaluated by some workers in terms of simplified blood plasma model.

VARIOUS FACTORS AFFECTING THE STABILITY OF COORDINATION COMPOUNDS

Following factors are affecting the stability of coordination compounds

(1) Nature of the Central Metal Ion

(i) Ionic Size

(ii) Ionic Charge

(2) Nature of the Ligand

- (i) Size and Charge
 - (ii) Basic Character
 - (iii) Ligand Concentration
- (3) Chelate Effect
- (i) Ring Size
 - (ii) Number of Rings
 - (iii) Effect of Substitution
 - (iv) Macrocyclic effect

[1] Nature of Central Metal Ion:

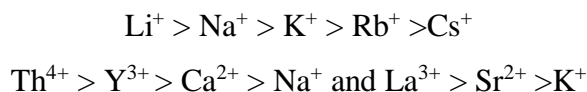
The important characteristics of the metal atom in determining stability of the complexes are given below.

(i) *Ionic Size:*

The stability of coordination compound (complex) decreases with increase in size of metal ion. Zn(II) forms more stable complexes than Cd(II). The size of Zn(II) ion is 0.74\AA and Cd(II) 0.97\AA .

(ii) *Ionic Charge:*

The effect of ionic charge of the central metal ion on the stability of coordination compounds may be described by comparing the change in stability in a series of complexes by changing the ionic charge on metal ion. If the charge of the central metal ion is more and the size is small, then the stability of the complex is more. In general, the small and highly charged cation can form more stable coordinate compounds because of most stable coordinate bonds.



[2] Nature of the Ligand:

Nature of the ligand or important characteristics of ligand affects to determine the stability of the compounds is explained in the following manner

(i) *Size and Charge:*

Ligands with less charge and more size are less stable and form less stable coordination compounds. Ligands with higher charge have small size and form more stable compounds.

More size \rightarrow Less Stable \leftarrow Less Charge

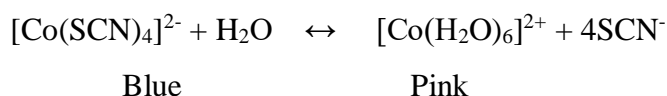
Small size \rightarrow More stable \leftarrow More Charge

(ii) Basic Character:

Calvin and Wilson suggested that the higher basic character or strength of the ligand, higher will be the stability of coordination compounds. It is defined that a strong base or higher basic strength of the ligand means it forms more stable compounds or its donating tendency of electron to central metal ion is higher. *e.g.* Aromatic diamines form unstable coordination compounds while aliphatic diamines form stable coordination compounds. Ligands like NH_3 , CN^- etc have more basic character that means they form more stable compounds.

(iii) Ligand Concentration:

Some coordination complexes exist in aqueous solution only in presence of higher concentration of coordination group. In some cases aqueous molecules show greater coordinating tendency than the coordinating group which is originally present. *e.g.* in presence of highly concentrated solution of SCN^- (thiocyanate ion), the Co^{2+} metal ion forms a stable blue colored coordination complex but on dilution in aqueous medium the blue complex is destroyed and a pink aqua complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is formed and then by further addition of ligand (SCN^-) pink color disappears.



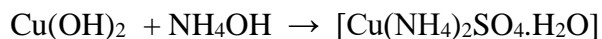
The color change indicates that there is a competition between $\text{H}_2\text{O}/\text{SCN}^-$ in formation of complex with $\text{Co}(\text{II})$ ion.

In the synthesis of tetra amine cupric sulphate complex at lower concentration of ammonia forms copper hydroxide, while at higher concentration of ligand form following complex.

Small concentration of ligand

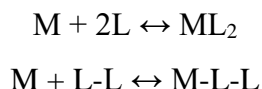


High concentration of ligand



[3] Chelate Effect:

The process of forming metal chelate by the attachment of multidentate ligand with central metal ion in which ligand act as chelating agent is known as chelation. Chelation is expressed by the following unidentate and bidentate ligand reaction.



Morgan proposed the term chelate to describe the cyclic structure which arises by multidentate (poly) ligand and a metal ion. The name chelate is derived from the Greek word 'CHELA' means 'CLAW OF LOBSTER OR CRAB'.

Multidentate ligands form more stable coordination compounds than monodentate ligands. In 1937 Dielh gave the comprehensive review of the chelate rings and more recent treatment is given by Martell and Calvin who gave the review of the unusually high stability of metal chelate compounds.

Following factors are of great importance in chelate formation.

(i) Ring Size:

The stability of chelate is depending on the size of chelate ring. The stability of coordination complex increases with number of chelate ring. It is found that 4-membered rings are unstable and rare than 5-membered rings which are common and stable. For chelate (saturated chelate) rings the following is the decreasing order of stability with increasing ring size

Five membered > Six membered > Seven membered

The stability of metal chelates decrease by increasing the chelate size.

UNIT V**Possible Questions****PART A – Objective type questions (Each carry 1 mark)**

- Another name of stable complexes is
a. **penetration** b. labile c. inert d. dilution
18. Labile complexes are belongs to stability
a. thermal b. **kinetic** c. stable d. none of these
- kinetic stability is based on the Of the reactions
a. order b. number c. **rate** d. degree
- Labile complexes are those whose ligands in which replaced
a. uniformly b. **rapidly** c. one by one d. doesn't replaced
- An ability to replace one or more ligand by other ligands are called
a. inert b. **labile** c. stability d. instability
- Labile and inert complexes are classified by
a. Biltz b. Stobe c. **Taube** d. Tanabe
- Square planar complexes formed by the Mechanism
a. S_N1 b. E^1CB c. E^1 d. **S_N2**
- The group Which direct the entering ligand to occupy the *trans* position
a. NO_2 b. Cl^- c. H_2O d. en
- Stability constant was introduced by
a. Sachey b. **Irving** c. Glasco d. Taffel
- Chelating effect present in membered complexes
a. Three b. four c. **five** d. none
- Determination of stability constants are calculated by using
a. ohm's law b. **Beer's law** c. Lambert's law d. Charles law
- Which ligand presents in the first of the trans effect series
a. CO b. F^- c. NO d. **CN^-**
- The stability constant is denoted as
a. μ b. **β** c. γ d. α
- Trans effect has been increased when polarisability
a. decreases b. **increases** c. zero d. no change

15. The main application of the Trans effect is to analyze the synthesis of complexes
a. Pt b. Cu c. Fe d. Co
16. Electrostatic polarization theory is not applicable for
 a. μ bond **b. π bond** c. σ bond d. α bond
17. When ionic radii is increased, the stability of the complexes are
 a. increased **b. decreased** c. no change d. maintained
18. Chelating ligands are formed Complexes
 a. unstable **b. stable** c. neutral d. semi stable
19. π -bonding theory is explained the complex
 a. octahedral b. tetrahedral **c. square planar** d. pyramidal
20. Which of the following is an example for non-conducting solvent?
 a. CCl_4 **b. C_6H_6** c. DMSO d. ROH

PART B (Each carry 2 marks)

1. What is Trans effect?
2. What is kinetic stability?
3. What is π -bonding theory?
4. Write any two applications of Trans effect
5. Write the theories of trans effect.
6. Define square planar complexes.

PART C (Each carry 6 marks)

1. Discuss the π -bonding and electrostatic theories with example
2. Discuss the factors affecting the stability of metal complexes
3. Explain Trans effect with example

4. Discuss the stability of the complexes with example
5. Discuss the factors are affecting the substitution reactions in square planar complexes
6. Explain how the nature of metal ion and ligand affect the stability of the complexes
7. Explain the theories of Trans effect with examples
8. Discuss the factors affecting the stability of metal complexes
9. What is Trans effect? How does it influence substitution in square planar complexes?

[16CHU302]

Batch: 2016-2019

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COIMBATORE-641 021

DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY

INORGANIC CHEMISTRY-II (Coordination Chemistry)

Semester –III

Multiple Choice Questions for on line examination (Each question carry one mark)

UNIT-V

S. No	Questions	Option 1	Option 2	Option 3	Option 4	Answer
1	Chelating ligands are formed Complexes	a. unstable	b. stable	c. neutral	d. semi stable	b. stable
2	The outermost configuration of La is	$5d^1 4s^2$	$5d^2 4s^2$	$5d^0 6s^2$	$4f^1 6s^2$	$5d^1 4s^2$
3	The radii of lanthanides are decrease because of	contraction	expansion	limitation	elongation	contraction
4	The no of unpaired electrons in La^{3+}	0	1	2	3	0
5	The no of unpaired electrons in Gd^{3+}	3	4	6	7	7
6	The bohr magneton value of La^{3+} is	1.1	2.3	0	3.5	0
7	The bohr magneton value of Dy^{3+} is	7.9	8.5	10.6	10.65	10.65
8	π -bonding theory is explained the complex	a. octahedral	b. tetrahedral	c. square planar	d. pyramidal	c. square planar
9	Which of the following is an example for non-conducting solvent?	a. CCl_4	d. ROH	b. C_6H_6	c. DMSO	a. CCl_4
10	The stability constant is denoted as	a. μ	b. β	c. γ	d. α	b. β
11	Trans effect has been increased when polarisability	a. decreases	b. increases	c. zero	d. no change	b. increases
12	The main application of the Trans effect is to analyze the synthesis of complexes	a. Pt	b. Cu	c. Fe	d. Co	a. Pt
13	Electrostatic polarization theory is not applicable for	a. μ bond	b. π bond	c. Σ bond	d. α bond	b. π bond

14	Stability constant was introduced by	a. Sachse	b. Irving	c. Glasco	d. Taffel	b. Irving
15	Chelating effect present in membered complexes	a. Three	b. four	c. five	d. none	c. five
16	Determination of stability constants are calculated by using	a. ohm's law	b. Beer's law	c. Lambert's law	d. Charles law	b. Beer's law
17	Which ligand presents in the first of the trans effect series	a. CO	b. F ⁻	c. NO	d. CN ⁻	d. CN ⁻
18	An ability to replace one or more ligand by other ligands are called	a. inert	b. labile	c. stability	d. instability	b. labile
19	Labile and inert complexes are classified by	a. Biltz	b. Stobe	c. Taube	d. Tanabe	c. Taube
20	Square planar complexes formed by the Mechanism	a. S _N 1	b. E ¹ CB	c. E ¹	d. S _N 2	d. S _N 2
21	The group Which direct the entering ligand to occupy the <i>trans</i> position	a. NO ₂	b. Cl ⁻	c. H ₂ O	d. en	NO ₂
22	Another name of stable complexes is	a. penetration	b. labile	c. inert	d. dilution	a. penetration
23	Labile complexes are belongs to stability	a. thermal	b. kinetic	c. stable	d. none of these	b. kinetic
24	kinetic stability is based on the Of the reactions	a. order	b. number	c. rate	d. degree	c. rate
25	Labile complexes are those whose ligands in which replaced	a. uniformly	b. rapidly	c. one by one	d. doesn't replaced	b. rapidly
26	CN ⁻ is more stable than	CO	F ⁻	NO ₂	NO	CO
27	The symbol for magnetic property is	μ	λ	β	Λ	μ
28	Coordination complexes undergo	Ligand substitution reactions	elimination reactions	addition reactions	Rearrangements	Ligand substitution reactions
29	The mechanism followed by Pt(II) complexes in substitution reactions is	a. S _N 1	b. E ¹ CB	c. E ¹	d. S _N 2	S _N 1
30	SN1 mechanism is followed in	Ligand substitution reactions	elimination reactions	addition reactions	Rearrangements	Ligand substitution reactions
31	the labilization (making more reactive) of ligands that are trans to certain other ligands	Trans effect	Hoffmann elimination	Zayteff effect	Emdes degradation	Trans effect
32	Trans effect is	the labilization (making more reactive) of ligands that	the labilization (making more reactive) of ligands that	the labilization (making more reactive) of ligands that	the labilization (making more reactive) of ligands that	the labilization (making more reactive) of ligands that

		are trans to certain other ligands	are cis to certain other ligands	are in the same side	are adjacent to certain other ligands	are trans to certain other ligands
33	Groups which direct the entering ligand to occupy the position trans to them are called	Trans directing group	strong ligands	weak ligands	hyperactive ligands	Trans directing group
34	The property of the groups due to which the groups lying trans to them are replaced far more readily by the entering ligand is called	Ortho directing character	meta directing character	trans directing character	para directing character	trans directing character
35	The effect of a coordinated group lying trans to it in a metal complex is called	Trans effect	Hoffmann elimination	Zayteff effect	Emdes degradatio n	Trans effect
36	Which is having high trans effect	cyanide ion	carbonyl	ethylene	Nitrosyl	cyanide
37	Which is having the least trans effect	cyanide ion	carbonyl	ethylene	Nitrosyl	Nitrosyl
38	Which is having high trans effect	Hydride ion	carbonyl	ethylene	Nitrosyl	Carbonyl
39	Which is having the least trans effect	cyanide ion	carbonyl	Nitrite ligand	Nitrosyl	Nitrite ligand
40	The ligands at the High end of the trans series have	vacant pi orbital	vacant sigma orbital	completely occupied pi orbital	completely occupied sigma orbital	vacant pi orbital
41	The ligands at the High end of the trans series have	vacant Π^* orbital	vacant sigma orbital	completely occupied pi orbital	completely occupied sigma orbital	vacant Π^* orbital
42	Example for a Pi bonding ligand	cyanide ion	carbonyl	ethylene	Nitrosyl	cyanide
43	The ligand which can accept electrons from metal orbital to form metal-ligand bond	cyanide ion	ammine	hydroxyl	aqua	cyanide
44	Which ligand does not accept electrons from metal orbital to form a metal ligand bond	cyanide ion	carbonyl	ethylene	aqua	aqua
45	Trans effect is less in	Fluoride	chloride	bromide	iodide	Iodide
46	Which is having low polarisability	Fluoride	chloride	bromide	iodide	Fluoride
47	Which is having high polarisability power	Fluoride	chloride	bromide	iodide	Iodide
48	Trans effect is used in	Synthesis of Pt(II) complexes	Nitrating reactions	In preparing trans geometrical isomer	Friedel Crafts alkylating reactions	Synthesis of Pt(II) complexes
49	trans effect is explained by	Arrehenius theory	Absolute reaction rate theory	electrostatic polarisation theory	Collision theory	Electrostatic polarisation theory
50	trans effect is explained by	Arrehenius theory	Absolute reaction rate theory	Pi bonding theory	Collision theory	Pi bonding theory

51	Electrostatic polarisation theory is to explain	Trans effect	Hoffmann elimination	Zayteff effect	Emdes degradation	Trans effect
52	Pi bonding theory is to explain	Trans effect	Hoffmann elimination	Zayteff effect	Emdes degradation	Trans effect
53	Which follows a thermodynamic approach	Electrostatic polarisation theory	Pi bonding theory	Arrhenius theory	Collision theory	Electrostatic polarisation theory
54	If the resultant dipole of the ligands is zero then it will	exhibit trans effect	will not exhibit trans effect	The trans effect will be very high	The trans effect will be moderate	Will not show trans effect
55	Metal ligand bond energies are used to explain the	Thermodynamic stability	Kinetic stability	lability of the complexes	Inertness of the complexes	thermodynamic stability
56	The stability constants are used to explain	Thermodynamic stability	Kinetic stability	lability of the complexes	Inertness of the complexes	thermodynamic stability
57	The complexes in which the ligands are rapidly replaced by others are called	Labile complexes	Inert complexes	Thermodynamically stable complexes	Thermodynamically non stable complexes	Labile complexes
58	The complexes in which the ligands are slowly replaced by other ligands are called	Labile complexes	Inert complexes	Thermodynamically stable complexes	Thermodynamically non stable complexes	Inert complexes

[16CHU302]

Reg. No.

KARPAGAM UNIVERSITY,
(Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

UG DEGREE EXAMINATION, JULY 2017
(For the candidates admitted from 2016 onwards)

DEPARTMENT OF CHEMISTRY
ODD SEMESTER

II B.Sc., CHEMISTRY

INTERNAL EXAM-I
INORGANIC CHEMISTRY-II (Coordination Chemistry)

Time: 2 hours
Date :

Maximum: 50 marks

PART- A (10 x 2=20 Marks)

Answer All the Questions

1. Colour of the complex is satisfactorily explained by
(a) Werner's theory (b) Valence bond theory
(c) Crystal field theory (d) Ligand field theory
2. The CFSE for a high spin d^4 octahedral complex ion is
(a) $-14Dq$ (b) $-6Dq$ (c) $-12Dq$ (d) Zero
3. The largest crystal field splitting will be for the ligand (same metal ion)
(a) Ox^{2-} (b) NO_2^- (c) NH_3 (d) CN^-
4. Which of the following is a ligand which causes maximum crystal field splitting?
(a) NH_3 (b) F^- (c) CO (d) Ox^{2-}
5. The order of splitting in cubic geometry is same as that in
(a) tetrahedral (b) Square planar (c) Octahedral
(d) tetragonally distorted octahedral
6. The number of unpaired electron in d^7 tetrahedral configuration is
(a) 3 (b) 2 (c) 1 (d) 7

- 85 copies
7. Stability of a complex does not depend upon
(a) nature of the central metal ion (b) Number of chelate rings
(c) steric effects (d) mass of the complex
 8. Maximum value of $\log \beta$ is that of
(a) AgI (b) $AgCl$ (c) $AgBr$ (d) AgF
 9. Who is Known as the father of Coordination Chemistry
(a) Werner (b) Hund (c) Mullikan (d) Coulson
 10. What is the coordination number of platinum in $[Pt(NH_3)_2Cl_2]$
(a) 3 (b) 2 (c) 1 (d) 4
 11. What is the oxidation number of central metal atom in $Na_3[Fe(C_2O_4)_3]$
(a) 3 (b) 2 (c) 1 (d) 4
 12. Among the following which is known as a neutral ligand
(a) NH_3 (b) ONO (c) Cl (d) CN
 13. Which of the following exhibits Geometrical isomerism
(a) $[Cr(en)_2Cl_2]^+$ (b) $[Cr(NH_3)_6][Co(CN)_6]$
(c) $[Co(NH_3)_4(NO_2)Cl]^+$ (d) $[Co(NH_3)_6]Cl_3$
 14. The number of unpaired electrons in $NiCl_4^{2-}$ (tetrahedral) are
(a) two (b) zero (c) one (d) four
 15. Which of the following does not show optical isomerism?
(a) $[Cr(ox)_3]^{3-}$ (b) $[Co(en)(NH_3)_2Cl_2]^+$ (c) $trans-[Pt(NH_3)_2Cl_2]$ (d) $[Co(EDTA)]^-$
 16. The IUPAC name of $Na_3[Fe(C_2O_4)_3]$ is
(a) Sodium trioxalatoferrate (III) (b) Sodium trioxalatoiron(III)
(c) Sodium tri(oxalate)ferrate (III) (d) Sodium tri(oxalate)iron(III)
 17. Which of the following ligand is bidentate?
(a) EDTA (b) Ethylenediamine (c) Acetato (d) Pyridine
 18. The number of ions per mole of the complex $CoCl_3 \cdot 5NH_3$ in aqueous solution will be
(a) three (b) four (c) two (d) Nine

19. Primary Valency indicates

- (a) Coordination number (b) Oxidation state (c) both (d) Neutral Ligands

20. If the oxidation state of the complex increase then the Δ_0 value

- (a) Decreases (b) Increases (c) As such (d) Moderate

PART- B (3 x 2=6 Marks)

Answer All the Questions

21. Calculate CFSE for d^9 tetrahedral complex.
22. What is meant by ligand? Give five examples of ligand.
23. Define John Teller Theorem.

PART- C (3 x 8=24 Marks)

Answer All the Questions

24. (a) What are the postulates of Werner's coordination theory? How does it account for non-ionic nature of $\text{CoCl}_2 \cdot 3\text{NH}_3$ complex.
(OR)
(b) How does valence bond theory explain,
(i) $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic and square planar.
(ii) $[\text{Ni}(\text{CO})_4]$ is diamagnetic and tetrahedral.
25. (a) What is crystal field splitting and crystal field stabilization energy? Discuss the structures of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions on the basis of crystal field theory.
(OR)
(b) Explain the factors affecting the magnitude of CFSE.
26. (a) Discuss geometrical isomerism in square planar complexes and octahedral complexes.
(OR)
(b) (i) Write the IUPAC name of the following compounds:
1. $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_3]$ 2. $\text{K}_4[\text{Ni}(\text{CN})_6]$
3. $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_4$ 4. $[\text{Co}(\text{en})_2\text{Br}_2]\text{Cl}$
(ii) Write the formula for the following compound
1. Sodium dicyanoaurate (I)
2. Potassium tetracyanonickelate(0)
3. Octaammine- μ -amido- μ -Nitrito-Odicobalt (III) nitrate
4. Hexaquaairon (II) sulphate

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DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY
INORGANIC CHEMISTRY-II (Coordination Chemistry)
Semester –III

Internal Test I- Answer Key

Part A

1. (c) Crystal field theory
2. (b) $-6Dq$
3. (d) CN^-
4. (c) CO
5. (a) tetrahedral
6. (a) 3
7. (d) mass of the complex
8. (a) AgI
9. (a) Werner
10. (d) 4
11. (a) 3
12. (a) NH_3
13. (b) $[Cr(NH_3)_6][Co(CN)_6]$
14. (a) two
15. (c) trans $[Pt(NH_3)_2Cl_2]$
16. (a) Sodium trioxalatoferrate (III)
17. (b) Ethylenediamine
18. (a) three
19. (b) Oxidation state
20. (b) Increases

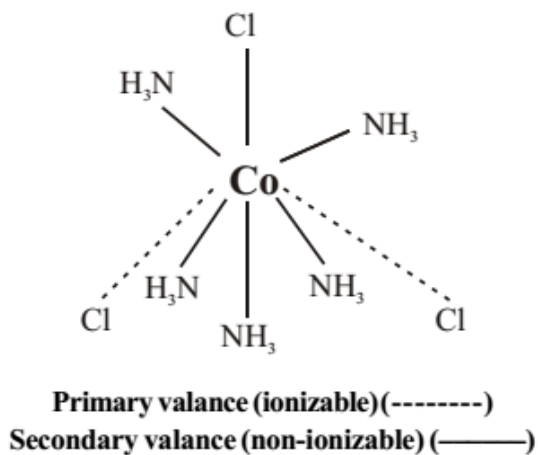
PART- B

21. Crystal field stabilization energy for d^9 tetrahedral complex : $\frac{2}{5} \Delta_t$
22. A ligand is an atom, ion, or molecule that donates or shares one or more of its electrons through a covalent bond with a central atom or ion
Five examples: CN^- , NH_3 , H_2O , Cl^- , Br^- .
23. Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy

PART- C

24. (a) Werner's Coordination Chemistry
Postulates of Werner's theory
1. In co-ordination compounds, central metal atoms exhibit primary valency and secondary valence.
- The primary valence is ionizable. Secondary valence is not ionizable. The primary valence corresponds to oxidation state. The secondary valence corresponds to coordination number. (the central metal ion and ligands are not ionizable)
2. Every metal atom has a fixed number of secondary valences (coordination number(s)).
 3. The metal atom tends to satisfy both its primary valence as well as its secondary valence. Primary valence is satisfied by negative ions (metal ion has a positive charge) whereas secondary valence (coordination number) is satisfied either by negative ions or by neutral molecules. (In certain case a negative ion may satisfy both types of valences).
 4. The coordination number or secondary valences are always directed towards the fixed positions in space and this leads to definite geometry of the coordination compound.
- The following formulas describe a series of three coordination compounds:

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, respectively, the species inside the square brackets being the complex ion and outside the square brackets the ionisable ions. On the basis of Werner's theory the structure of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is:

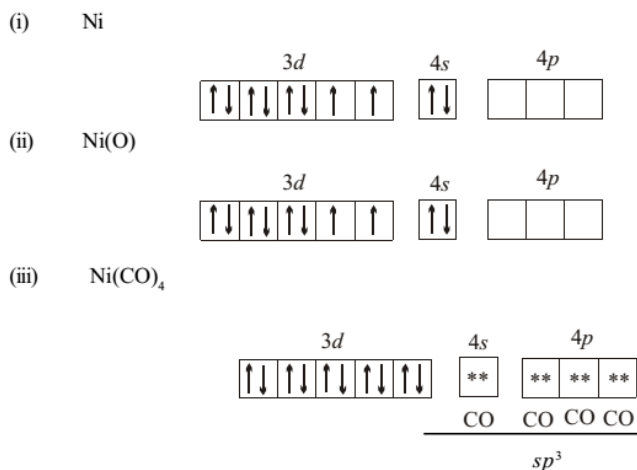


(OR)

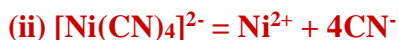
(b) VBT Theory:

(i) $\text{Ni}(\text{CO})_4 = \text{Ni} + 4\text{CO}$

- * The valence shell electronic configuration of ground state Ni atom is $3d^8 4s^2$.
- * All of these 10 electrons are pushed into 3d orbitals and get paired up when strong field CO ligands approach Ni atom. The empty 4s and three 4p orbitals undergo sp^3 hybridization and form bonds with CO ligands to give $\text{Ni}(\text{CO})_4$. Thus $\text{Ni}(\text{CO})_4$ is diamagnetic.

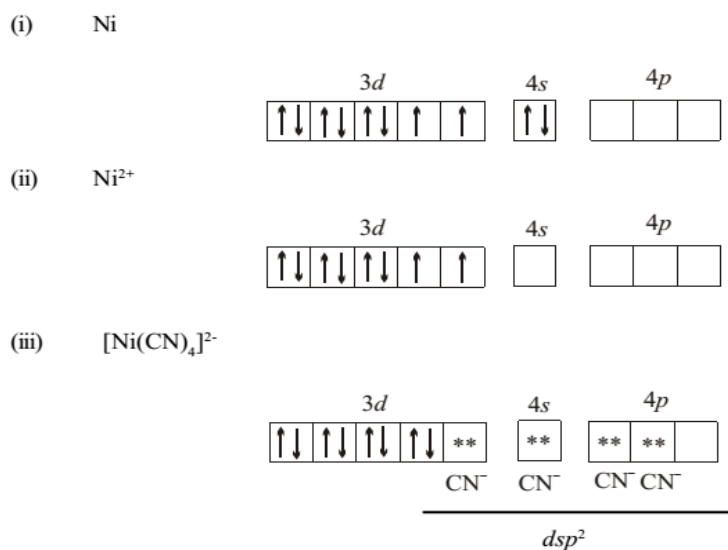


The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.



* In $[\text{Ni}(\text{CN})_4]^{2-}$, there is Ni^{2+} ion for which the electronic configuration in the valence shell is $3d^8 4s^0$.

* In presence of strong field CN^- ions, all the electrons are paired up. The empty $4d$, $3s$ and two $4p$ orbitals undergo dsp^2 hybridization to make bonds with CN^- ligands in square planar geometry. Thus $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.



The resulting complex is square planar and diamagnetic.

25. (a) Crystal field splitting

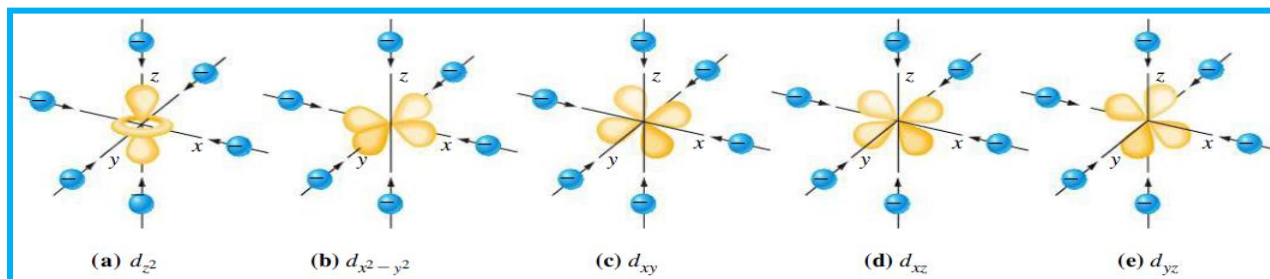
In an octahedral complex, the d orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy, Δ . (A) When Δ is large, it is energetically more favourable for electrons to occupy the lower set of orbitals.

Crystal field stabilization energy

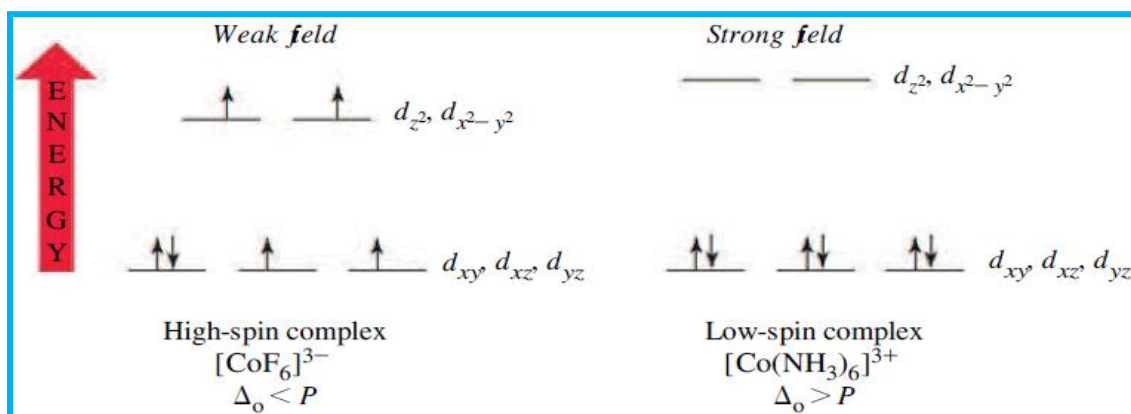
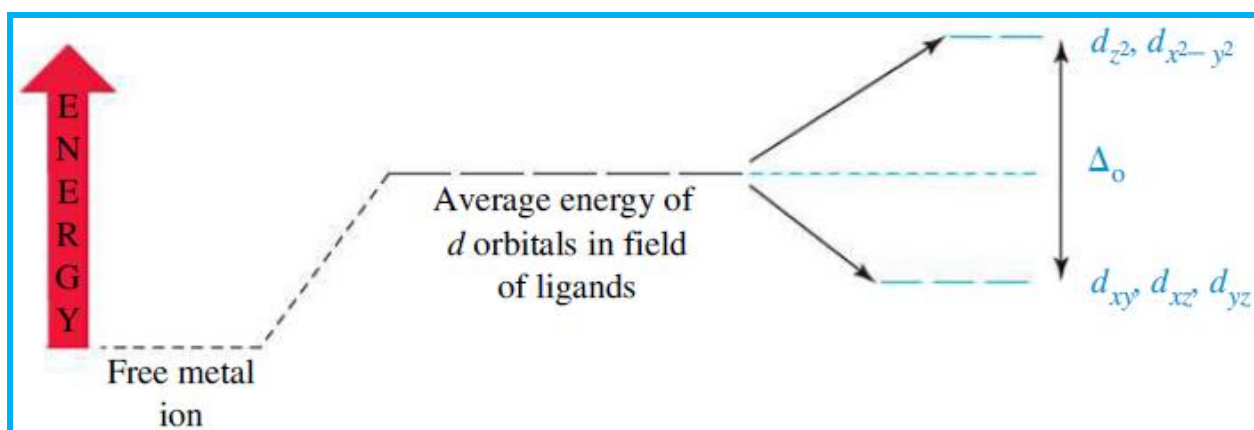
Crystal Field Stabilisation Energy (CFSE) A consequence of Crystal Field Theory is that the distribution of electrons in the d orbitals can lead to stabilisation for some electron configurations. It is a simple matter to calculate this stabilisation since all that is needed is the electron configuration.

Crystal Field Theory: Octahedral Complexes

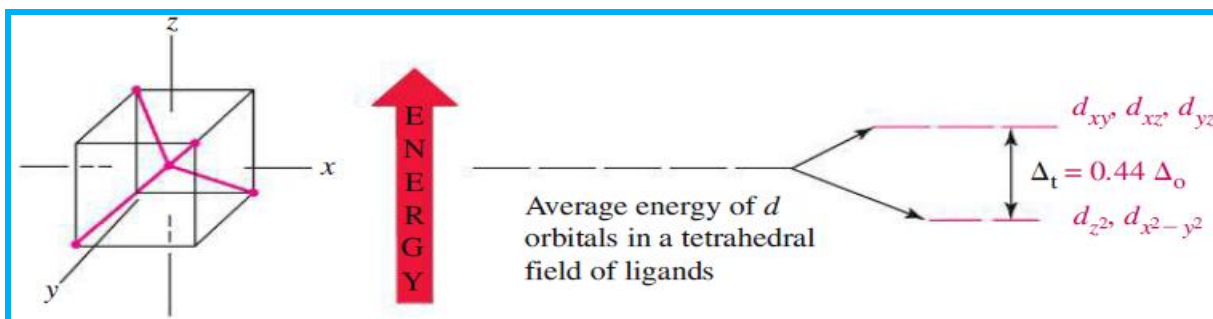
Approach of six anions to a metal to form a complex ion with octahedral structure



Splitting of d energy levels in the formation of an octahedral complex ion



Crystal Field Theory: Tetrahedral Complexes



- Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.
- The two 'e' ($d_{x^2-y^2}$ and d_{z^2}) orbitals point to the center of the face of the cube while the three 't₂' (d_{xy} , d_{yz} and d_{zx}) orbitals point to the center of the edges of the cube.
- Thus, the t₂ orbitals are nearer to the direction of approach of the ligands than the e orbitals. (The ligands do not directly approach any of the metal d orbitals)

(OR)

(b)

Factors Affecting the Magnitude of Δ

- Higher oxidation states of the metal atom correspond to larger Δ .

$$\Delta = 10,200 \text{ cm}^{-1} \text{ for } [\text{CoII}(\text{NH}_3)_6]^{2+} \text{ and } 22,870 \text{ cm}^{-1} \text{ for } [\text{CoIII}(\text{NH}_3)_6]^{3+}$$

$$\Delta = 32,200 \text{ cm}^{-1} \text{ for } [\text{FeII}(\text{CN})_6]^{4-} \text{ and } 35,000 \text{ cm}^{-1} \text{ for } [\text{FeIII}(\text{CN})_6]^{3-}$$

- In groups, heavier analogues have larger Δ .

For hexa ammine complexes $[\text{MIII}(\text{NH}_3)_6]^{3+}$:

$$\Delta = 22,870 \text{ cm}^{-1} (\text{Co})$$

$$34,100 \text{ cm}^{-1} (\text{Rh})$$

$$41,200 \text{ cm}^{-1} (\text{Ir})$$

- Geometry of the metal coordination unit affects Δ greatly.

Tetrahedral complexes ML_4 have smaller Δ than octahedral ones ML_6 :

$$\Delta = 10,200 \text{ cm}^{-1} \text{ for } [\text{CoII}(\text{NH}_3)_6]^{2+}$$

$$5,900 \text{ cm}^{-1} \text{ for } [\text{CoII}(\text{NH}_3)_4]^{2+}$$

4. Nature of the ligands.

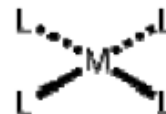
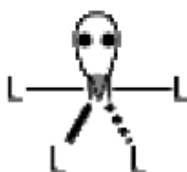
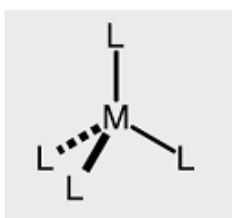
For $[\text{Co}^{\text{III}}\text{L}_6]$ Δ in cm^{-1} : 13 100 (F^-); 20 760 (H_2O); 22 870 (NH_3)

For $[\text{Cr}^{\text{III}}\text{L}_6]$, Δ in cm^{-1} : 15,060 (F^-); 17,400 (H_2O); 26,600 (CN^-)

26. (a)

Square planar

- known for p-block metals with four ligands and two non-bonding electron pairs
- common for transition metals with a d^8 electron count and a low spin configuration: central metal has four non-bonding electron pairs but one pair resides in d_{z^2}



Octahedral

Coordination number six.

Very common for transition metal ions.

octahedral is the basic structure

- all M–L distances equivalent
- all L–M–L angles are 90°



(OR)

(b) (i)

1. $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$: triamminetrinitrocobalt(III)
2. $\text{K}_4[\text{Ni}(\text{CN})_4]$: potassium tetracyanonickelate(IV)
3. $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$: hexaammineplatinum(IV) chloride
4. $[\text{Co}(\text{en})_2\text{Br}_2]\text{Cl}$: dichlorodiakis(ethylenediammine)cobalt(III) chloride

(ii) Write the formula for the following compound

1. Sodium dicyanoaurate (I) : $\text{NaAu}(\text{CN})_2$

2. Potassium tetracyanonickelate(0) : $\text{K}_2\text{Ni}(\text{CN})_4$

3. Octaammine- μ -amido- μ -Nitrito-Odicobalt (III) nitrate: $[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]^{3+}\text{NO}_3$

4. Hexaaquairon (II) sulphate : $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}\text{SO}_4^{2-}$,

[16CHU302]

Reg. No.

KARPAGAM UNIVERSITY
KARPAGAM ACADEMY OF HIGHER EDUCATION
(Under Section 3 of UGC Act 1956)
COIMBATORE-641 021
(For the candidates admitted from 2016 & onwards)
II B.Sc. Chemistry
INTERNAL EXAM II
INORGANIC CHEMISTRY III
(Coordination Chemistry)

Time: 2 hours
Date: 08-08-2017

Maximum: 50 Marks

PART A (20 x 1 = 20 Marks)
Answer all the questions

- Stability of a complex does not depend upon nature of the
 - Number of chelate rings
 - steric effects
 - mass of the complex
 - central metal ion
- Maximum value of $\log \beta$ is that of
 - AgI
 - AgCl
 - AgBr
 - AgF
- What is the coordination number of platinum in $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 - 3
 - 2
 - 4
 - 1
- What is the oxidation number of central metal atom in $\text{Na}_2[\text{Fe}(\text{C}_2\text{O}_4)_2]$
 - 3
 - 2
 - 1
 - 4
- Among the following which is known as a neutral ligand
 - NH_3
 - ONO
 - Cl
 - CN
- Among the following which is known as negative ligand
 - NH_3
 - H_2O
 - CO
 - CN
- Which of the following exhibits Geometrical isomerism
 - $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$
 - $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
 - $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^+$
 - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

8. Which of the following does not show optical isomerism?

- $[\text{Cr}(\text{ox})_3]^-$
- $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
- trans $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- $[\text{Co}(\text{EDTA})]^-$

9. The IUPAC name of $\text{Na}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ is

- Sodium trioxalatoferrate (III)
- Sodium trioxalatoiron(III)
- Sodium tri(oxalato)ferrate (III)
- Sodium tri(oxalato)iron(III)

10. Which of the following ligand is bidentate?

- EDTA
- Ethylenediamine
- Acetato
- Pyridine

11. The number of ions per mole of the complex $\text{CoCl}_2 \cdot 5\text{NH}_3$ in aqueous solution will be

- Three
- Four
- Nine
- Two

12. Which factor does not affect the labile and inertness of the complex

- Size of the central metal ion
- Charge on the central metal ion
- d-electron configuration
- Geometry of the complex

13. Which of the following has lowest oxidation state of central atom?

- $\text{Na}_3[\text{Fe}(\text{CN})_6]$
- $\text{Na}[\text{Co}(\text{CO})_4]$
- $\text{Fe}(\text{CO})_5$
- $[\text{Co}(\text{en})_2]\text{Cl}_3$

14. The complexes $[\text{Co}(\text{NH}_3)_2\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_3(\text{ONO})]\text{Cl}_2$ are examples of

- Geometrical isomerism
- Coordination isomerism
- Linkage isomerism
- Position isomerism

15. The formula of the complex tris(ethylene diamine)cobalt (III) sulphate is

- $[\text{Co}(\text{en})_3]\text{SO}_4$
- $[\text{Co}(\text{en})_3]_2\text{SO}_4$
- $[\text{Co}(\text{en})_3]\text{SO}_4$
- $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_2$

16. The IUPAC name of $\text{K}_4[\text{Ni}(\text{CN})_6]$ is

- Potassium tetracyanonickel (III)
- Potassium tetracyanonickel (II)
- Potassium tetracyanonickelate(0)
- Potassium tetracyanonickelate(IV)

17. The IUPAC name of $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ is

- Hexaammine platinum(IV) Chloride
- Hexaammine platinum(II) Chloride
- Hexaammine platinate(IV) Chloride
- Hexaammine platinate(0) Chloride

18. The IUPAC name of $\text{K}_4[\text{Fe}(\text{CN})_6]$ is

n. Potassium hexacyanoferrate (III) b. Potassium ferrocyanide c. Potassium hexacyanoiron(III) d. Potassium hexacyanoferrate (II)

19. If a ligand is attached to the central metal atom only by one coordination bond then the ligand is called as

a. Monodentate ligand b. Bidentate ligand c. Tridentate ligand d. Tetra dentate ligand

20. Chlorophyll is a

a. Cobalt complex b. Copper complex c. Iron complex d. Magnesium Porphyrin complex

PART-II (3 x 2= 6 Marks)
Answer ALL the Questions

21. Why transition metal complexes are coloured?

22. Illustrate with examples what are linkage isomers

23. Define a labile complex. Give an example.

PART-C (3 x 8= 24 Marks)
Answer ALL the Questions

24. a. What are chelates and chelating ligands. What are the factors affecting the stability of chelates.

OR

24. b. Differentiate labile and inert complexes. Explain the factors affecting the inertness of complexes.

25. a. What are polynuclear complexes. Give examples each for binuclear, trinuclear and tetranuclear complexes.

OR

25. b. Discuss the electronic configuration, colour, variable valency, magnetic and catalytic properties of transition elements

26. a. Differentiate between the first, second and third transition series

OR

26. b. Write down the preparation of potassium ferricyanide and sodium nitroprusside.

[16CHU302]

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(Deemed to be University Under Section 3 of UGC Act 1956)
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DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY
INORGANIC CHEMISTRY-II (Coordination Chemistry)
INTERNAL EXAM-II (Answer Key)

Answers

1. (C) mass of the complex
2. (a) AgI
3. (c) 4
4. (a) 3
5. (a) NH_3
6. CN
7. (b) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
8. (c) trans $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
9. (a) Sodium trioxalatoferrate (III)
10. (b) Ethylenediamine
11. (a) three
12. (d) Geometry of the complex
13. (c) $[\text{Fe}(\text{CO})_5]$
14. (c) Linkage isomerism
15. (d) $[\text{Co}(\text{en})_3] (\text{SO}_4)_2$
16. (c) potassium tetracyanonickelate(0)
17. (a) Hexammine platinum(IV) chloride
18. (d) potassium hexacyano ferrate (II)
19. (a) monodentate ligand
20. (d) magnesium porphyrin complex

PART- B

21.

- Transition elements have partially filled d orbitals.
- Property of unpaired d-electrons

22.

Linkage isomerism is the existence of coordination compounds that have the same composition differing with the connectivity of the metal to a ligand.

Typical ligands that give rise to linkage isomers are:

- thiocyanate, SCN^- – isothiocyanate, NCS^-
- selenocyanate, SeCN^- – isoselenocyanate, NCSe^-
- nitrite, NO_2^-
- sulfite, SO_3^{2-}

Examples of linkage isomers are violet-colored $[(\text{NH}_3)_5\text{Co-SCN}]^{2+}$ and orange-colored $[(\text{NH}_3)_5\text{Co-NCS}]^{2+}$.

23.

Transition metal complexes which undergo rapid substitution of one ligand for another are labile, whereas complexes in which substitutions proceed slowly or not at all are inert.

PART- C (3 x 8=24 Marks)

Answers

24.

(a) Chelation is a process in which a polydentate ligand bonds to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating agent.

Following factors are affecting the stability of coordination compounds

(1) Nature of the Central Metal Ion

(i) Ionic Size

(ii) Ionic Charge

(2) Nature of the Ligand

(i) Size and Charge

(ii) Basic Character

(iii) Ligand Concentration

(3) Chelate Effect

(i) Ring Size

(ii) Number of Rings

(iii) Effect of Substitution

(iv) Macrocyclic effect

[1] Nature of Central Metal Ion:

The important characteristics of the metal atom in determining stability of the complexes are given below.

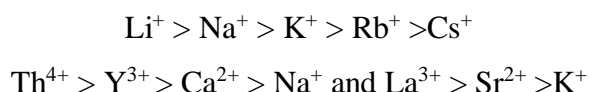
(i) *Ionic Size:*

The stability of coordination compound (complex) decreases with increase in size of metal ion. Zn(II) forms more stable complexes than Cd(II). The size of Zn(II) ion is 0.74\AA and Cd(II) 0.97\AA

(ii) *Ionic Charge:*

The effect of ionic charge of the central metal ion on the stability of coordination compounds may be described by comparing the change in stability in a series of complexes by changing the ionic charge on metal ion. If the charge of the central metal ion is more and the size is small, then the stability of the complex is more. In general, the small and

highly charged cation can form more stable coordinate compounds because of most stable coordinate bonds.

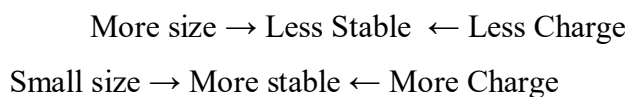


[2] Nature of the Ligand:

Nature of the ligand or important characteristics of ligand affects to determine the stability of the compounds is explained in the following manner

(i) *Size and Charge:*

Ligands with less charge and more size are less stable and form less stable coordination compounds. Ligands with higher charge have small size and form more stable compounds.

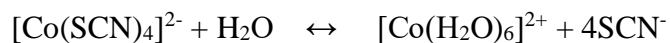


(ii) *Basic Character:*

Calvin and Wilson suggested that the higher basic character or strength of the ligand, higher will be the stability of coordination compounds. It is defined that a strong base or higher basic strength of the ligand means it forms more stable compounds or its donating tendency of electron to central metal ion is higher. *e.g.* Aromatic diamines form unstable coordination compounds while aliphatic diamines form stable coordination compounds. Ligands like NH_3 , CN^- etc have more basic character that means they form more stable compounds.

(iii) *Ligand Concentration:*

Some coordination complexes exist in aqueous solution only in presence of higher concentration of coordination group. In some cases aqueous molecules show greater coordinating tendency than the coordinating group which is originally present. *e.g.* in presence of highly concentrated solution of SCN^- (thiocyanate ion), the Co^{2+} metal ion forms a stable blue colored coordination complex but on dilution in aqueous medium the blue complex is destroyed and a pink aqua complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is formed and then by further addition of ligand (SCN^-) pink color disappears.



Blue

Pink

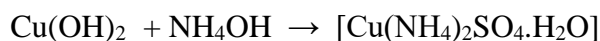
The color change indicates that there is a competition between $\text{H}_2\text{O}/\text{SCN}^-$ in formation of complex with Co(II) ion.

In the synthesis of tetra amine cupric sulphate complex at lower concentration of ammonia forms copper hydroxide, while at higher concentration of ligand form following complex.

Small concentration of ligand

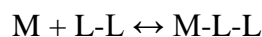
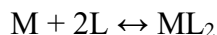


High concentration of ligand



[3] Chelate Effect:

The process of forming metal chelate by the attachment of multidentate ligand with central metal ion in which ligand act as chelating agent is known as chelation. Chelation is expressed by the following unidentate and bidentate ligand reaction.



Morgan proposed the term chelate to describe the cyclic structure which arises by multidentate (poly) ligand and a metal ion. The name chelate is derived from the Greek word 'CHELA' means 'CLAW OF LOBSTER OR CRAB'.

Multidentate ligands form more stable coordination compounds than monodentate ligands. In 1937 Dielh gave the comprehensive review of the chelate rings and more recent treatment is given by Martell and Calvin who gave the review of the unusually high stability of metal chelate compounds.

Following factors are of great importance in chelate formation.

(i) Ring Size:

The stability of chelate is depending on the size of chelate ring. The stability of coordination complex increases with number of chelate ring. It is found that 4-membered

rings are unstable and rare than 5-membered rings which are common and stable. For chelate (saturated chelate) rings the following is the decreasing order of stability with increasing ring size

Five membered > Six membered > Seven membered

The stability of metal chelates decrease by increasing the chelate size.

23. (b). Labile and inert complexes

Labile complex

In these complexes, the rate of substitution of ligands is relatively high.
Example:

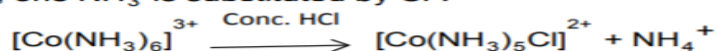
$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is labile. Its aqueous solution is blue in color. When concentrated hydrochloric acid is added to this solution, the blue solution immediately turns green giving $[\text{CuCl}_4]^{2-}$.

Inert complex

In this case, ligands are not exchanged easily. The rate of exchange is very slow.

Example:

$[\text{Co}(\text{NH}_3)_6]^{3+}$ reacts slowly. When this complex is treated with concentrated HCl, no reaction takes place. Only when it is heated with 6M HCl for many hours, one NH_3 is substituted by Cl^- .



Factors affecting stability of metal complexes

1. Size of the central metal ion

Smaller the size of the metal ion, greater will be the inertness because the ligands are held tightly by the metal ion.

2. Charge on the central metal ion

Greater the charge on the metal ion, greater will be the inertness of the complex.

3. d-electron configuration

If electrons are present in the antibonding eg^* orbitals, the

complex will be labile because the ligands will be weakly bonded to the metal and hence can be substituted easily.

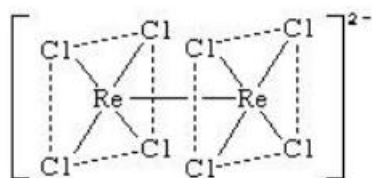
If the complex contains empty t_{2g} orbitals, then it will be labile because ligands can approach easily without much repulsion. In short, if the complex contains less than three d-electrons, it will be labile. Or, if one or more eg electrons are present, it will be labile.

No. of d electrons & electron configuration	Nature		Example
d^0	Labile		$[\text{CaEDTA}]^{2-}$
$d^1; t_{2g}^1 e_g^0$	Labile		$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
$d^2; t_{2g}^2 e_g^0$	Labile		$[\text{V}(\text{phen})_3]^{3+}$
$d^3; t_{2g}^3 e_g^0$		Inert	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$
d^4 (high-spin); $t_{2g}^3 e_g^1$	Labile		$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
d^4 (low-spin); $t_{2g}^4 e_g^0$		Inert	$[\text{Cr}(\text{CN})_6]^{4-}$
d^5 (high-spin); $t_{2g}^3 e_g^2$	Labile		$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
d^5 (low-spin); $t_{2g}^5 e_g^0$		Inert	$[\text{Mn}(\text{CN})_6]^{4-}$
d^6 (high-spin); $t_{2g}^4 e_g^2$		Inert	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
d^6 (low-spin); $t_{2g}^6 e_g^0$		Inert	$[\text{Fe}(\text{CN})_6]^{4-}$
d^7, d^8, d^9, d^{10}	Labile		

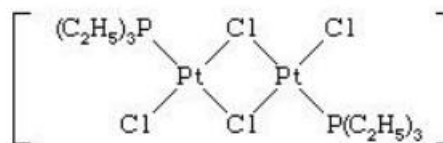
25. (a) Polynuclear complexes

Polynuclear complexes are coordination compounds containing two or more metal atoms, or ions, in a single coordination sphere. The two atoms may be held together through direct metal-metal bonds, through bridging ligands, or both.

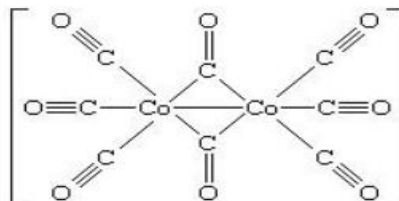
Binuclear complex:



complex with metal-metal bond (Re is rhenium)



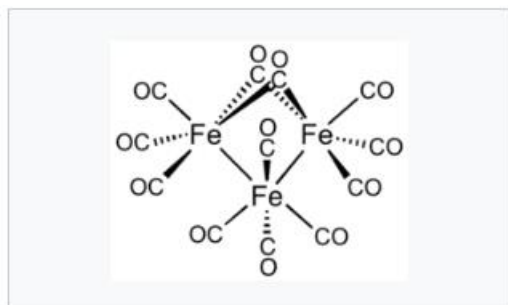
complex with bridging ligands
(C_2H_5 is ethyl radical, Pt is platinum, P is phosphorus, and Cl is chlorine)



complex with metal-metal bonds and bridging ligands

Trinuclear complexes:

In triiron dodecarbonyl, two CO ligands are bridging and ten are terminal ligands. The terminal and bridging CO ligands interchange rapidly.



25. (b)

Coloured Complexes

The compounds of transition elements are usually coloured both in solid state and in aqueous solution. The colour of these complexes is due to absorption of some radiation from visible light, which is used in promoting an electron from one of the d-orbitals to another. This can be explained as under:

The d-orbitals in the transition elements do not have same energy in their complexes. Under the influence of the ligands attached, the d-orbitals split into two sets of orbitals having slightly different energies. In the transition elements, which have partly filled d-orbitals, the transition of electron can take place from one of the lower d-orbitals to some higher d-orbital within the same subshell. The energy required for this transition falls in the visible region. So when white light falls on these complexes they absorb a particular colour from the radiation for the promotion of electron and the remaining colours are emitted. The colour of the complex is due to this emitted radiation. For example, copper(II) salts are bluish green due to absorption of red light. Ti^{3+} salts appear purple due to absorption of yellow light.

The energy difference between the two sets of d-orbitals in the central atom of the complex depends on the nature of ligands and the structure of the complex ion. As a result different complexes of the same metal ion, with different ligands, may have different colours. For example, $[\text{CoCl}_4]^{2-}$ is blue in colour whereas $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is pink.

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is green in colour whereas $[\text{Fe}(\text{CN})_6]^{4-}$ is yellow.

Zn^{2+} and Ti^{4+} salts are white because they do not absorb any radiation in the visible region. In these compounds, d-d transitions are not possible because in Zn^{2+} all the d-orbitals are fully filled whereas in Ti^{4+} all the d-orbitals are vacant. The colours of some transition metal ions in aqueous solutions are given in Table 19.7.

Table. The Colours of Some Transition Metal Ions in Aqueous Solution

<i>Metal Ion</i>	<i>Configuration</i>	<i>Colour</i>
Sc ³⁺	3d ⁰	Colourless
Ti ⁴⁺	3d ⁰	Colourless
Ti ³⁺	3d ¹	Purple
V ⁴⁺	3d ¹	Blue
V ³⁺	3d ²	Green
Cr ³⁺	3d ³	Violet
Mn ³⁺	3d ⁴	Violet
Mn ²⁺	3d ⁵	Pink
Fe ³⁺	3d ⁵	Yellow
Fe ²⁺	3d ⁶	Green
Co ²⁺	3d ⁷	Pink
Ni ²⁺	3d ⁸	Green
Cu ²⁺	3d ⁹	Blue
Zn ²⁺	3d ¹⁰	Colourless
Cd ²⁺	4d ¹⁰	Colourless

Magnetic property of transition elements

Paramagnetism

The substances, which contain some species (atoms, ions or molecules) with unpaired electrons in their orbitals, behave as paramagnetic substances. Such substances are weakly attracted by magnetic field. On the other hand, the substances whose constituent particles do not contain any unpaired electrons are repelled by magnetic field and are called diamagnetic.

The transition metal ions generally contain one or more unpaired electrons in them and hence their complexes are generally paramagnetic. The paramagnetic character increases with increase in number of unpaired electrons.

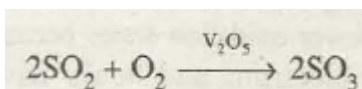
Catalytic Properties

Many transition metals and their compounds are known to act as catalysts. For example, finely divided iron acts as catalyst in the manufacture of ammonia by Haber Process. vanadium pentoxide (V₂O₅) or platinum act as catalyst for the oxidation of SO₂ to SO₃ in Contact Process, ferrous sulphate and hydrogen peroxide (Fenton's reagent) are used for the oxidation of alcohols to aldehydes.

The catalytic activity of transition metals is attributed to the following reasons:

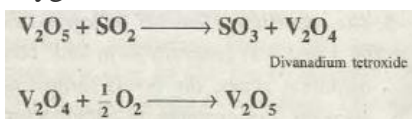
1. Because of their variable oxidation states transition metals sometimes form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.

For example, V₂O₅ catalyses the oxidation of SO₂ to SO₃.

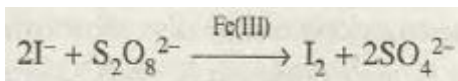


The catalytic action of V_2O_5 can be understood as follows:

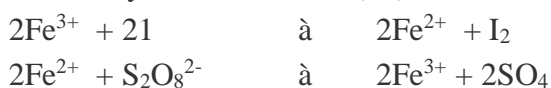
During the conversion of SO_2 to SO_3 , V_2O_5 adsorbs SO_2 molecule on its surface and gives oxygen to it to form SO_3 , and V_2O_4 . V_2O_4 then reacts with oxygen to form V_2O_5



Similarly, iron(III) catalyses the reaction between iodide and persulphate ions.



The catalytic action of iron(III) in this reaction is explained as follows



2. In some cases transition metals provide a suitable surface of the reaction to take place. The reactant are adsorbed on the surface of the catalyst where reaction occurs.

Adsorption results in increased concentration of reactants at the surface and also weakens the bonds between atoms in the reactant molecules.

26. (a).

First Transition Series

It is a part of the fourth period and consists of 10 elements from Scandium (At no: 21) to zinc (at no 30) in which 3d - sub-shells are progressively filled. This is also called as 3d series which corresponds to the filling of the 3d orbital.

Element	Atomic number	Symbol	Electronic configuration
Scandium	21	Sc	$[\text{Ar}] 3d^1 4s^2$
Titanium	22	Ti	$[\text{Ar}] 3d^2 4s^2$
Vanadium	23	V	$[\text{Ar}] 3d^3 4s^2$
Chromium	24	Cr	$[\text{Ar}] 3d^5 4s^1$
Manganese	25	Mn	$[\text{Ar}] 3d^5 4s^2$
Iron	26	Fe	$[\text{Ar}] 3d^6 4s^2$
Cobalt	27	Co	$[\text{Ar}] 3d^7 4s^2$
Nickel	28	Ni	$[\text{Ar}] 3d^8 4s^2$

Element	Atomic number	Symbol	Electronic configuration
Copper	29	Cu	[Ar] 3d ¹⁰ 4s ¹
Zinc	30	Zn	[Ar] 3d ¹⁰ 4s ²

Second Transition Series

Second transition series is a part of the fifth period and consists of 10 elements from Yttrium (At no: 39) to cadmium (At no: 48) in which 4d- sub-shells are being progressively filled. This is also called 4d series which corresponds to the filling of the 4d orbital.

Element	Atomic Number	Symbol	Electronic configuration
Yttrium	39	Y	[Kr] 4d ¹ 5s ²
Zirconium	40	Zr	[Kr] 4d ² 5s ²
Niobium	41	Nb	[Kr] 4d ⁴ 5s ¹
Molybdenum	42	Mo	[Kr] 4d ⁵ 5s ¹
Technetium	43	Tc	[Kr] 4d ⁵ 5s ²
Ruthenium	44	Ru	[Kr] 4d ⁷ 5s ¹
Rhodium	45	Rh	[Kr] 4d ⁸ 5s ¹
Palladium	46	Pd	[Kr] 4d ¹⁰ 5s ⁰
Silver	46	Ag	[Kr] 4d ¹⁰ 5s ¹
Cadmium	48	Cd	[Kr] 4d ¹⁰ 5s ²

Third Transition Series

It is a part of the sixth period and consists of 10 elements from Lanthanum (At no: 57) and Hafnium (At no: 72) to Mercury (At no: 80) in which the 5d sub-shell is progressively filled. This is also called as 5d series which corresponds with the filling of 5d orbital.

Element	Atomic number	Symbol	Electronic configuration
Lanthanum	57	La	[Xe] 5d ¹ 6s ²

Element	Atomic number	Symbol	Electronic configuration
Hafnium	72	Hf	[Xe] 4f ¹⁴ 5d ² 6s ²
Tantalum	73	Ta	[Xe] 4f ¹⁴ 5d ³ 6s ²
Tungsten	74	W	[Xe] 4f ¹⁴ 5d ⁴ 6s ²
Rhenium	75	Re	[Xe] 4f ¹⁴ 5d ⁵ 6s ²
Osmium	76	Os	[Xe] 4f ¹⁴ 5d ⁶ 6s ²
Iridium	77	Ir	[Xe] 4f ¹⁴ 5d ⁷ 6s ²
Platinum	78	Pt	[Xe] 4f ¹⁴ 5d ⁹ 6s ¹
Gold	79	Au	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
Mercury	80	Hg	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²

Transition metal charges

The valence electrons of transition metals are responsible for the charges that these metals carry or show and has been explained below. The valence or the electrons in the ultimate shell enter the 'd' orbital. The first element in each series starts with one valence electron or 'd' electron and the last element will have 10 'd' electrons. Variable oxidation state or variable valency is one of the most striking features of the transition elements. All transition elements, except the first and last member of each series exhibit variable valency, related to its electronic structure. These elements lose both the 's' and the 'd' electrons and thus have a lot of valencies. Consequently, all transition elements in general exhibit variable valencies. Valencies of first transition series are

Element	Oxidation state/valency
Sc	+2, +3
Ti	+2, +3, +4
V	+2, +3, +4, +5
Cr	+1 to +6 (+4 and +5 are unstable)
Mn	+2 to +6 (+4, +5 and +6 are unstable)
Fe	+2 to +6 (+4, +5 and +6 are unstable)
Co	+2 to +6 (+4 is unstable)

Ni	+2, +3, +4
Cu	+1, +2
Zn	+2

Characteristics of Transition Metals

Transition elements have partly filled d- orbitals. These elements show several interesting properties like variable oxidation state or variable valency, formation of colored complexes and paramagnetic behavior. These metals and their compounds also exhibit catalytic properties.

Some of the important properties of transition metals are

1. Electronic Configuration

The electronic configuration of transition elements may in general be represented as

$$(n-1) d^{1-10} ns^{1 \text{ or } 2}$$

The (n-1) means penultimate or next to the outermost shell and d- orbital may have 1 to 10 electrons and the s- orbital of the outermost shell (n) may have 1 or 2 electrons. The electronic configurations of all the four series of elements are given in a table above.

2. Atomic and ionic radii

The atomic and ionic radii of the elements of a particular transition series decreases from left to right. In the first series, the atomic radii become almost constant for chromium, because of two factors-Increase in nuclear charge and increase in the screening effect which just balance each other.

Atomic radii of Chromium is - 117pm. Mn, the next element has an atomic radii of 117 pm. The next three elements, Co, Ni and Cu has 116. 115 and 117 respectively. To summarize, atomic and ionic radii decrease with increase in atomic number, due to increase in nuclear charge.

3. Magnetic Properties

Magnetic character is of two types.

- Paramagnetic
- Diamagnetic

Those which are attracted by the magnetic field are termed as paramagnetic and those repelled by the magnetic field are diamagnetic. Transition elements and their compounds are paramagnetic in nature, they conduct electricity.

Paramagnetism is due to the presence of **unpaired electrons** in the d- orbitals of the transition metal atoms, ions or molecules. The greater the number of unpaired electrons, the greater will be its magnetic behavior. So, all transition metals with at least one unpaired electron are paramagnetic.

4. Color

Most d- block compounds are colored in the solid or in solution states. The color of the transition metal ions is due to the presence of unpaired or incomplete (n-1) d orbitals and the ability to promote an electron from one energy level to another. In these ions d- electrons are promoted to the higher energy levels within the same d- sub-shell. The color exhibited depends upon the complementary color of light observed by these ions.

Colors of some transition metals are

Ions	Color observed
Fe^{2+}	Green
Ni^{2+}	Green
Cu^{2+}	Blue
Fe^{3+}	Yellow
Mn^{2+}	Pink

5. Complex formation

Complex formation or complexation is a typical behavior of transition metals. In these complex compounds, the transition metal ions form co-ordinate bonds with a number of neutral or negatively charged ions which are capable of donating electrons to the metal atom.

A few examples are $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, etc.

6. Catalytic behavior

Most of the transition elements and their compounds are good catalysts. Platinum, cobalt, nickel, chromium, manganese, vanadium pent-oxide, etc are good examples. They are used as catalysts since they have incomplete d- orbitals and can form unstable intermediates which can then change into products.

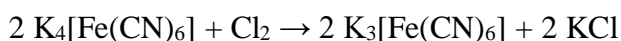
26. (b)

Potassium ferricyanide

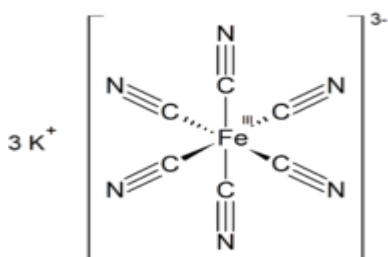
Potassium ferricyanide is the chemical compound with the formula $K_3[Fe(CN)_6]$. This bright red salt contains the octahedrally coordinated $[Fe(CN)_6]^{3-}$ ion. It is soluble in water and its solution shows some green-yellow fluorescence. It was discovered in 1822 by Leopold Gmelin and was initially used in the production of ultramarine dyes.

Preparation

Potassium ferricyanide is manufactured by passing chlorine through a solution of potassium ferrocyanide. Potassium ferricyanide separates from the solution:



Structure



Like other metal cyanides, solid potassium ferricyanide has a complicated polymeric structure. The polymer consists of octahedral $[Fe(CN)_6]^{3-}$ centers crosslinked with K^+ ions that are bound to the CN ligands. The $K^+ \cdots NCFe$ linkages break when the solid is dissolved in water.

Sodium nitroprusside

Sodium nitroprusside (SNP), sold under the brand name **Nitropress** among others, is a medication used to lower blood pressure. This may be done if the blood pressure is very high and resulting in symptoms, in certain types of heart failure, and during surgery to decrease bleeding. It is used by continuous injection into a vein. Onset is typically immediate and effects last for up to ten minutes.

Common side effects include low blood pressure and cyanide toxicity. Other serious side effects include methemoglobinemia. It is not generally recommended during pregnancy due to concerns of side effects. High doses are not recommended for more than ten minutes. It works by causing the dilation of blood vessels.

[16CHU302]

Reg. No.

KARPAGAM UNIVERSITY,
(Under Section 3 of UGC Act 1956)
COIMBATORE-641 021
UG DEGREE EXAMINATION, 2017
(For the candidates admitted from 2016 onwards)

DEPARTMENT OF CHEMISTRY
ODD SEMESTER

II B.Sc., CHEMISTRY

INTERNAL EXAM- III
INORGANIC CHEMISTRY-II (Coordination Chemistry)

Time: 2 hours

Maximum: 50 marks

Date :

PART- A (10 x 2=20 Marks)

Answer All the Questions

1. The lanthanide contraction will affect the
a) acidity b) basicity c) conductivity d) neutrality
2. The most common oxidation state of lanthanides are known as
a) +2 b) +1 c) +3 d) +4
3. Another name of stable complex is known as
a) penetration b) labile c) inert d) dilution
4. Labile complexes are belongs to stability
a) thermal b) kinetic c) stable d) none of these
5. Kinetic stability is based on the Of the reactions
a) order b) number c) rate d) degree
6. Labile complexes are those whose ligands in which replaced
a) uniformly b) rapidly c) one by one d) doesn't replaced
7. The elements in which the extra electron enters (n-2)f orbitals are called
a) s block elements b) p block elements
c) d block elements d) f block elements
8. The Lanthanides contraction is due to
a) Perfect shielding of 4f electron b) imperfect shielding of 4f electron
c) Perfect shielding of 3d electron d) imperfect shielding of 3d electron
9. Ceria is used in
a) toys b) Tracer bullets c) gas lamp materials d) Insulators
10. An ability to replace one or more ligand by other ligands are called
a) inert b) labile c) stability d) instability
11. The highest oxidation state of lanthanides are
a) +3 b) +4 c) +5 d) +8
12. Alloys of lanthanides are called
a) Mish metals b) pyroboric alloy c) brass d) nichrome
13. Stability constant was introduced by
a) Sachey b) Irving c) Glasco d) Taffel
14. Chelating effect present in membered complexes
a) Three b) four c) five d) none
15. Determination of stability constants are calculated ny using
a) ohm's law b) Beer's law c) Lambert's law d) Charles law
16. The main ore of uranium is
a) carnitite b) bauxite c) carnotite d) zincite
17. Actinide contraction is caused by due to
a) 6d orbital b) 5f orbital c) 5d orbital d) 4f orbital
18. The stability constant is denoted by the symbol of
a) μ b) β c) γ d) α
19. Trans effect has been increased when polarisability
a) decreases b) increases c) zero d) no change
20. The main application of the trans effect is to analyze the synthesis of complexes
a) Pt b) Cu c) Fe d) Co

No of copies - 95

PART- B (3 x 2=6 Marks)

Answer All the Questions

21. Why lanthanides are paramagnetic in nature?
22. Write any two uses of lanthanides and actinides.
23. Write the utility of Trans effect.

PART- C (3 x 8=24 Marks)

Answer All the Questions

24. a). What are lanthanides? Describe ion exchange method for the separation of lanthanides
(OR)
b). Write note on lanthanide contraction
25. a) Explain the magnetic property of Lanthanides and Actinides.
(OR)
b) Discuss the factors are affecting the substitution reactions in square planar complexes
26. a) Discuss the factors affecting the stability of metal complexes.
(OR)
b) What is Trans effect? How does it influence substitution in square planar complexes?

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
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DEPARTMENT OF CHEMISTRY
II B.Sc., CHEMISTRY
INORGANIC CHEMISTRY-II (Coordination Chemistry)
Semester –III

Internal Test III- Answer Key

Part A

1. b) basicity
2. c) +3
3. a) penetration
4. b) kinetic
5. c) rate
6. b) rapidly
7. d) f block elements
8. b) imperfect shielding of 4f electron
9. c) gas lamp materials
10. b) labile
11. b) +4
12. a) Misch metals
13. b) Irving
14. c) five
15. b) Beer's law
16. a) carotene
17. b) 5f orbital
18. b) β
19. b) increases
20. a) Pt

PART- B

21.

The 4f electrons are responsible for the strong magnetism exhibited by the metals and compounds of the lanthanides. In the incomplete 4f sub shell the magnetic effects of the different electrons do not cancel out each other as they do in a completed sub shell, and this factor gives rise to the interesting magnetic behaviour of these elements

22.

1. Use as catalysts: Lanthanide catalysts have been repeatedly recommended for use in numerous organic reactions, including the hydrogenation of ketones to form secondary alcohols, the hydrogenation of olefins to form alkanes, the dehydrogenation of alcohols and butanes, and the formation of polyesters.
2. Plutonium is used in the manufacture of nuclear weapons and as the power source in nuclear power plants.

23.

The trans effect is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.

PART- C

24. a).

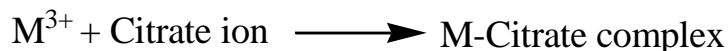
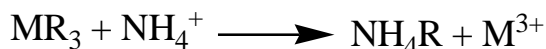
Separation of Lanthanides - Ion exchange method:

A synthetic ion-exchange resin with functional groups like -COOH and $\text{-SO}_3\text{H}$ is packed in a long column fixed in a vertical position. The steady decrease in size and consequent decrease in basicity causes the steady increase the complexing ability with increasing atomic number of lanthanides. When an aqueous solution containing the mixture of trivalent lanthanide ion $\text{M}^{+3}(\text{aq})$ is passed through a column having synthetic cation-exchange resin (HR)solid, the M^{+3} ions replace H^+ ion of the resin and thus get fixed on that



Small Lu^{3+} gets more hydrated than La^{3+} and is bigger in size. So $\text{La}^{3+}(\text{aq})$ gets strongly bound to the resin column than others. In order to recover M^{3+} ions fixed on the resin, the

column is eluted with a citric acid–ammonium citrate solution (eluant). During elution process NH_4^+ ions replace M^{3+} ion and M-citrate complexes are formed.



A citrate buffer (citric acid/ammonium citrate) solution (which complexes with the lanthanide ions) is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution. Since the smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column. By the correct choice of conditions the lutetium ion, $\text{Lu}^{+3}(\text{aq})$, emerges first from the column, followed by the cations ytterbium, thulium, erbium, etc, in order of increasing ionic radius. By using a long ion-exchange column, the elements may be obtained at 99.9% with one pass. The bigger aquated ion is least strongly held and comes out first. Other ions remain on the column and can be separated by repeated elution.

(OR)

b). Lanthanide Contraction (or Atomic and ionic radii):

The energies of 4f and 5d -orbitals are nearly same, beginning near to atomic number 57 La. Similar behavior is also observed for 5f and 6d - orbitals at atomic number 89 Ac.

The shielding of one f- electron by another from the effect of nuclear charge is quite weak due to shape of f-orbitals and hence with increasing atomic number the effective nuclear charge experienced by each 4f e increases, because of this there is contraction of atomic or ionic - radii proceeding from La to Lu. This decrease in atomic or ionic radii is called Lanthanide Contraction. Due to Lanthanide contraction the chemical properties of Lanthanides are almost similar.

Case of Lanthanide Contraction:

In Lanthanides the additional electrons enters 4f-sub shell but not in the valence shell namely sixth shell. The shielding effect of one electron in 4f- sub shell by another in the same sub-shell (i.e. mutual shielding effect of 4f- electrons) is being even smaller than that of d-electrons, because the shape of f sub-shell is very much diffused. The nuclear charge (i.e.

atomic number) increases by unity at each step. Thus the nuclear charge increases at each step, while there is no comparable increase in the mutual shielding effect of 4f-electron. This results in that electrons in the outermost shell experience increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic- radii go on decreasing as we move from La₅₇ to Lu₇₁.

Consequences of lanthanide contraction:

Some important consequences of lanthanides contraction are as under:

(i) *High density of post lanthanide elements:*

Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. The arrangement of atoms in metallic lattice is much compact that the densities are very high. The density of 2nd transition series is slightly higher than 1st transition series, while the densities of 3rd transition series is almost double than 2nd transition series.

(ii) *Basic character of oxides, Ln₂O₃ and hydroxides, Ln(OH)₃:*

There is decrease in basic strength of oxides and hydroxides of lanthanides with increase in atomic number. The basicity decreases as ionic radii decreases. The basicity of Ln⁺³ ions may be expected to decrease in the order, La⁺³ > Ce⁺³ > Pr⁺³ > Lu⁺³. These differences in basicity are reflected in (a) thermal decomposition of oxy-salts. *i.e.* more basic oxy-salts decompose less easily (b) hydrolysis of ions-more basic ions hydrolyse less readily (c) solubilities of salts (d) formation of complexes and (e) decreasing ease of oxidation of the metals with increasing atomic number—oxidation potential for the couple $\text{Ln} \rightarrow \text{Ln}^{+3} + 3\text{e}^-$ regularly goes on decreasing.

Due to lanthanide contraction the decrease in size of Ln⁺³ ions from La⁺³ to Lu⁺³ increases the covalent character (*i.e.* decreases the ionic character) between Ln⁺³ and OH ions in Ln(III) hydroxides. Thus La(OH)₃ is the most basic while Lu(OH)₃ is the best basic.

Similarly there is a decrease in the basic strength of the oxides, Ln₂O₃ with the increase of atomic number of Ln-atom.

(iii) Small variation in the properties on account of Lanthanide contraction allows the separation of Lanthanides by the methods based on fractional crystallization and basicity differences.

(iv) The pair of elements i.e. Zr-Hf, Nb-Ta, have almost similar size and they are much closer to one another in properties than the pairs of elements of 1st and 2nd transition series, e.g. solubilities of their salts are very much similar to one another.

(v) *Occurrence of Y with heavy Lanthanides:*

The crystal radii of Y^{+3} and Er^{+3} are equal ($Y^{+3}=0.93 \text{ \AA}$ and $Er^{+3}=0.96 \text{ \AA}$). This similarities in atomic size of these two cations coupled with the equality in ionic charge ($= +3$ in both the ions) accounts for the invariable occurrence of Y with heavier Lanthanides.

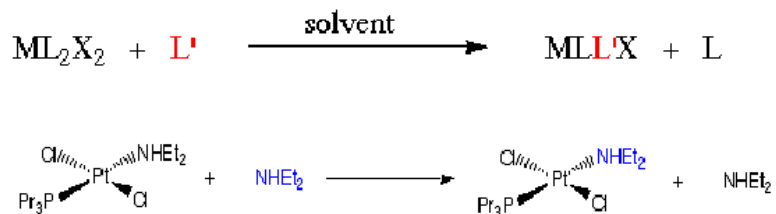
25. a) **Magnetic properties of Lanthanides and Actinides.**

The 4f electrons are responsible for the strong magnetism exhibited by the metals and compounds of the lanthanides. In the incomplete 4f sub shell the magnetic effects of the different electrons do not cancel out each other as they do in a completed sub shell, and this factor gives rise to the interesting magnetic behaviour of these elements. At higher temperatures, all the lanthanides except lutetium are paramagnetic (weakly magnetic), and this paramagnetism frequently shows a strong anisotropy. As the temperature is lowered, many of the metals exhibit a point below which they become antiferromagnetism (i.e., magnetic moments of the ions are aligned but some are opposed to others), and, as the temperatures are lowered still further, many of them go through a series of spin rearrangements, which may or may not be in conformity with the regular crystal lattice. Finally, at still lower temperatures, a number of these elements become ferromagnetic (i.e., strongly magnetic, like iron). Some of the metals have saturation moments (magnetism observed when all the magnetic moments of the ions are aligned) greater than iron, cobalt, or nickel. They also show a strong anisotropy in their magnetic behaviour depending on the crystal direction. Study of the magnetism of rare-earth elements has had great influence on present-day theories of magnetism.

(OR)

b)

Factors are affecting the substitution reactions in square planar complexes



The following factors are affecting the substitution reaction in square planar complexes

- i). Role of the Entering Group
- ii). The Role of The Leaving Group
- iii). The Nature of the Other Ligands in the Complex
- iv). Effect of the Metal Centre

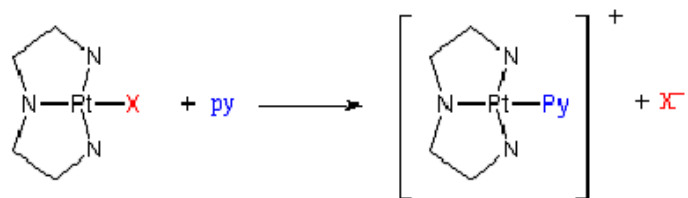
i). Role of the Entering Group

„ The rate of substitution is proportional to the nucleophilicity of entering group i.e. for most reactions of Pt(II). The rate constant increases in the order: $\text{H}_2\text{O} < \text{NH}_3 = \text{py} < \text{Br}^- < \text{I}^- < \text{CN}^-$. The ordering is consistent with Pt(II) being a soft metal centre.

ii). The Role Of The Leaving Group



For the reaction in H_2O at 250 C the sequence of lability is; $\text{H}_2\text{O} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{N}_3^- > \text{SCN}^- > \text{NO}_2^- > \text{CN}^-$ with a spread of over 10^6 in rate across series.



The leaving group does not affect the nucleophilic discrimination factors only the intrinsic reactivity. The series tend to parallel the strength of the Metal-L bond

iii). The nature of other ligands in the complex

Nature of the ligands present in the complex also affects the substitution reactions.

26. a)

VARIOUS FACTORS AFFECTING THE STABILITY OF COORDINATION COMPOUNDS

Following factors are affecting the stability of coordination compounds

(1) Nature of the Central Metal Ion

- (i) Ionic Size
- (ii) Ionic Charge

(2) Nature of the Ligand

- (i) Size and Charge
- (ii) Basic Character
- (iii) Ligand Concentration

(3) Chelate Effect

- (i) Ring Size
- (ii) Number of Rings
- (iii) Effect of Substitution
- (iv) Macrocyclic effect

[1] Nature of Central Metal Ion:

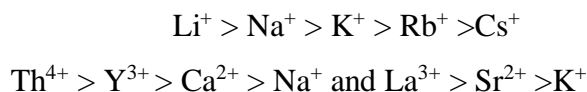
The important characteristics of the metal atom in determining stability of the complexes are given below.

(i) Ionic Size:

The stability of coordination compound (complex) decreases with increase in size of metal ion. Zn(II) forms more stable complexes than Cd(II). The size of Zn(II) ion is 0.74\AA and Cd(II) 0.97\AA .

(ii) Ionic Charge:

The effect of ionic charge of the central metal ion on the stability of coordination compounds may be described by comparing the change in stability in a series of complexes by changing the ionic charge on metal ion. If the charge of the central metal ion is more and the size is small, then the stability of the complex is more. In general, the small and highly charged cation can form more stable coordinate compounds because of most stable coordinate bonds.

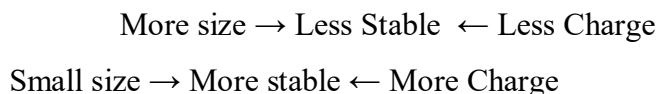


[2] Nature of the Ligand:

Nature of the ligand or important characteristics of ligand affects to determine the stability of the compounds is explained in the following manner

(i) *Size and Charge:*

Ligands with less charge and more size are less stable and form less stable coordination compounds. Ligands with higher charge have small size and form more stable compounds.

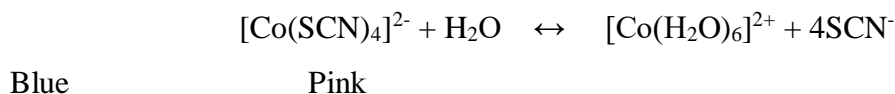


(ii) *Basic Character:*

Calvin and Wilson suggested that the higher basic character or strength of the ligand, higher will be the stability of coordination compounds. It is defined that a strong base or higher basic strength of the ligand means it forms more stable compounds or its donating tendency of electron to central metal ion is higher. *e.g.* Aromatic diamines form unstable coordination compounds while aliphatic diamines form stable coordination compounds. Ligands like NH_3 , CN^- etc have more basic character that means they form more stable compounds.

(iii) *Ligand Concentration:*

Some coordination complexes exist in aqueous solution only in presence of higher concentration of coordination group. In some cases aqueous molecules show greater coordinating tendency than the coordinating group which is originally present. *e.g.* in presence of highly concentrated solution of SCN^- (thiocynate ion), the Co^{2+} metal ion forms a stable blue colored coordination complex but on dilution in aqueous medium the blue complex is destroyed and a pink aqua complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is formed and then by further addition of ligand (SCN^-) pink color disappears.



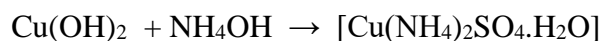
The color change indicates that there is a competition between $\text{H}_2\text{O}/\text{SCN}^-$ in formation of complex with Co(II) ion.

In the synthesis of tetra amine cupric sulphate complex at lower concentration of ammonia forms copper hydroxide, while at higher concentration of ligand form following complex.

Small concentration of ligand

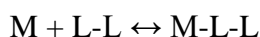
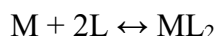


High concentration of ligand



[3] Chelate Effect:

The process of forming metal chelate by the attachment of multidentate ligand with central metal ion in which ligand act as chelating agent is known as chelation. Chelation is expressed by the following unidentate and bidentate ligand reaction.



Morgan proposed the term chelate to describe the cyclic structure which arises by multidentate (poly) ligand and a metal ion. The name chelate is derived from the Greek word 'CHELA' means 'CLAW OF LOBSTER OR CRAB'.

Multidentate ligands form more stable coordination compounds than monodentate ligands. In 1937 Dielh gave the comprehensive review of the chelate rings and more recent treatment is given by Martell and Calvin who gave the review of the unusually high stability of metal chelate compounds.

Following factors are of great importance in chelate formation.

(i) Ring Size:

The stability of chelate is depending on the size of chelate ring. The stability of coordination complex increases with number of chelate ring. It is found that 4-membered rings are unstable and rare than 5-membered rings which are common and stable. For chelate

(saturated chelate) rings the following is the decreasing order of stability with increasing ring size

Five membered > Six membered > Seven membered

The stability of metal chelates decrease by increasing the chelate size.

(OR)

b)

Trans effect

Definition

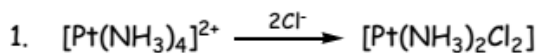
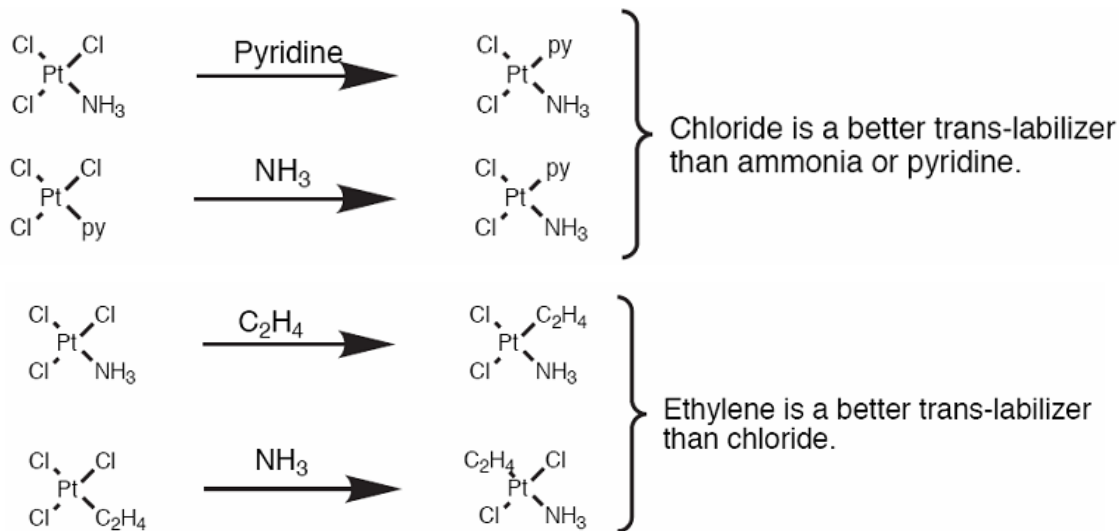
“The trans effect is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.”

OR

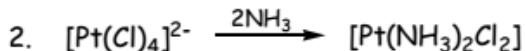
“The ability of a ligand in a square planar complex to direct the replacement of the ligand trans to it.”

The trans effect is given as the following series:

$\text{CN}^- > \text{NO}_2^- > \text{I}^- = \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{NH}_3 > \text{H}_2\text{O}$



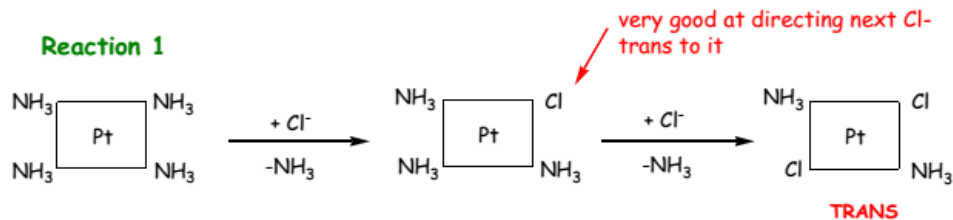
TRANS



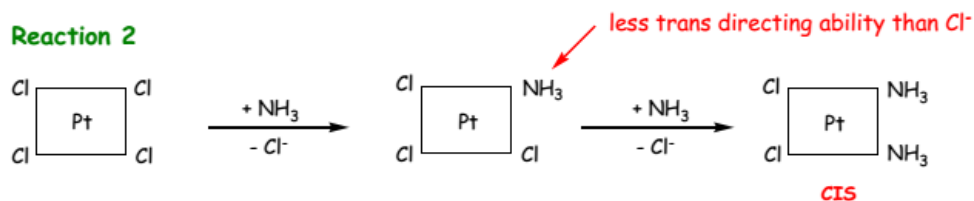
CIS

why the different isomers ?

Reaction 1



Reaction 2



Conclusion:

- Cl⁻ has a greater *trans* directing effect than NH₃. Trans directing series Cl⁻ > NH₃.
- Depends on order in which the reagents are added as to which geometric isomer is formed so has uses for devising synthesis of Pt(II) complexes.
- e.g. consider the preparation of *cis* and *trans* PtCl₂I(py) from PtCl₄²⁻, I⁻ and py.

