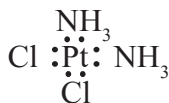


9. COORDINATION COMPOUNDS

9.1 Introduction : A coordination compound consists of central metal atom or ion surrounded by ions or molecules. For example, a chemotherapy drug, cisplatin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, is a coordination compound in which the central platinum metal ion is surrounded by two ammonia molecules and two chloride ions. The species surrounding the central metal atom or ion are called ligands. The ligands are linked directly to central metal ion through coordinate bonds. A formation of coordinate bond occurs when the shared electron pair is contributed by ligands. A coordinate bond is conveniently represented by an arrow \rightarrow , where the arrow head points to electron acceptor. The central metal atom or ion usually an electron deficient species, accepts an electron pair while the ligands serve as electron donors. Coordination compounds having a metal ion in the centre are common. In cisplatin two ammonia molecules and two chloride ligands utilize their lone pairs of electrons to form bonds with the $\text{Pt}(\text{II})$.



The donor nitrogen and chlorine atoms of the ligands are directly attached to and form bonds with platinum.

Can you recall ?

What are Lewis acids and bases ?

Formation of a coordination compound can be looked upon as the Lewis acid-base interaction. The ligands being electron pair donors are Lewis bases. The central metal ion being electron pair acceptor serves as Lewis acid.

9.2 Types of ligands : The ligands can be classified as monodentate and polydentate

ligands depending on the number of electron donor atoms they have.

9.2.1 Monodentate ligands : A monodentate ligand is the one where a single donor atom shares an electron pair to form a coordinate bond with the central metal ion. For example: the ligands Cl^\ominus , OH^\ominus or CN^\ominus attached to metal have electron pair on Cl, O and N, respectively which are donor atoms :



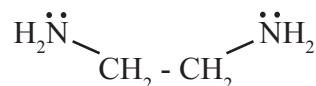
Use your brain power

Draw Lewis structure of the following ligands and identify the donor atom in them : NH_3 , H_2O

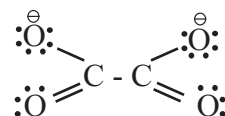


9.2.2 Polydentate ligands : A polydentate ligand has two or more donor atoms linked to the central metal ion. For example, ethylenediamine and oxalate ion. Each of these ligands possesses two donor atoms. These are **bidentate** ligands.

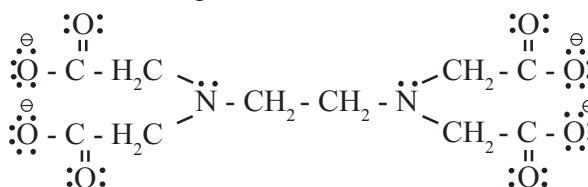
i. Ethylenediamine binds to metal using electron pair on each of its two nitrogens.



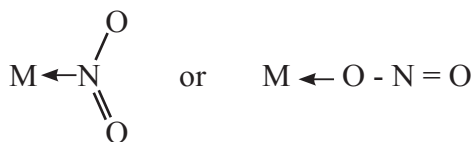
Similarly oxalate ion $(\text{C}_2\text{O}_4)^{2\ominus}$ utilizes electron pair on each of its negatively charged oxygen atoms upon linking with the metal.



ii. Ethylenediaminetetraacetate ion $(\text{EDTA})^{4\ominus}$ binds to metal ion by electron pairs of four oxygen and two nitrogen atoms. It is a **hexadentate** ligand.



9.2.3 Ambidentate ligand : The ligands which have two donor atoms and use the electron pair of either donor atoms to form a coordinate bond with the metal ion, are ambidentate ligands. For example, the ligand NO_2^\ominus links to metal ion through nitrogen or oxygen.



Similarly, SCN^\ominus has two donor atoms nitrogen and sulfur either of which links to metal depicted as $\text{M} \leftarrow \text{SCN}$ or $\text{M} \leftarrow \text{NCS}$.

9.3 Terms used in coordination chemistry: The following terms are used for describing coordination compounds.

9.3.1 Coordination sphere : The central metal ion and ligands linked to it are enclosed in a square bracket. This is called a coordination sphere, which is a discrete structural unit. When the coordination sphere comprising central metal ion and the surrounding ligands together carry a net charge, it is called the complex ion. The ionisable groups shown outside the bracket are the counter ions. For example, the compound $\text{K}_4[\text{Fe}(\text{CN})_6]$ has $[\text{Fe}(\text{CN})_6]^{4-}$ coordination sphere with the ionisable K^\oplus ions representing counter ions. The compound ionizes as :



Try this...

Can you write ionisation of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$? Identify coordination sphere and counter ions.



9.3.2 Charge number of complex ion and oxidation state of metal ion :

The net charge residing on the complex ion is its charge number. It is algebraic sum of the charges carried by the metal ion and the ligands. The charge carried by the metal ion is its oxidation state (O.S.). The complex

$[\text{Fe}(\text{CN})_6]^{4-}$ has charge number of -4. It can be utilised to calculate O.S. of Fe. Thus,

charge number of complex = -4

= (O.S. of Fe + charge of ligands)

= (O.S. of Fe + $6 \times$ charge of CN^\ominus ion)

= (O.S. of Fe + $6 \times (-1)$)

Therefore, O.S. of Fe = $-4 + 6 = +2$.

Can you tell ?

A complex is made of Co(III) and consists of four NH_3 molecules and two Cl^\ominus ions as ligands. What is the charge number and formula of complex ion ?



9.3.3 Coordination number (C.N.) of central metal ion : Look at the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^\oplus$.

Here four ammonia molecules and two chloride ions, that is, total six ligands are attached to the cobalt ion. All these are monodentate since each has only one donor atom. There are six donor atoms in the complex. Therefore, the coordination number of Co^{3+} ion in the complex is six. Thus, the coordination number of metal ion attached to monodentate ligands is equal to number of ligands bound to it.

Consider the bidentate ligand $\text{C}_2\text{O}_4^{2-}$ or ethylenediamine (en). The complexes, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Co}(\text{en})_3]^{3+}$, have three bidentate ligands each. The total donor atoms in three of ligands is six and the C.N. of Fe^{3+} and Co^{3+} in these complexes is six.

C.N. of metal ion in a complex is the number of ligand donor atoms directly attached to it or the number of electron pairs involved in the coordinate bond.

Use your brain power

Coordination number used in coordination of compounds is somewhat different than that used in solid state. Explain



Can you tell ?

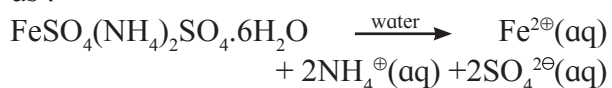
What is the coordination number of Co in $[\text{CoCl}_2(\text{en})_2]^{\oplus}$, of Ir in $[\text{Ir}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3\oplus}$ and of Pt in $[\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2]$?



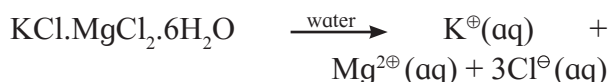
9.3.4 Double salt and coordination complex

Combination of two or more stable compounds in stoichiometric ratio can give two types of substances, namely, double salt and coordination complexes.

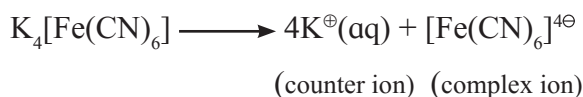
Double salt : A double salt dissociates in water completely into simple ions. For example (i) Mohr's salt, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ dissociates as :



ii. Carnalite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ dissociates as



Coordination complex : A coordination complex dissociates in water with at least one complex ion. For example, $\text{K}_4[\text{Fe}(\text{CN})_6]$ dissociates as the complex ion and counter ion.



9.3.5 Werner theory of coordination complexes : The first attempt to explain nature of bonding in coordination compounds was put forth by Werner. The postulates of Werner theory are as follows.

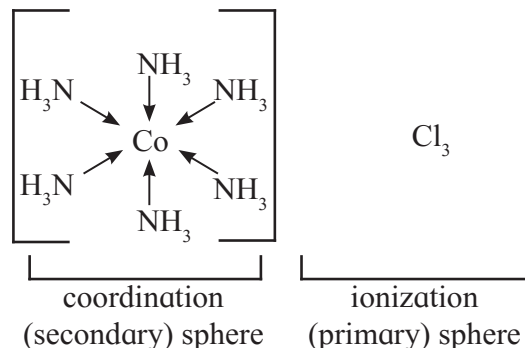
Postulate (i) Unlike metal salts, the metal in a complex possesses two types of valencies : primary (ionizable) valency and secondary (nonionizable) valency.

Postulate (ii) The ionizable sphere consists of entities which satisfy the primary valency of the metal. Primary valencies are generally satisfied by anions.

Postulate (iii) The secondary coordination sphere consists of entities which satisfy the secondary valencies and are non ionizable.

The secondary valencies for a metal ion are fixed and satisfied by either anions or neutral ligands. Number of secondary valencies is equal to the coordination number.

Postulate (iv) The secondary valencies have a fixed spatial arrangement around the metal ion. Two spheres of attraction in the complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are shown.



Remember...

When a complex is brought into solution it does not dissociate into simple metal ions. When $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is dissolved in water it does not give the test for $\text{Co}^{3\oplus}$ or NH_3 . However, on reacting with AgNO_3 a curdy white precipitate of AgCl corresponding to 3 moles is observed.



Problem 9.1 : One mole of a purple coloured complex CoCl_3 and NH_3 on treatment with excess AgNO_3 produces two moles AgCl . Write the formula of the complex if the coordination number of Co is 6.

Solution : One mole of the complex gives 2 moles of AgCl . It indicates that two Cl^{\ominus} ions react with Ag^{\oplus} ions. The complex has two ionisable Cl^{\ominus} ions. The formula of the complex is then $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

Can you tell ?

One mole of a green coloured complex of CoCl_3 and NH_3 on treatment with excess of AgNO_3 produces 1 mole of AgCl . What is the formula of the complex ? (Given : C.N. of Co is 6)



A complex with coordination number six has **octahedral** structure. When four coordinating groups are attached to the metal ion the complex would either be with **square planar** or **tetrahedral** structure.

9.4 Classification of complexes: The coordination complexes are classified according to types of ligands and sign of charge on the complex ion.

9.4.1 Classification on the basis of types of ligands

i. Homoleptic complexes : Consider $[\text{Co}(\text{NH}_3)_6]^{3+}$. Here only one type of ligands surrounds the Co^{3+} ion. The complexes in which metal ion is bound to only one type of ligands are homoleptic.

ii. Heteroleptic complexes : Look at the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. There are two types of ligands, NH_3 and Cl attached to Co^{3+} ion. Such complexes in which metal ion is surrounded by more than one type of ligands are heteroleptic.

Use your brain power

Classify the complexes as homoleptic and heteroleptic
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$, $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$
 $[\text{CoCl}(\text{NH}_3)(\text{en})_2]^{2+}$ and $[\text{Cu}(\text{C}_2\text{O}_4)_3]^{3-}$.



9.4.2 Classification on the basis of charge on the complex

i. Cationic complexes : A positively charged coordination sphere or a coordination compound having a positively charged coordination sphere is called cationic sphere complex.

For example: the cation $[\text{Zn}(\text{NH}_3)_4]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ are cationic complexes. The latter has coordination sphere $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$; the anion SO_4^{2-} makes it electrically neutral.

ii. Anionic sphere complexes : A negatively charged coordination sphere or a coordination compound having negatively charged coordination sphere is called

anionic sphere complex. For example, $[\text{Ni}(\text{CN})_4]^{2-}$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$ have anionic coordination sphere; $[\text{Fe}(\text{CN})_6]^{3-}$ and three K^+ ions make the latter electrically neutral.

iii. Neutral sphere complexes : A neutral coordination complex does not possess cationic or anionic sphere. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ or $[\text{Ni}(\text{CO})_4]$ have neither cation nor anion but are neutral sphere complexes.

Use your brain power

Classify the complexes as cationic, anionic or neutral.
 $\text{Na}_4[\text{Fe}(\text{CN})_6]$, $\text{Co}(\text{NH}_3)_6\text{Cl}_2$,
 $\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2^{3-}$, $\text{PtCl}_2(\text{en})_2$ and
 $\text{Cr}(\text{CO})_6$.



9.5 IUPAC nomenclature of coordination compounds: Tables 9.1, 9.2 and 9.3 summarize the IUPAC nomenclature of coordination compounds.

Rules for naming coordination compounds recommended by IUPAC are as follows:

1. In naming the complex ion or neutral molecule, name the ligand first and then the metal.
2. The names of anionic ligands are obtained by changing the ending -ide to -o and -ate to -ato.
3. The name of a complex is one single word. There must not be any space between different ligand names as well as between ligand name and the name of the metal.
4. After the name of the metal, write its oxidation state in Roman number which appears in parentheses without any space between metal name and parentheses.
5. If complex has more than one ligand of the same type, the number is indicated with prefixes, di-, tri-, tetra-, penta-, hexa- and so on.
6. For the complex having more than one type of ligands, they are written in an alphabetical order. Suppose two ligands with prefixes

Table 9.1 : IUPAC names of anionic and neutral ligands

Anionic ligand	IUPAC name	Anionic ligand	IUPAC name
Br^\ominus , Bromide	Bromo	$\text{CO}_3^{2\ominus}$, Carbonate	Carbonato
Cl^\ominus , Chloride	Chloro	OH^\ominus , Hydroxide	Hydroxo
F^\ominus , Fluoride	Fluoro	$\text{C}_2\text{O}_4^{2\ominus}$, Oxalate	Oxalato
I^\ominus Iodide	Iodo	NO_2^\ominus , Nitrite	Nitro (For N - bonded ligand)
CN^\ominus , Cyanide	Cyano	ONO^\ominus , Nitrite	Nitrito (For O-bonded ligand)
$\text{SO}_4^{2\ominus}$, Sulphate	Sulphato	SCN^\ominus , Thiocyanate	Thiocyanato (For ligand donor atom S)
NO_3^\ominus , Nitro	Nitrato	NCS^\ominus , Thiocyanate	Isothiocyanato (For ligand donor atom N)
Neutral ligand	IUPAC name	Neutral ligand	IUPAC names
NH_3 , Ammonia	Ammine (Note the spelling)	H_2O , water	Aqua
CO, Carbon monoxide	Cabonyl	en, Ethylene diamine	Ethylenediamine

Table 9.2 : IUPAC names of metals in anionic complexes

Metal	IUPAC name	Metal	IUPAC name
Aluminium, Al	Aluminate	Chromium, Cr	Chromate
Cobalt, Co	Cobaltate	Copper, Cu	Cuprate
Gold, Au	Aurate	Iron, Fe	Ferrate
Manganese, Mn	Maganate	Nickel, Ni	Nickelate
Platinum, Pt	Platinate	Zinc, Zn	Zincate

Table 9.3 : IUPAC names of some complexes

Complex	IUPAC name
i. Anionic complexes : a. $[\text{Ni}(\text{CN})_4]^{2\ominus}$ b. $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3\ominus}$ c. $[\text{Fe}(\text{CN})_6]^{4\ominus}$	Tetracyanonickelate(II) ion Trioxalatocobaltate(III) ion Hexacyanoferrate(II) ion
ii. Compounds containing complex anions and metal cations : a. $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ b. $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ c. $\text{Na}_3[\text{AlF}_6]$	Sodium hexanitrocobaltate(III) Potassium trioxalatoaluminate(III) Sodium hexafluoroaluminate(III)
iii. Cationic complexes : a. $[\text{Cu}(\text{NH}_3)_4]^{2\oplus}$ b. $[\text{Fe}(\text{H}_2\text{O})_5(\text{NCS})]^{2\oplus}$ c. $[\text{Pt}(\text{en})_2(\text{SCN})_2]^{2\oplus}$	Tetraamminecopper(II) ion Pentaaquaisothiocyanatoiron(III) ion, Bis(ethylenediamine)dithiocyanatoplatinum(IV).
iv. Compounds containing complex cations and anion : a. $[\text{PtBr}_2(\text{NH}_3)_4]\text{Br}_2$ b. $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$ c. $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{I}_3$	Tetraamminedibromoplatinum(IV) bromide, Pentaamminecarbonatocobalt(III) chloride, Pentaammineaquacobalt(III) iodide.
v. Neutral complexes : a. $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$ b. $\text{Fe}(\text{CO})_5$ c. $[\text{Rh}(\text{NH}_3)_3(\text{SCN})_3]$	Triamminetrinitrocobalt(III) Pentacarbonyliron(0) Triamminetrithiocyanatorhodium(III)

are tetraaqua and dichloro. While naming in alphabetical order, tetraaqua is first and then dichloro.

- If the name of ligand itself contains numerical prefix then display number by prefixes with bis for 2, tris for 3, tetrakis for 4 and so forth. Put the ligand name in parentheses. For example, (ethylenediamine)₃ or (en)₃ would appear as tris(ethylenediamine) or tris(ethane-1, 2-diamine).
- The metal in cationic or neutral complex is specified by its usual name while in the anionic complex the name of metal ends with 'ate'.

Try this...

Write the representation of

- Tricarbonatocobaltate(III) ion.
- Sodium hexacyanoferrate(III).
- Potassium hexacyanoferrate (II)
- Aquachlorobis(ethylenediamine) cobalt(III).
- Tetraaquadichlorochromium(III) chloride.
- Diamminedichloroplatinum(II).



9.6 Effective Atomic Number (EAN) Rule :

An early attempt to explain the stability of coordination compounds was made by Sidgwick who proposed an empirical rule known as effective atomic number (EAN) rule. EAN equals total number of electrons around the central metal ion in the complex. EAN

rule states that a metal ion continues to accept electrons pairs till it attains the electronic configuration of the next noble gas. Thus if the EAN is equal to 18 (Ar), 36 (Kr), 54 (Xe), or 86 (Rn) then the EAN rule is obeyed.

EAN can be calculated with the following formula

$$\begin{aligned}\text{EAN} &= \text{number of electrons of metal ion} + \text{total} \\ &\quad \text{number of electrons donated by ligands} \\ &= \text{atomic number of metal (Z)} - \text{number} \\ &\quad \text{of electrons lost by metal to form the} \\ &\quad \text{ion (X)} + \text{number of electrons donated} \\ &\quad \text{by ligands (Y)} \\ &= Z - X + Y\end{aligned}$$

Consider $\text{Co}[\text{NH}_3]_6^{3+}$

Oxidation state of Cobalt is +3, six ligands donate 12 electrons.

$$Z = 27; X = 3; Y = 12$$

$$\text{EAN of } \text{Co}^{3+} = 27 - 3 + 12 = 36.$$

Try this...

Find out the EAN of $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$



$\text{Cr}(\text{CO})_6$ and $[\text{Fe}(\text{CN})_6]^{4-}$ are some examples of coordination compounds which obey the EAN rule. Certain other coordination compounds however do not obey the EAN rule. For example, $[\text{Fe}(\text{CN})_6]^{3-}$ and $\text{Cu}[\text{NH}_3]_4^{2+}$ have EAN 35.

Use your brain power

Do the following complexes follow the EAN rule ? $\text{Cr}(\text{CO})_4$, $\text{Ni}(\text{CO})_4$, $\text{Mn}(\text{CO})_5$, $\text{Fe}(\text{CO})_5$.

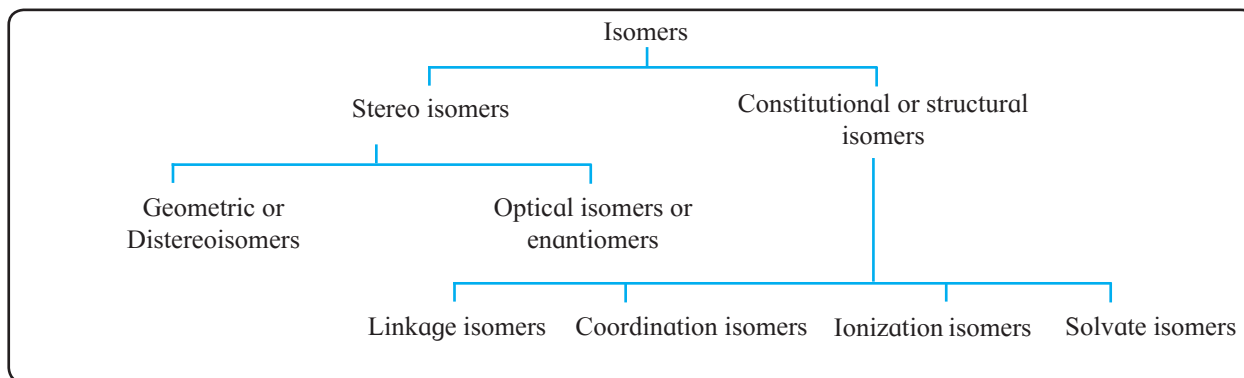


Fig. 9.1 : Classification of isomers in coordination compounds

9.7 Isomerism in coordination compounds :

One of the interesting aspects of coordination chemistry is existence of isomers. Isomers are different compounds that have the same molecular formula. Their chemical reactivities and physical properties such as colour, solubility and melting point are different.

Broadly speaking, isomers are classified into two types namely stereoisomers and constitutional (or structural) isomers as displayed in Fig. 9.1.

9.7.1 Stereoisomers : Stereoisomers have the same links among constituent atoms however the arrangements of atoms in space are different.

There are two kinds of stereoisomers in coordination compounds: (a) geometric isomers or distereoisomers and (b) enantiomers or optical isomers.

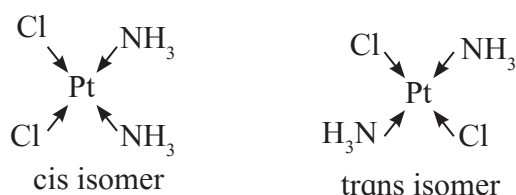
a. Geometric isomers or distereoisomers : These are nonsuperimposable mirror image isomers. These are possible in heteroleptic complexes. In these isomers, there are cis and trans types of arrangements of ligands.

Cis-isomers : Identical ligands occupy adjacent positions.

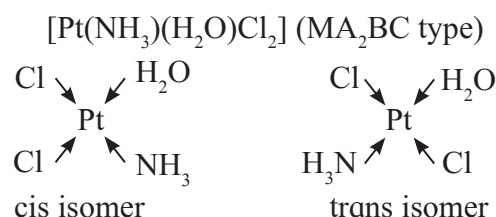
Trans-isomer : Identical ligands occupy the opposite positions.

Cis and trans isomers have different properties. Cis trans isomerism is observed in square planar and octahedral complexes.

i. Cis and trans isomers in square planar complexes : The square planar complexes of MA_2B_2 and MA_2BC type exist as cis and trans isomers, where A, B and C are monodentate ligands, M is metal. For example : $Pt(NH_3)_2Cl_2$, (MA_2B_2 type)

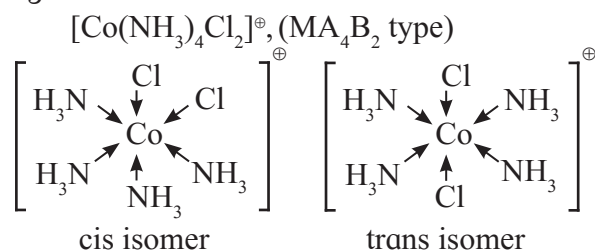


Here the cis isomer is more soluble in water than the trans isomer. The cis isomer named cisplatin is an anticancer drug while the trans isomer is physiologically inactive. The cis isomer is polar with non-zero dipole moment. The trans isomer has zero dipole moment as a result of the two opposite Pt - Cl and two Pt-NH₃ bond moments, which cancel each other.

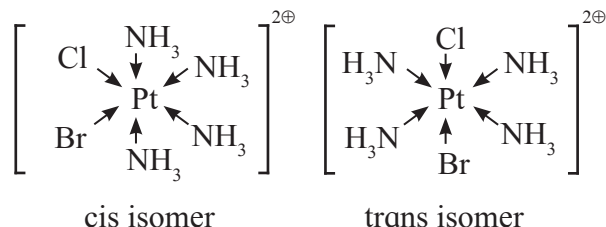


Four coordinate tetrahedral complexes do not show cis and trans isomers.

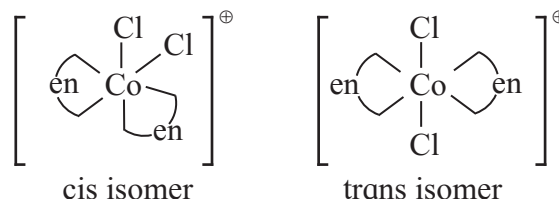
iii. Cis and trans isomers in octahedral complexes : The octahedral complexes of the type MA_4B_2 , MA_4BC and $M(AA)_2B_2$ exist as cis and trans isomers. (AA) is a bidentate ligand.



$[Pt(NH_3)_4ClBr]^{2+}$, (MA_4BC type)



$[Co(en)_2Cl_2]^+$, ($M(AA)_2B_2$ type)



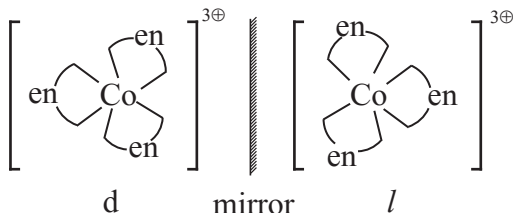
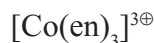
Try this...

Draw structures of the cis and trans isomers of $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^\ominus$

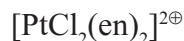
**b. Optical isomers (Enantiomers) :**

The complex molecules or ions that are nonsuperimposable mirror images of each other are enantiomers. The nonsuperimposable mirror images are chiral. (A more elaborate discussion on chirality and optical isomerism is included in Chapter 10.)

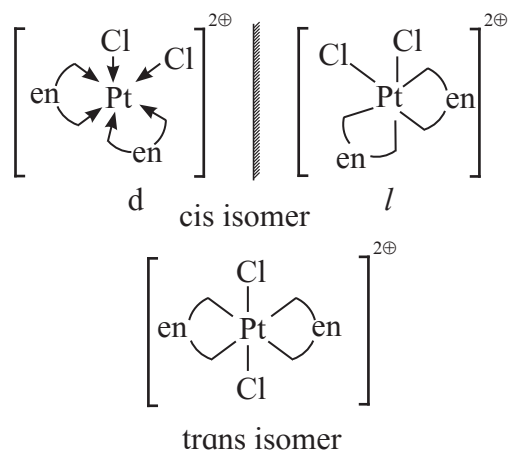
Enantiomers have identical properties however differ in their response to the plane-polarized light. The enantiomer that rotates the plane of plane-polarized light to right (clockwise) is called the dextro (*d*) isomer, while the other that rotates the plane to left (anticlockwise) is called laevo (*l*) isomer.

i. Optical isomers in octahedral complexes**Remember...**

Our hands are non superimposable mirror images. When you hold your left hand upto a mirror the image looks like right hand.

**ii. Octahedral complexes existing as both geometric and optical isomers**

In this type of complex, only the cis isomer exists as pair of enantiomers



Square planar complexes do not show enantiomers since they have mirror plane and axis of symmetry.

Try this...

1. Draw enantiomers of $[\text{Cr}(\text{ox})_3]^{3\ominus}$
2. Draw enantiomers and cis and trans isomers of $[\text{Cr}(\text{H}_2\text{O})_2(\text{ox})_2]^\ominus$ (where $\text{ox} = \text{C}_2\text{O}_4^{2\ominus}$)



9.7.2 Structural isomers (Constitutional isomers) : Structural isomers possess different linkages among their constituent atoms and have, their chemical formulae to be the same.

They can be classified as linkage isomers, ionization isomers, coordination isomers and solvate isomers.

a. Linkage isomers : These isomers are formed when the ligand has two different donor atoms. It coordinates to the metal via different donor atoms. Thus the nitrite ion NO_2^\ominus having two donor atoms show isomers as :



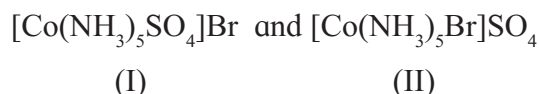
The nitro complex has Co-N bond and the nitrito complex is linked through Co-O bond. These are linkage isomers.

Can you tell ?

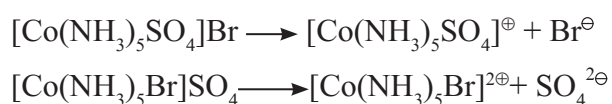
Write linkage isomers of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^\oplus$. Write their IUPAC names.



b. Ionization isomers : Ionization isomers involve exchange of ligands between coordination and ionization spheres. For example:



In compound I, anion SO_4^{2-} , bonded to Co is in the coordination sphere while Br^- is in the ionization sphere. In compound II, anion Br^- is in the coordination sphere linked to Co while SO_4^{2-} is in the ionisation sphere. These complexes in solution ionize to give different ions.



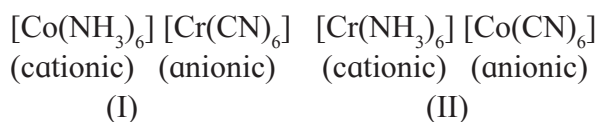
I and II are examples of ionization isomers.

Can you tell ?

Can you write IUPAC names of isomers I and II?



c. Coordination isomers : Coordination isomers show interchange of ligands between cationic and anionic spheres of different metal ions. For example :



In isomer I, cobalt is linked to ammine ligand and chromium to cyanide ligand. In isomer II the ligands coordinating to metals are interchanged. Cobalt coordinates with cyanide ligand and chromium to NH_3 ligand. I and II are examples of coordination isomers.

d. Solvate isomers (Hydrate isomers when water is solvent) : These are similar to ionization isomers. Look at the complexes.



In compound I the solvent water is directly bonded to Cr. In compound II, H_2O appears as

the free solvent molecule. I and II represent solvate (hydrate) isomers.

9.8 Stability of the coordination compounds:

The stability of coordination compounds can be explained by knowing their stability constants. The stability is governed by metal-ligand interactions. In this the metal serves as electron-pair acceptor while the ligand as Lewis base (since it is electron donor). The metal-ligand interaction can be realized as the Lewis acid-Lewis base interaction. Stronger the interaction greater is stability of the complex.

Consider the equilibrium for the metal ligand interaction :

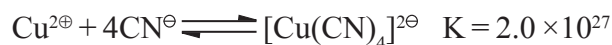


where a , x , $[a+ + nx-]$ denote the charge on the metal, ligand and the complex, respectively. Now, the equilibrium constant K is given by

$$K = \frac{[\text{ML}_n]^{a+ + nx-}}{[\text{M}^{a+}][\text{L}^{x-}]^n}$$

Stability of the complex can be explained in terms of K . Higher the value of K larger is the thermodynamic stability of the complex.

The equilibria for the complex formation with the corresponding K values are given below.



From the above data, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is more stable than $[\text{Ag}(\text{CN})_2]^{-}$ and $[\text{Cu}(\text{CN})_4]^{2-}$.

9.8.1 Factors which govern stability of the complex : Stability of a complex is governed by (a) charge to size ratio of the metal ion and (b) nature of the ligand.

a. charge to size ratio of the metal ion

Higher the ratio greater is the stability. For the divalent metal ion complexes their stability shows the trend : $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Cd}^{2+}$. The above stability order

is called Irving-William order. In the above list both Cu and Cd have the charge +2, however, the ionic radius of Cu^{2+} is 69 pm and that of Cd^{2+} is 97 pm. The charge to size ratio of Cu^{2+} is greater than that of Cd^{2+} . Therefore the Cu^{2+} forms stable complexes than Cd^{2+} .

b. Nature of the ligand.

A second factor that governs stability of the complexes is related to how easily the ligand can donate its lone pair of electrons to the central metal ion that is, the basicity of the ligand. The ligands those are stronger bases tend to form more stable complexes.

Use your brain power

The stability constant K of the $[\text{Ag}(\text{CN})_2]^\ominus$ is 5.5×10^{18} while that for the corresponding $[\text{Ag}(\text{NH}_3)_2]^\oplus$ is 1.6×10^7 . Explain why $[\text{Ag}(\text{CN})_2]^{2\ominus}$ is more stable.



9.9 Theories of bonding in complexes :

The metal-ligand bonding in coordination compounds has been described by Valence Bond Theory (VBT) and Crystal Field Theory (CFT).

9.9.1 Valence bond theory (VBT)

Can you recall ?

What is valence bond theory and the concept of Hybridisation?



The hybridized state is a theoretical step that describes how complexes are formed. VBT is based on the concept of hybridization. The hybrid orbitals neither exist nor can be detected spectroscopically. These orbitals, however, help us to describe structure of coordination compounds. The steps involved in describing bonding in coordination compounds using the VBT are given below.

- Metal ion provides vacant d orbitals for formation of coordinate bonds with ligands.
- The vacant d orbitals along with s and p orbitals of the metal ion take part in hybridisation.

- The number of vacant hybrid orbitals formed is equal to the number of ligand donor atoms surrounding the metal ion which equals the coordination number of metal.
- Overlap between the vacant hybrid orbitals of the metal and filled orbitals of the ligand leads to formation of the metal-ligand coordinate bonds.
- The hybrid orbitals used by the metal ion point in the direction of the ligand.
- The (n-1)d or nd orbitals used in hybridisation allow the complexes to be classified as (a) inner orbital and (b) outer orbital complexes respectively.

Type of hybridisation decides the structure of the complex. For example when the hybridisation is d^2sp^3 the structure is octahedral. Steps to understand the metal-ligand bonding include :

- Find oxidation state of central metal ion
- Write valence shell electronic configuration of free metal ion.
- See whether the complex is low spin or high spin. (applicable only for octahedral complexes with d^4 to d^8 electronic configurations).
- From the number of ligands find the number of metal ion orbitals required for bonding.
- Identify the orbitals of metal ion available for hybridisation and the type of hybridisation involved.
- Write the electronic configuration after hybridisation.
- Show filling of orbitals after complex formation.
- Determine the number of unpaired electrons and predict magnetic behaviour of the complex.

Remember...

Complete the missing entries.

Coordination number	Geometry of complex	Hybridisation
2		sp
4	Tetrahedral	
4	Square planar	
6		d^2sp^3 / sp^3d^2

Try this...

Give VBT description of bonding in each of following complexes.

- $[ZnCl_4]^{2-}$
- $[Co(H_2O)_6]^{2+}$ (high spin)
- $[Pt(CN)_4]^{2-}$ (square planar)
- $[CoCl_4]^{2-}$ (tetrahedral)
- $[Cr(NH_3)_6]^{3+}$

9.9.2 Octahedral, complexes

a. $[Co(NH_3)_6]^{3+}$ low spin

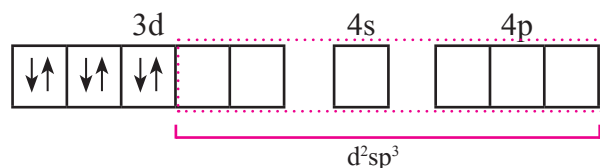
- Oxidation state of Cobalt is +3
- Valence shell electronic configuration of Co^{3+} is represented in box diagram as shown below :



- Number of ammine ligands is 6, number of vacant metal ion orbitals required for bonding with ligands must be six.
- Complex is low spin, so pairing of electrons will take place prior to hybridisation.
- Electronic configuration after pairing would be

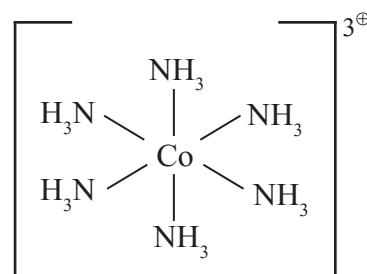
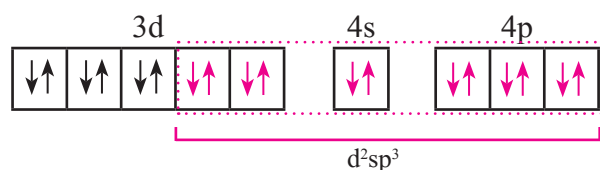


- Six orbitals available for hybridisation are two 3d, one 4s, three 4p orbitals



The orbitals for hybridization are decided from the number of ammine ligands which is six. Here (n-1)d orbitals participate in hybridization since it is the low spin complex.

- Electronic configuration after complex formation.



- As all electrons are paired the complex is diamagnetic.

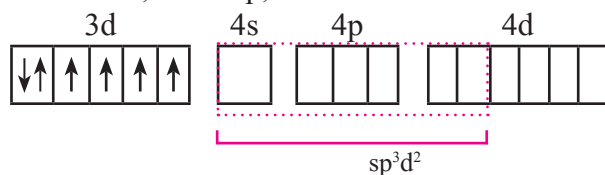
b. $[CoF_6]^{3-}$ high spin

- Oxidation state of central metal Co is +3
- Valence shell electronic configuration of Co^{3+} is



- Six fluoride F^- ligands, thus the number of vacant metal ion orbitals required for bonding with ligands would be six.
- Complex is high spin, that means pairing of electrons will not take place prior to hybridisation. Electronic configuration would remain the same as in the free state shown above.

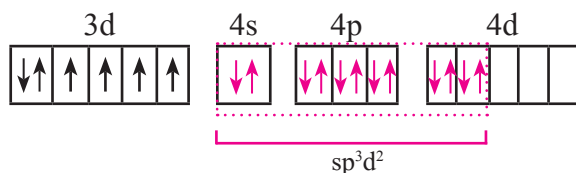
v. Six orbitals available for the hybridisation are one 4s, three 4p, two of 4d orbitals



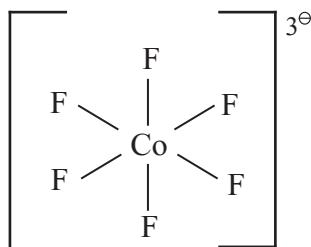
Six metal orbitals after bonding with six F^- ligands led to the sp^3d^2 hybridization. The d orbitals participating in hybridisation for this complex are nd.

vi. Six vacant sp^3d^2 hybrid orbital of Co^{3+} overlap with six orbitals of fluoride forming Co - F coordinate bonds.

vii. Configuration after complex formation.



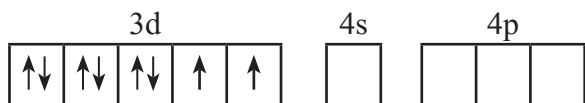
viii. The complex is octahedral and has four unpaired electrons and hence, is paramagnetic.



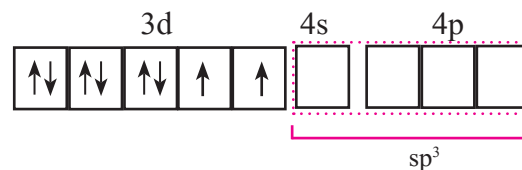
9.9.3 Tetrahedral complex



- Oxidation state of nickel is +2
- Valence shell electronic configuration of Ni^{2+}

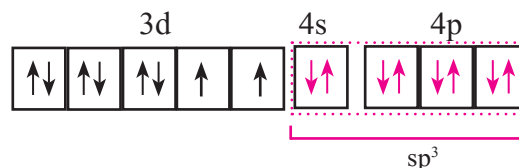


- number of Cl^- ligands is 4. Therefore number of vacant metal ion orbitals required for bonding with ligands must be four.
- Four orbitals on metal available for hybridisation are one 4s, three 4p. The complex is tetrahedral.

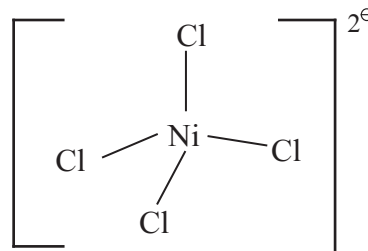


The four metal ion orbitals for bonding with Cl^- ligands are derived from the sp^3 hybridization.

- Four vacant sp^3 hybrid orbitals of Ni^{2+} overlap with four orbitals of Cl^- ions.
- Configuration after complex formation would be.



vii. The complex has two unpaired electrons and hence, paramagnetic.



9.9.4 Square planar complex



- Oxidation state of nickel is +2
- Valence shell electronic configuration of Ni^{2+}



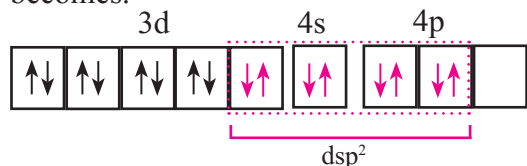
- Number of CN^- ligands is 4, so number of vacant metal ion orbitals required for bonding with ligands would be four.
- Complex is square planar so Ni^{2+} ion uses dsp^2 hybrid orbitals.
- 3d electrons are paired prior to the hybridisation and electronic configuration of Ni^{2+} becomes :



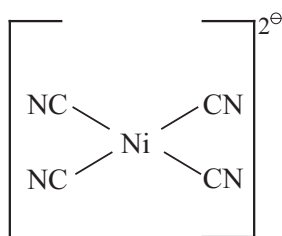
vi. Orbitals available for hybridisation are one 3d, one 4s and two 4p which give dsp^2 hybridization.

vii. Four vacant dsp^2 hybrid orbitals of Ni^{2+} overlap with four orbitals of CN^\ominus ions to form Ni - CN coordinate bonds.

viii. Configuration after the complex formation becomes.



viii. The complex has no unpaired electrons and hence, diamagnetic.



Try this...

Based on the VBT predict structure and magnetic behavior of the $[Ni(NH_3)_6]^{3+}$ complex.



9.9.5 Limitations of VBT

i. It does not explain the high spin or low spin nature of the complexes. In other words, strong and weak field nature of ligands can not be distinguished.

ii. It does not provide any explanation for the colour of coordination compounds.

iii. The structure of the complexes predicted from the VBT would not always match necessarily with those determined from the experiments.

To overcome these difficulties in VBT, the Crystal field theory has been proposed which has widely been accepted.

9.9.6 Crystal Field theory (CFT)

C.F.T. is based on following assumptions

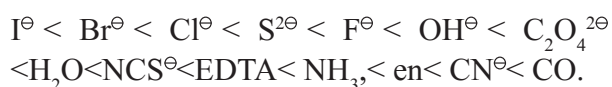
i. The ligands are treated as point charges. The interaction between metal ion and ligand is purely electrostatic or there are no orbital interactions between metal and ligand.

In an isolated gaseous metal ion the five d orbitals, $d_{x^2-y^2}$, d_{z^2} , d_{xy} , d_{yz} , d_{zx} have the same energy i.e. they are degenerate.

ii. When ligands approach the metal ion they create crystal-field around the metal ion. If it were symmetrical the degeneracy of the d orbitals remains intact.

Usually the field created is not symmetrical and the degeneracy is destroyed. The d orbitals thus split into two sets namely, (d_{xy} , d_{yz} , d_{xz}) usually referred by t_{2g} and ($d_{x^2-y^2}$, d_{z^2}) called as e_g . These two sets of orbitals now have different energies. A separation of energies of these two sets of d orbitals is the **crystal field splitting** parameter. This is denoted by Δ_o (O for octahedral).

iii. The Δ_o depends on strength of the ligands. The ligands are then classified as (a) strong field and (b) weak field ligands. Strong field ligands are those in which donor atoms are C, N or P. Thus CN^\ominus , NC^\ominus , CO, NH_3 , EDTA, en (ethylenediamine) are considered to be strong ligands. They cause larger splitting of d orbitals and pairing of electrons is favoured. These ligands tend to form low spin complexes. Weak field ligands are those in which donor atoms are halogens, oxygen or sulphur. For example, F^\ominus , Cl^\ominus , Br^\ominus , I^\ominus , SCN^\ominus , $C_2O_4^{2-}$. In case of these ligands the Δ_o parameter is smaller compared to the energy required for the pairing of electrons, which is called as electron pairing energy. The ligands then can be arranged in order of their increasing field strength as



Let us understand **splitting of d orbitals and formation of octahedral complexes**

In octahedral environment the central metal ion is surrounded by six ligands.

Ligands approach the metal ion along the x, y, z axes. As the ligands approach the metal ion the degeneracy of d orbitals is resolved.

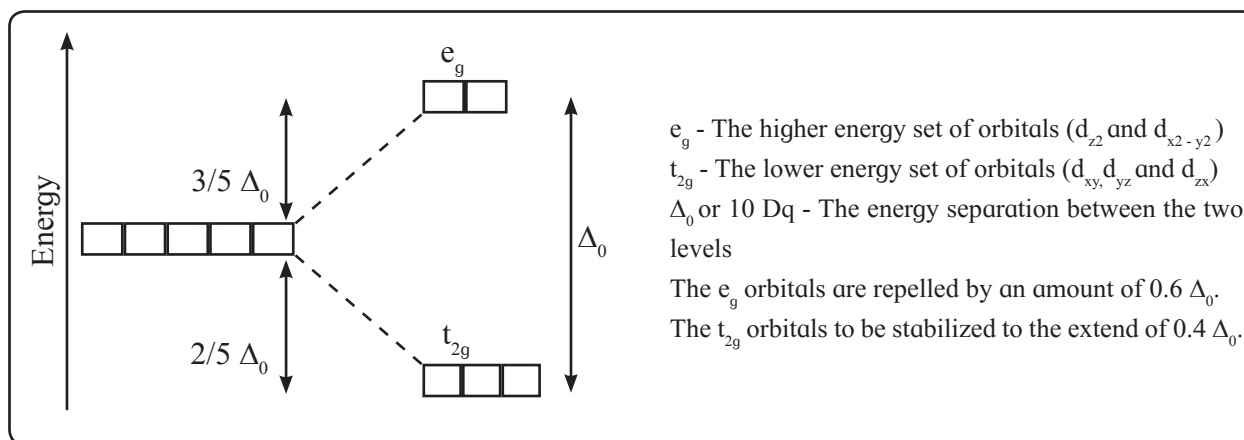


Fig. 9.2 : Crystal field Splitting in an octahedral complex

With closer approach of ligands along the axes, the doubly degenerate $d_{x^2-y^2}$ and d_{z^2} (e_g) orbitals experience larger repulsion than the triply degenerate t_{2g} orbitals. As shown in Fig. 9.2, the e_g set has higher energy than the t_{2g} set by the amount Δ_0 . The Δ_0 parameter is equal to 10 Dq units of splitting of t_{2g} and e_g levels. For electronic configurations d^1 , d^2 , d^3 the electrons occupy t_{2g} orbitals and obey the Hund's rules. For electronic configurations d^1 , d^2 , d^3 and d^8 , d^9 , d^{10} the high spin and low spin configurations cannot be distinguished. Only the electronic configurations d^4 to d^7 render the high and low spin complexes. These are depicted in Table 9.5.

Table 9.5 : d orbital diagrams for high spin and low spin complexes.

d orbital electronic configuration		High spin	Low spin
d^4	e_g	\uparrow — —	— — —
	t_{2g}	\uparrow \uparrow \uparrow	$\uparrow\downarrow$ \uparrow \uparrow
d^5	e_g	\uparrow \uparrow —	— — —
	t_{2g}	\uparrow \uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow
d^6	e_g	\uparrow \uparrow —	— — —
	t_{2g}	$\uparrow\downarrow$ \uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$
d^7	e_g	\uparrow \uparrow —	\uparrow — —
	t_{2g}	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$

9.9.7 Factors affecting Crystal Field Splitting parameter (Δ_0)

- The magnitude of crystal field splitting depends on strength of the ligands. The strong ligands those appear in spectrochemical series approach closer to the central metal which results in a large crystal field splitting.
- Oxidation state of the metal :** A metal with the higher positive charge is able to draw ligands closer to it than that with the lower one. Thus the metal in higher oxidation state results in larger separation of t_{2g} and e_g set of orbitals. The trivalent metal ions cause larger crystal field splitting than corresponding divalent ones.

9.9.8 Colour of the octahedral complexes

As discussed above, the formation of an octahedral complex is accompanied by splitting of d orbitals into t_{2g} and e_g sets. A separation of these two sets of orbitals is Δ_0 , which can be measured from experiments. The Δ_0 corresponds to a certain frequency of electromagnetic radiation usually in the visible region. A colour complementary to the absorbed frequency is thus observed. Consider the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex. The central metal ion titanium has electronic configuration $3d$ and the electron occupies one of the t_{2g} orbitals (Figure 9.3).

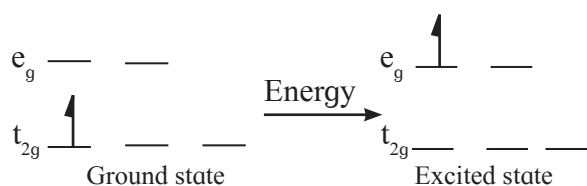


Fig. 9.3 : d - d transition in d system

The absorption of the wavelength of light corresponding to Δ_o parameter promotes an electron from the t_{2g} level. Such energy gap in case of the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex is $20,300 \text{ cm}^{-1}$ (520 nm , 243 kJ/mol) and a complimentary colour to this is imparted to the complex. A violet color of the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex arises from such d-d transition.

9.9.9 Tetrahedral complexes

A pattern of splitting of d orbitals, which is a key in the crystal field theory, is dependent on the ligand field environment. This is illustrated for the tetrahedral ligand field environment.

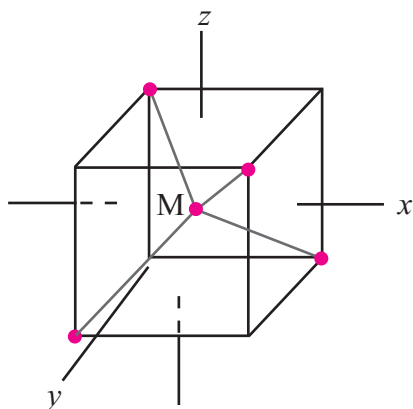


Fig. 9.4 : Tetrahedral structure

The tetrahedral structure having the metal atom M at the centre and four ligands occupying the corners of a tetrahedron is displayed along with in Fig. 9.4.

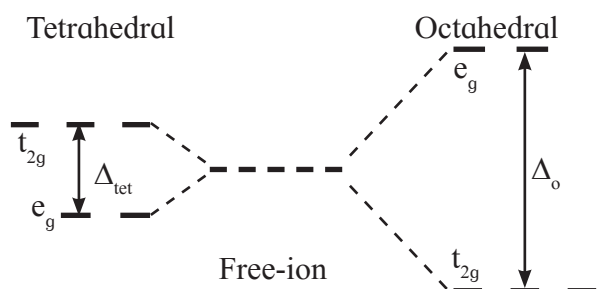


Fig. 9.5 : Splitting of d orbitals in tetrahedral and octahedral complexes

Try this...



Sketch qualitatively crystal field d orbital energy level diagrams for each of the following complexes:

- a. $[\text{Ni}(\text{en})_3]^{2+}$ b. $[\text{Mn}(\text{CN})_6]^{3-}$
c. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Predict whether each of the complexes is diamagnetic or paramagnetic.

The d_{xy} , d_{yz} , d_{zx} orbitals with their lobes lying in between the axes point toward the ligands. On the other hand, $d_{x^2-y^2}$ and d_{z^2} orbitals lie in between metal-ligand bond axes. The d_{xy} , d_{yz} and d_{zx} orbitals experience more repulsion from the ligands compared to that by $d_{x^2-y^2}$ and d_{z^2} orbitals.

Due to larger such repulsions the d_{xy} , d_{yz} and d_{zx} orbitals are of higher energy while the $d_{x^2-y^2}$ and d_{z^2} orbitals are of relatively lower energy.

Each electron entering in one of the d_{xy} , d_{yz} and d_{zx} orbitals raises the energy by $4 Dq$ whereas that occupying $d_{x^2-y^2}$ and d_{z^2} orbitals lowers it by $6 Dq$ compared to the energy of hypothetical degenerate d orbitals in the ligand field.

A splitting of d orbitals in tetrahedral crystal fields (assumed to be $10 Dq$) thus is much less (typically $4/9$) compared to that for the octahedral environment. The crystal field splitting of d orbitals in a tetrahedral ligand field is compared with the octahedral one in Fig. 9.5. Thus the pairing of electrons is not favoured in tetrahedral structure. For example, in d^4 configuration an electron would occupy one of the t_{2g} orbitals. The low spin tetrahedral complexes thus are not found.

Typically metal complexes possessing the central metal ion with d^8 electronic configuration, for example, $\text{Ni}(\text{CO})_4$, favours the tetrahedral structure.

9.10 Applications of coordination compounds

a. In biology : Several biologically important natural compounds are metal complexes. They play important role in a number of processes occurring in plants and animals.

For example, chlorophyll present in plants is a complex of Mg. Haemoglobin present in blood is a complex of iron.

b. In medicines

- Pt complex cisplatin is used in the treatment of cancer.
- EDTA is used for treatment of lead poisoning.

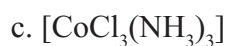
c. To estimate hardness of water : Hardness of water is due to the presence of Ca^{2+} and Mg^{2+} ions. The ligand EDTA forms stable complexes with Ca^{2+} and Mg^{2+} . It can, therefore, be used to estimate hardness of water.

d. In electroplating : Usually stable coordination complexes on dissolution dissociate to small extent and furnish a controlled supply of metal ions. The metal ions when reduced clump together to form the clusters or nanoparticles. When the coordination complexes are used the ligands in the complex keep the metal atoms well separated from each other. These metal atoms tend to form a protective layer on the surface. Certain cyanide complexes $\text{K}[\text{Ag}(\text{CN})_2]$ and $\text{K}[\text{Au}(\text{CN})_2]$ find applications in the electroplating of these noble metals.

Exercises

1. Choose the most correct option.

- The oxidation state of cobalt ion in the complex $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ is
 - +2
 - +3
 - +1
 - +4
- IUPAC name of the complex $[\text{Pt}(\text{en})_2(\text{SCN})_2]^{2+}$ is
 - bis (ethylenediamine) dithiocyanatoplatinum (IV) ion
 - bis (ethylenediamine) dithiocyanatoplatinate (IV) ion
 - dicyanatobis (ethylenediamine) platinate IV ion
 - bis (ethylenediammine)dithiocynato platinate (IV) ion
- Formula for the compound sodium hexacyanoferrate (III) is
 - $[\text{NaFe}(\text{CN})_6]$
 - $\text{Na}_2[\text{Fe}(\text{CN})_6]$
 - $\text{Na}[\text{Fe}(\text{CN})_6]$
 - $\text{Na}_3[\text{Fe}(\text{CN})_6]$
- Which of the following complexes exist as cis and trans isomers ?
 - $[\text{Cr}(\text{NH}_3)_2\text{Cl}_4]^\ominus$
 - $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2\oplus}$
 - $[\text{PtCl}_2\text{Br}_2]^{2\ominus}$ (square planar)
 - $[\text{FeCl}_2(\text{NCS})_2]^{2\ominus}$ (tetrahedral)
 - 1 and 3
 - 2 and 3
 - 1 and 3
 - 4 only
- Which of the following complexes are chiral ?
 - $[\text{Co}(\text{en})_2\text{Cl}_2]^\oplus$
 - $[\text{Pt}(\text{en})\text{Cl}_2]$
 - $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3\ominus}$
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^\oplus$
 - 1 and 3
 - 2 and 3
 - 1 and 4
 - 2 and 4
- On the basis of CFT predict the number of unpaired electrons in $[\text{CrF}_6]^{3\ominus}$.
 - 1
 - 2
 - 3
 - 4
- When an excess of AgNO_3 is added to the complex one mole of AgCl is precipitated. The formula of the complex is
 - $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$
 - $[\text{CoCl}(\text{NH}_3)_4]\text{Cl}_2$



viii. The sum of coordination number and oxidation number of M in $[\text{M}(\text{en})_2\text{C}_2\text{O}_4]\text{Cl}$ is

- a. 6 b. 7 c. 9 d. 8

2. Answer the following in one or two sentences.

i. Write the formula for tetraammineplatinum (II) chloride.

ii. Predict whether the $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ complex is chiral. Write structure of its enantiomer.

iv. Name the Lewis acids and bases in the complex $[\text{PtCl}_2(\text{NH}_3)_2]$.

v. What is the shape of a complex in which the coordination number of central metal ion is 4?

vi. Is the complex $[\text{CoF}_6]$ cationic or anionic if the oxidation state of cobalt ion is +3?

vii. Consider the complexes $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$. What type of isomerism these two complexes exhibit?

viii. Mention two applications of coordination compounds.

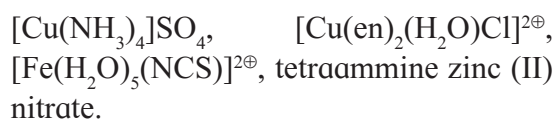
3. Answer in brief.

i. What are bidentate ligands? Give one example.

ii. What is the coordination number and oxidation state of metal ion in the complex $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^\ominus$?

iii. What is the difference between a double salt and a complex? Give an example.

iv. Classify following complexes as homoleptic and heteroleptic



v. Write formulae of the following complexes

a. Potassium amminetrichloroplatinate (II)

b. Dicyanoaurate (I) ion

vi. What are ionization isomers? Give an example.

vii. What are the high-spin and low-spin complexes?

viii. $[\text{CoCl}_4]^{2\ominus}$ is tetrahedral complex. Draw its box orbital diagram. State which orbitals participate in hybridization.

ix. What are strong field and weak field ligands? Give one example of each.

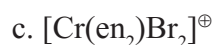
x. With the help of crystal field energy-level diagram explain why the complex $[\text{Cr}(\text{en})_3]^{3\oplus}$ is coloured?

4. Answer the following questions.

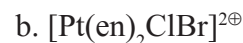
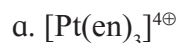
i. Give valence bond description for the bonding in the complex $[\text{VCl}_4]^\ominus$. Draw box diagrams for free metal ion. Which hybrid orbitals are used by the metal? State the number of unpaired electrons.

ii. Draw qualitatively energy-level diagram showing d-orbital splitting in the octahedral environment. Predict the number of unpaired electrons in the complex $[\text{Fe}(\text{CN})_6]^{4\ominus}$. Is the complex diamagnetic or paramagnetic? Is it coloured? Explain.

iii. Draw isomers in each of the following



iv. Draw geometric isomers and enantiomers of the following complexes.

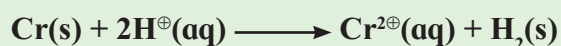


- v. What are ligands ? What are their types ? Give one example of each type.
- vi. What are cationic, anionic and neutral complexes? Give one example of each.
- vii. How stability of the coordination compounds can be explained in terms of equilibrium constants ?
- viii. Name the factors governing the equilibrium constants of the coordination compounds.

Activity :



1. The reaction of chromium metal with H_2SO_4 in the absence of air gives blue solution of chromium ion.



Cr^{2+} forms octahedral complex with H_2O ligands.

- a. Write formula of the complex
- b. Describe bonding in the complex using CFT and VBT.

Draw crystal field splitting and valence bond orbital diagrams.

2. Reaction of complex $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ with HCl gives a complex

$[\text{Co}(\text{NH}_3)_3\text{H}_2\text{OCl}_2]^+$ in which two chloride ligands are trans to one another.

- a. Draw possible stereoisomers of starting material
- b. Assuming that NH_3 groups remain in place, which of two starting isomers would give the observed product ?