Coordination Compounds

Addition Compounds

When two or more than two simple salts are allowed to chemically combine in a fix ratio then addition compound is formed.

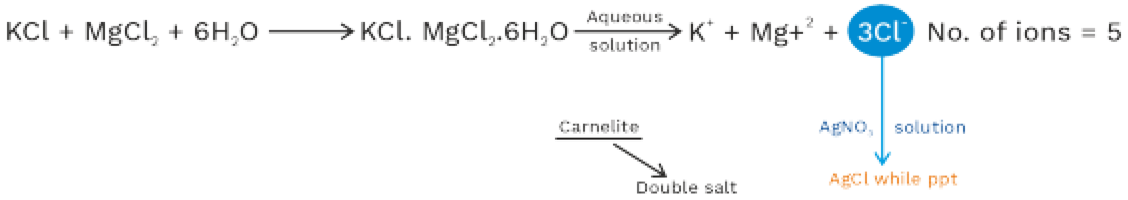
On the basis of behaviour in aqueous solution they are of the following two types.

1. **Double salt: -** Addition compound in which simple salts don't loss their identity and its aqueous solution give test of its all constitute ions.

- Double salts loss their identity in aqueous solution.

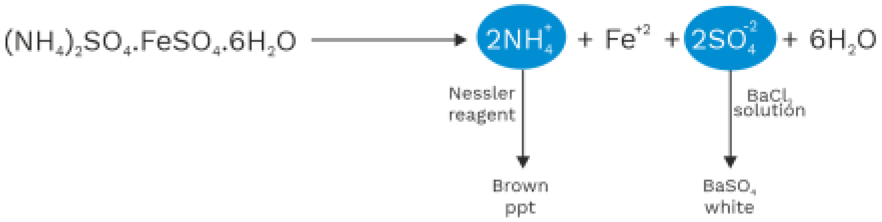
Concept Ladder

The concept of coordination compounds originates from teh tendency for complex formation of transition elements.



$$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.\ MgCl_2.6H_2O \xrightarrow[\text{solution}]{\text{Aqueous}} K^+ + Mg+^2 + \boxed{3Cl^-}$$

No. of ions = 5



$$(NH_4)_2SO_4.FeSO_4.6H_2O \longrightarrow \boxed{2NH_4^+} + Fe^{+2} + \boxed{2SO_4^{-2}} + 6H_2O$$

- All Alums are double salt.

2. **Complex compound: -** Addition compound in which simple salts loss their identity and it's aqueous solution doesn't give test of its all constitute ions.

- Complex compound don't loss their identify in aqueous solution.

$$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

Does not ionize to give Fe^{2+} and CN^- ions

Rack your Brain

State whether the given complexes are double salt or complex compound

(i) $K_4[FeCN_6]$

(ii)$NaCl.NaF.2Na_2SO_4$

Classification of Complex Compound

1. On basis of type of ligands

(i) Homoleptic complex: - Same type of ligands

Ex.

$$[\underbrace{Cu}_{\text{Central metal atom (CMA)}}\underbrace{(NH_3)_4}_{\text{Ligand}}]SO_4$$

(ii) Heteropoietic Complex: - Different type of ligands

$$[\underbrace{Pt}_{\text{(CMA)}}\underbrace{(NH_3)_4Cl}_{\text{Ligand}}]SO_4$$

Concept Ladder

First coordination compound is **Prussian blue**, which was accidently prepared in 1704 by a Berlin colour maker, prepared by strong heating animal waste and sodium carbonate in an iron container.

2. On the basis of degree of dissociation

(i) Perfect complex compound : Relatively more stable and its aqueous solution doesn't give test of its all constitutive ions.

$$3KCN + CuCN \xrightarrow[\text{Solution}]{\text{Aqueous}} K_3[Cu(CN_4)] \xrightarrow[\text{Solution}]{\text{Aqueous}} 3K^+ + [Cu(CN_4)^{-3}]$$

Perfect Complex compound complexion

$$[Cu^+][S^{-2}] < Ksp \qquad \text{No. ppt.} \xleftarrow[\text{gas}]{H_2S} \underset{\text{less conc.}}{Cu^+} + 4CN^-$$

(ii) Imperfect complex compound: - Relatively less stable and its aqueous solution gives test of its all constitute ions.

$$2KCN + Cd(CN)_2 \longrightarrow \underbrace{K_2[Cd(CN)_4]}_{\text{Imperfect complex compound}} \xrightarrow[\text{Solution}]{\text{Aqueous}} 2K^+ + \underbrace{[Cd(CN)_4]^{-2}}_{\text{Complexion}} \text{ less stable}$$

$$\Big\Updownarrow \text{ More ionisation}$$

$$\underset{\text{yellow ppt}}{Cds} \xleftarrow[\text{gas}]{H_2S} Cd^{+2} + 4CN^-$$

- Imperfect complex compound which undergoes 100% ionisation is known as double salt.
- There is no sharp line between perfect and imperfect complex compound.
- Complex forming tendency decreases down a group in s-block because size increases.

Concept Ladder

d-Block metals have strong complex forming tendency due to smaller size, high charge and presence of vacant orbitals.

Representation of complex ion

Coordination sphere: -

$[Mlx]^{\pm n}$

$\swarrow$

A/T alphabet order

Outside region: -

- Ionisation sphere
- Free ion
- Cation

Naming of ligands

- —O—suffix provided to the name of anionic ligands.
- —ium suffix provided to the name of cationic ligands.

Anionic ligands ending with -ide are named by replacing -ide with suffix -o or replacing -e by -o.

Ligands whose names end in -ite or -ate become -ito or -ato, i.e., by replacing the ending -e with -o.

Definitions

The neutral molecules; cations or anions which are directly linked with the centred metal atom or ion in complex ion are called ligands.

Q.1 Green colour of leaves is due to presece of chlorophyll which is a complex compound. Which metal is present in it?

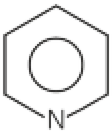
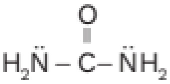
A.1 Magnesium

Classification of ligands

(a) On the basis of denticity

1. Monodentate ligand

(i) Neutral ligands

H_2O	aqua	PH_3	Phosphene
NH_3	Ammine	$p(Ph)_3$	Triphenyl phosphene
CO	Carbonyl	O_2	Dioxygen
CS	Thiocabonyl	N_2	Dinitrogen
NO	Nitrosyl		Pyridine(Py)
CH_3NH_2	Methyl Amine	 $H_2\ddot{N}-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2$	Urea

$H_2N—NH_2$ Hydrazine

- Hydrozine never acts as bidentate ligand.

(ii) Cationic ligand: -

O_2^+	Oxygenium
NO^+	Nitrosyliium Or Nitrosonium
$H_2N—NH_3$	Hydrazinium

(iii) Anionic ligands

F^-	Flurido Or fluro	S^{-2}	Sulphido Or sulpho
Cl^-	Chlorido Or chloro	OH^-	hydroxide Or hydroxo
Br^-	Bromido Or bromo	CH_3O^-	Methoxido Or methoxo
I^-	Iodido Or Ido	O_2^-	Superoxido Or superoxol
O^{-2}	Oxido	O_2^{-2}	Peroxido Or peroxo
NO_2^-	Nitro	N^{-3}	Nitrido
N_3^-	Azido	NH_2^-	Amido
H^-	Hydrido		

Definitions

The ligands that have one donar atom i.e. they only donate one electron pair to central metal atom or ion are known as monodentate ligands.

Concept Ladder

Denticity of the ligands is termed as the nubmer of coordianting or ligating groups present in a ligand.

Previous Year's Questions

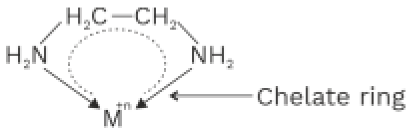
Which of these cannot act as a ligand?

[AIPMT]

(1) NH_3 (2) H_2O
(3) CO (4) NH_4^+

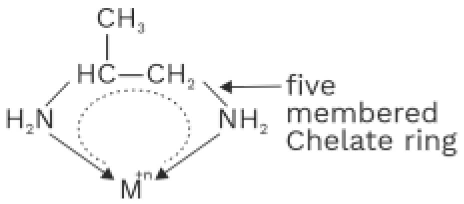
2. Bidentate ligands

(i) Ethylene diamine (en)
Or (ethane 1, 2–diamine)

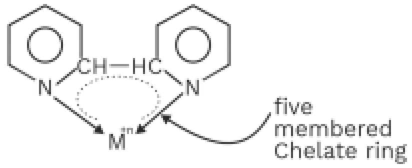


Symmetrical Complex

(ii) Propane 1,2–diamine
Or propylene diamine (Pn)

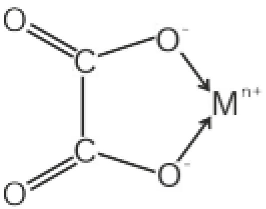


(iii) Dipyridyl (dipy)

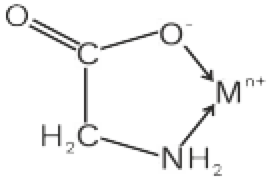


Symmetrical Complex

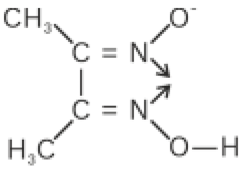
(iv) Oxalato (OX)$^{-2}$



(v) Glycenato (gly)$^-$



(vi) Dimethyl glyoximato (dmg)$^-$



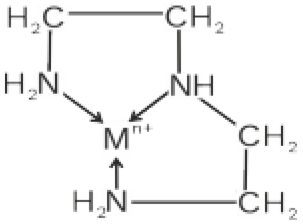
3. Polydentate ligands

All bidentate and polydentate ligand are chelating ligands.

No of chelate ring = Denticity – 1

(i) Diethylenetriamine (dien)

Denticity = 3
No. of rings = 2
Neutral



Previous Year's Questions

The anion of acetylacetone (acac) forms Co (acac)$_3$ chelate with Co^{3+}. The rings of the chelate are **[NEET-2013]**

(1) five membered
(2) four membered
(3) six membered
(4) three membered

(ii) (trien) – Triethylene tetramine

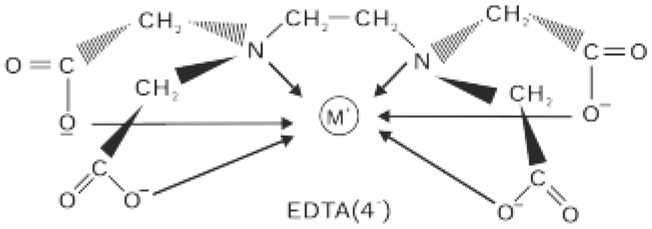
Denticity = 4
Chelate rings = 3
Neutral

(iii) Terpyridine

Denticity = 3
Chelate rings = 2
Neutral

(iv) Ethylenediamine tetracetato $(EDTA)^{-4}$

2N 4(O)
Denticity = 6
Chelate rings = 5



(v) Ethylenediamine triacetato $(EDTA)^{-3}$

Denticity = 5
Chelate rings = 4

Concept Ladder

Chelating ligands form more stable complexes than the unidentate analogs. This is called chelating effect.

4. Ambidentate ligands

- Ligands which have two different donor atoms but at time of coordination such ligand can be coordinate CMA by either of two donor atoms.

(a)

$M^{n+}\longleftarrow C^{-}\equiv N$
Cynido (CN)
Cynido—C

$M^{n+}\longleftarrow N\equiv C^{-}$
Isocynido (NC)
Cynido — N

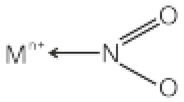
(b)

$M^{n+}\longleftarrow O^{-}—C\equiv N$
Cynido (OCN)
Cynido—O

$M^{n+}\longleftarrow N\equiv C—O^{-}$
Isocynido (NCO)
Cynido — N

(c)

$M^{n+}\longleftarrow O^{-}—N=O$
Nilito (ONO)
Nitrilo — O



Nilito (NO_2)
Nitrilo — N

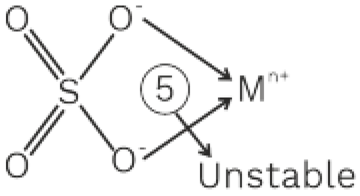
Rack your Brain

Explain how dithicoxalate behaves as ambidentate ligand.

5. Flexi dentate

Ligands which can change their denticity

Ex. $CO_3^{-2}, PO_4^{-3}, SO_4^{-2}, CH_3-COO^-, NO_3^-$ etc.



Ex. $\left[Co(NH_3)_5\,SO_4\right]Cl$

$X + 0 - 2 = 0$ $\quad X \Rightarrow +3$

$C.N \Rightarrow 6$

5 by NH_3 + 1 by SO_4

Monodentate

(b) On the basis of e⁻ donating and e⁻ accepting nature

1. Normal Or classical ligands

Ligands which only donate e⁻ pair to CMA and form coordinate σ bond.

Ex. $NH_2^-, OH^-, N^{-3}, Cl^-, O^{-2}$

2. Non classical or π acid or π acceptor ligands

Ligands which donate e⁻ pair to CMA and form coordinate bond but simultaneously they accept e⁻ pair from CN through back bonding (synergic bonding)

Ex. $CO, NO^+, CN^-, C_6H_6, C_5H_5^-, C_2H_4$

Concept Ladder

Coordination number = Σ number of ligands × Dentate character of ligands

Rack your Brain

Why CO is a stronger ligand than NH_3 for many metals?

Q.2 Why only transition metals are known to form π complexes?

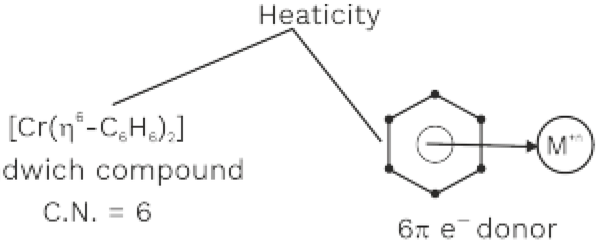
A.2 Transition metals/ions have empty d-orbitals into which the electron-pairs can be donated by ligands containing π electron-pairs can be donated by ligands contianing p electrons, i.e, electrons in their π moleculear orbitals, e.g., $CH_2=CH_2$, C_5H_5, C_6H_6 etc.

3. π donor and π acceptor ligand

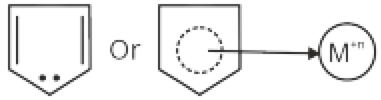
Ligands which donate π e^- to CMA and also accept e^- density from CMA though synergic bonding.

Ex. $C_6H_6, C_5H_5^-$

(i)



(ii) $[Fe(\eta^5\text{-}C_5H_5)_2]$ Ferrocene



$6\pi\ e^-$ chonor

(η^5-Cyclopentadienyl)]

Coordination Number

Total no of e^- pair accepted by CMA

1. $[Ni(dmg)_2]$ = 4
2. $[Pt(trien)]Cl_2$ = 4
3. $[Fe(EDTA)]^-$ = 6
4. $[Co(en)_2Ox]Cl$ = 6

Some important points

1. Generally C.N of monovalent cation is two and four except

Ex. $\underset{\substack{O.S.=+1\\ C.N=2}}{\left[Cu\left(CN_2\right)\right]^-} \xrightarrow[\text{excess}]{CN^-} \underset{C.N=4}{\left[Cu\left(CN_4\right)\right]^{-3}}$

2. Generally C.N of bivalent cation is four and six except.

$Pt^{+2}, Pd^{+2} \rightleftharpoons$ only 4

3. Generally C.N. of trivalent cation is six except some exceptions.

Concept Ladder

As per VBT and MOT, it is implicit that the bond order of C—O bond decreases but the C—O bond length increases due to synergic effect.

Definitions

The number of atoms in a ligand that directly bonded to the central metal atom or ion by coordinate bond is called coordination number of metal atom or ion.

Previous Year's Questions

Coordination number of Ni in $[Ni(C_2O_4)_3]^{4-}$ is

[AIPMT]

(1) 3 (2) 6
(3) 4 (4) 2

4. C.N of tetravalent cation is 6.
5. C.N of CMA depends upon charge of CMA, six of CMA size of ligands and concentration of ligand.

Effective Atomic Number (EAN)

Total number of e^- of CMA after accepting e^- pair from ligands

ENA = Z–(0.5) + 2 × C.N.

1. $K_4\left[Fe\left(CN\right)_6\right] \Rightarrow 26-\left(+2\right)+2\times6 \Rightarrow 36$ [K]r

   O.S. = +2, C.N. = 6
2. $K_3\left[Fe\left(CN\right)_6\right] \Rightarrow 26-\left(+3\right)+2\times6 \Rightarrow 35$ [Kr]

   O.S. = +3, C.N. = 6
3. $\left[Fe\left(\eta^5-C_5H_5\right)_2\right] \Rightarrow 26-\left(+2\right)+2\times6 \Rightarrow 36$ [Kr]

   O.S. = +2, C.N. = 6

Concept Ladder

The effective atomic number generally coincides with the atomic number of next inert gas in some cases.

Sidgwick rule

- If EAN of CMA in metal carbonyl is equal to Atomic number of nearest inert gas then the stability of metal is high.

(a) $\underset{EAN\,=\,35}{\left[Mn\left(CO\right)_5\right]} < \underset{EAN\,=\,36}{\left[Mn\left(CO\right)_5\right]^-}$ Stability

(b) $\underset{EAN\,=\,35}{\left[V\left(CO\right)_6\right]} \xrightarrow[\text{reduction}]{+e^-} \underset{EAN\,=\,36}{\left[V\left(CO\right)_6\right]^-}$ More stable

(c) $\left[Fe\left(CO\right)_5\right] \Rightarrow$ neither oxidising nor reducing

- Sidgwick rule is appliable only for metal carbonyl.

Rack your Brain

Calculate the EAN of the metal atom in the following

(i) $[Cr(CO)_6]$

(ii) $[Ni(NH_3)_6]^+$

Q.3 Write the coordination number and oxidation state of Platinum in the complex $[Pt(en)_2Cl_2]$.

A.3 As en is bidentate ligand, coordination number of Pt = 6

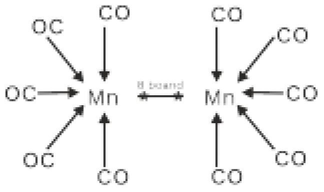
$$[\overset{x}{Pt}(\overset{0}{en})_2\,\overset{-1}{Cl_2}]$$

$\therefore$ x – 2 = 0, x = +2

Oxidation state of Pt = 2

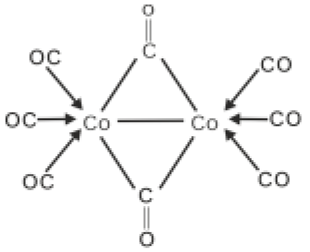
EAN Of Polynuclear Metal Carbonyl

(a) $$\underset{\text{EAN} = 35}{2\left[\text{Mn}(\text{CO})_5\right]} \xrightarrow{\text{Dimer}} \underset{\text{EAN} = 36}{\left[\text{Mn}(\text{CO})_{10}\right]}$$



σ bond =20

(b) $$\underset{\text{EAN} = 35}{2\left[\text{Co}(\text{CO})_4\right]} \xrightarrow{\text{Dimer}} \underset{\text{EAN} = 36}{\left[\text{CO}_2(\text{CO})_8\right]}$$



FORMULA AND IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

1. Formula of a Complex

(a) In formulas of both simple and complex salts, cation precedes the anion. Nonionic compounds are written as single units.

(b) Complex ions are written inside square brackets without any space between the ions.

(c) Metal atom and ligands are written in the following order:

- (i) In the complex part, the metal atom is written first followed by ligands in the order, anionic → neutral → cationic.
- (ii) If more than one ligand of one type (anionic, neutral or cationic) are present, then they are arranged in English alphabetical order, e.g. between H_2O and NH_2, H_2O should be written first. Similarly, order of NO_2^-, SO_3^{2-} and OH^- will be NO_2^-

Concept Ladder

In the old system, (i) the ligands are named in the order of negative, neutral and positive without separation by hyphens. (ii) when there are several ligands of same kind, these are listed alphabetically.

(iii) When ligands of the same type have similar name for the first atom, then the ligand with less number of such atoms is written first. Sometimes the second atom may be used to decide the order. When number of atoms are also same e.g., Out of NO_2^- , NH_2^- will be written first. In H_3 and $\ddot{N}_2$, $\ddot{N}H_3$ will be written first as it contains only one N-atom.

(iv) Polyatomic ligands and abbreviations for ligands are always written in lower case letters. e.g. (en), (py), etc.

(v) Charge of a complex ion is represented as over script or square bracket.

Examples,

$K_4[Fe(CN)_6]$ — First cation and then anion

$[CrCl_2(H_2O)_4]$ Br—Cl^- (negative ligand) before H_2O

Previous Year's Questions

The name of complex ion, $[Fe(CN)_6]^{3-}$ is

[NEET-2015]

(1) hexacyanitoferrate (III) ion
(2) tricyanoferrate (III) ion
(3) hexacyanidoferrate (III) ion]
(4) hexacyanoiron (III) ion

Q.4 Write the formulae of the following:
(i) bis (acetylacetonato) oxovanedium (IV)
(ii) dichloridoplatinum (IV) tetrachloridoplatinate (II)

A.4 (i) $[V (acac)_2\ O]$
(ii) $[PtCl_2][PtCl_4]$

Q.5 Give the IUPAC names of the complexes
(i) $K[BF_4]$
(ii) $[Fe(C_5H_5)_2]$
(iii) $[Mn_3(CO)_{12}]$

A.5 (i) potassium tetrafluoridoborate (III)
(ii) bis (cyclopentadienyl) iron
(iii) dodecacarbonyl trimagnaese (0)

2. Nomenclature of Coordination Compounds

Mononuclear coordination compounds are named by following these rules:

(a) In both the positively and negatively charged coordination compounds, the cation is named first followed by the anion.

(b) The name of the central atom/ion is written after the ligands are named in alphabetical order. (This procedure is reversed in writing its formula).

(c) Names of the anionic ligands end in –o.

Rack your Brain

Write the name for iron metal when it is used as complex anion?

Symbol	Name as ligand	Symbol	Name as ligand
N^{3-}	Azido	OH^-	Hydroxo
Cl^-	Chloro	CO_3^{2-}	Carbonato
O^{2-}	Peroxo	$C_2O_4^{-2}$	Oxalato
Br^-	Bromo	SO_4^{-2}	Sulphato
O_2H^-	Perhydroxo	NO_3^-	Nitrato
CN^-	Cyano	SO_3^{2-}	Sulphito
S^{2-}	Sulphido	CH_3COO^-	Acetato
O_2^{2-}	Peroxo	NO_2^-	(Bonded through oxygen) nitrite
NH_2^-	Amido		(Bonded through nitrogen) nitro

(d) Names of neutral and cationic ligands are the same except for aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. These are placed within parentheses ( ).

Symbol	Name as ligand	Symbol	Name as ligand
H_2O	Aqua	NO	Nitrosyl
NH_3	Ammine	CS	Thiocarbonyl
CO	Carbonyl		

(e) Positive ligands are named as:

Symbol	Name as ligand
NH^{+4}	
NO^{+}	Nitrosylium
$NH_2NH_3^{+}$	Hydrazinium

(f) Oxidation state of the metal in a cation, anion or a neutral coordination compound is indicated by a Roman numeral in parenthesis.

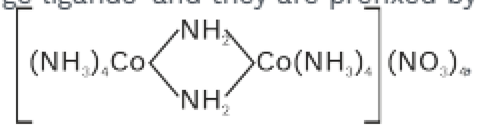
(g) When the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. In an anion, Co is called cobaltate. For some metals, their Latin names are used in the complex anions, e.g. ferrate for Fe.

(h) Nomenclature of a neutral complex molecule is done in the similar way as that of a complex cation.

The following examples illustrate the nomenclature for coordination compounds:

- $[Cr(NH_3)_3(H_2O)_3]$ Cl_3 is named as: Triamminetriaquachromium (III) chloride
- $[Co\ (H_2NCH_2CH_2NH_2)_3]_2$ SO_4 is named as: Tris (ethane-1, 2-diammine) cobalt (III) sulphate
- $[Ag\ (NH_3)_2]$ $[Ag(CN)_2]$ is named as: Diamminesilver (I) dicyanoargentate (I)

(i) Ligands which join two metals are known as 'Bridge ligands' and they are prefixed by 'μ' (mu).

E.g. 

$$\left[(NH_3)_4Co\begin{matrix}NH_2\\ \\NH_2\end{matrix}Co(NH_3)_4\right](NO_3)_4$$

in this complex.

Concept Ladder

- Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands in a coordination compound.
- When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, and the ligand to which they refer is placed in parentheses.

Rack your Brain

Explain with an example how the name of the metal differs in cation and anion even though they contain the same metal ions.

3. Nomenclature of Complexes

(I) Cationic Complex

$[Cr(NH_3)_3(H_2O)_3]Cl_2$

triamminetriaquachromium (III) chloride

(i) The number of the individual ligands are indicated by prefix like mono, di, tri, etc. and ligands are named in an alphabetical order.

(ii) Central metal atom and oxidation state indicated by Roman numeral in parenthesis.

(iii) Name of ionisable anion.

(II)Anionic Complex

$K_3[Fe(CN)_6]$

Potassium hexacyanoferrate (III)

(i) Name of ionisable metal and oxidation state

(ii) Name of ligand in an alphabetical order

(iii) Central metal atom + ate and oxidation state

(III) Neutral Complex

$[Pt(NH_3)_2Cl(NO_2)]$

Diammine chloronitrito-N-platinum (II)

(i) Name of ligands in an alphabetical order

(ii) Central metal atom and oxidation states.

Concept Ladder

Polyatomic ligands are enclosed in parentheses but all ligands are formulated without any space in between.

Previous Year's Questions

The hypothetical complex chlorodiaquatriammine cobalt (III) chloride can be represented as **[AIPMT]**

(1) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$
(2) $[Co(NH_3)_3(H_2O)Cl_3]$
(3) $[Co(NH_2)_3(H_2O)_2Cl]$
(4) $[Co(NH_3)_3(H_2O)_3]Cl_3$

Q.6 Give the IUPAC names of the complexes

(i) $K[BF_4]$ (ii) $[Fe(C_5H_5)_2]$
(iii) $[Mn_3(CO)_{12}]$

A.6 (i) potassium tetrafluoridoborate (III)
(ii) bis (cyclopentadienyl) iron
(iii) dodecacarbonyl trimagnaese (0)

Magnetic Nature

Ferromagnetic : Fe, Co, NO_2

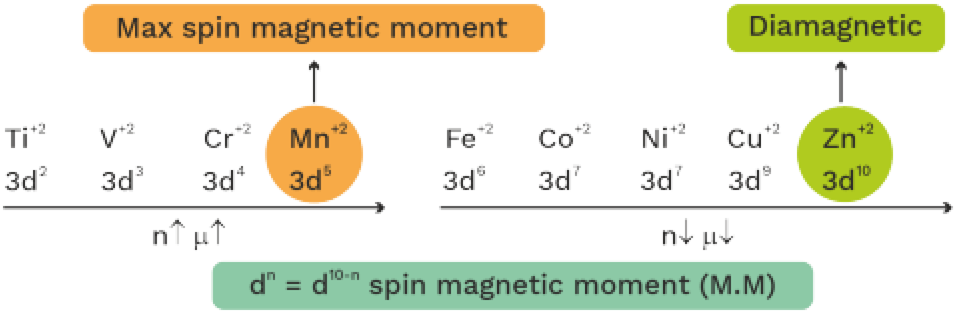
Spin magnetic moment = (μ) = $\sqrt{n(n+2)}$ B.M.

$n = 1$	$\mu = 1.73$
$n = 2$	$\mu = 2.83$
$n = 3$	$\mu = 3.87$
$n = 4$	$\mu = 4.90$
$n = 5$	$\mu = 5.92$

Concept Ladder

The magnetic property depends upon oxidation state of central metal atom or ion and nature of ligand.

Spin magnetic moment of bivalent cation of 3d series



Spin magnetic moment of trivalent lanthanoids

- 'Na' (Neodymium) has max. M.M. among lanthanoids due to sum of spin magnetic moment + orbital magnetic moment.

Bonding in complex compound

1. Werner's Theory

According to Werner, central metal atom has two types of valencies

Primary valency	Secondary Valency
Equal to O.S. of CMA	Equal to C.N. of CMA
Satisfied by anions	Satisfied by legends
Non directional and ionisable	Directional and non ionisable
Not helpful in geometry prediction	Helpful in geometry prediction

- All secondary valencies have specific arrangement according to C.N.

  CN = 2 → Linear
  CN = 3 → Trigonal planar
  CN = 4 → Tetrahedral or square planar
  CN = 5 → TBP or square pyramidal
  CN = 6 → Octahedral

  $\left[Co\left(H_2O\right)_6\right]Cl_3$

  O.S. $\Rightarrow$ +3CN = 6
  Primary valency =+3
  Secondary valency =6
  Satisfied by 3Cl Satisfied by $6H_2O$

- Possible complex of $CaCl_3 \cdot 6H_2O$
  O.S = +3 C.N. = 6

  (a) $\left[Ca\left(H_2O\right)_6\right]Cl_3 = 4$ ions

  (b) $\left[Co\left(H_2O\right)_5 Cl\right]Cl_2.H_2O = 3\text{ions}$

  (c) $\left[Co\left(H_2O\right)_4 Cl_2\right]Cl.2H_2O = 2\text{ions}$

  (d) $\left[Co\left(H_2O\right)_3 Cl_3\right]3H_2O$ not possible

- $PtCl_4 \cdot 4NH_3 \xrightarrow{AgNO_3 solution}$ 2 mol AgCl ppt
  O.S = +4 C.N. = 6
  $[Pt(NH_3)_4Cl_2]Cl_2$

- $PtCl_4 \cdot 2HCl \xrightarrow[Solution]{AgNO_3}$ No. ppt
  O.S = +4 C.N = 6
  $H_2\left[PtCl_6\right]$
  Hexachloro platinic (IV) acid

- $PtCl_2 \cdot 4NH_3 \xrightarrow[Solution]{AgNO_3}$ 2 mole AgCl ppt
  O.S = +2 C.N. = 4
  $[Pd(NH_3)_4]Cl_2$

Concept Ladder

In 1898, Werner proposed the concept of a primary valence and a secondary valence for a metal ion.

Rack your Brain

Waht are the limitation of Werner's theory?

Previous Year's Questions

Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?

[AIPMT-2012]

(1) $[Ni(NH_3)_6]^{2+}$
(2) $[Zn(NH_3)_6]^{2+}$
(3) $[Cr(NH_3)_6]^{3+}$
(4) $[Co(NH_3)_6]^{3+}$

Valence Bond Theory

- Central metal atom releases e⁻ according to its O.S.
- Central metal atom will provide vacant orbitals according to its coordination number.
- These vacant orbital undergo histrion and form coordinate σ bond with donor atoms.
- Hybridisation state of central metal atom depends upon C.N. and nature of ligand M.M. dipole moment, isomerism etc. are also helpful in hybridisation prediction.

C.N = 2	sp	linear
C.N = 3	sp^2	Trigonal planar
C.N = 4	sp^3	Tetrahedral
	dsp^2	square planar
C.N = 5	sp^3d	TBP
	dsp^3	(i) TBP
		(ii) Square pyramidal (dx^2y^2)
C.N = 6	sp^3d^2	Octahedral (SBP)
	d^2sp^3	Octahedral (SBP)

- In presence of strong field ligand (SFL), the pairing of (n-1)d e⁻ is possible before hybridisation but this pairing is not possible in presence of WFL.

Concept Ladder

According to VBT, the atomic orbitals of the metal ion hybridize to form hybrid with definite directional properties. There hybrid orbitals tend to form strong chemical bonds with the ligand orbitals.

S or S-donor		O-donor		N-donor		C-donor
$I^- < Br^- < SN^- < Cl < S^{-2} < F^-$	<	$OH^- < C_2O_4^{-2} < H_2O$	<	$NCS^- < EDTA < NH_3 < en < NO_2^-$	<	$CN^- < CO$

X or S-donor < O-donor

WFL

N – Donor < C-donor

SFL

For 3d series Metal

- All ligands acts as SFL with 4d and 5d series metal ions.
- P^- acts as SFL with Ni^{+4}
- H_2O and $C_2O_4^{-2}$ acts as SFL with CO^{+3}
- NH_3 act as WFL with Fe^{+2} and Mn^{+2}.
- H_2O act as SFL with Cu^{+2} (C.N = 4)

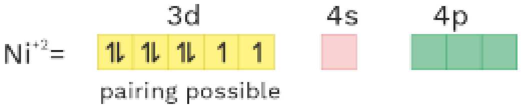
Rack your Brain

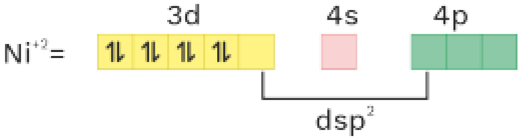
Name the type of spin complex involved for hybridisation of inner (n – 1)d orbital.

(1) $\left[Ni(CN)_4\right]^{-2}$

O.S. = +2 C.N = 4 ligand = SFL

Ni = $3d^8 4s^2$



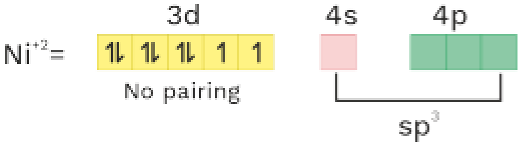


square planar
diamagnetic

(2) $\left[Ni(Cl_4)\right]^{-2}$ or $\left[Ni(SCN)_4\right]^{-2}$

O.S = +2 C.N = 4 ligand = WFL

Ni = $3d^8 4s^2$

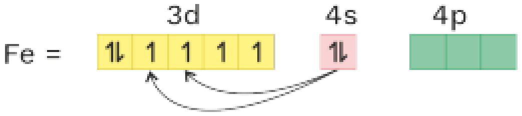


Tetrahedral
paramagnetic

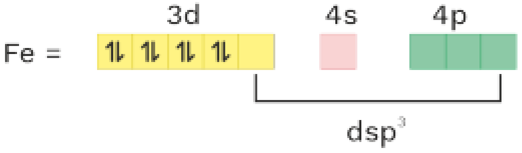
$\mu = \sqrt{8}$

(3) $\left[Fe(CO)_5\right]$ D.M. = 0

O.S. = 0 C.N. = 5 Ligand = SFL



s-e shifting
(not depends on strength of ligand)



diamagnetic
μ = 0 so Trigonal Bipyramidal
inner orbital complex
low spin complex

Concept Ladder

The number of unapaired electrons in the complex, determins the geometry of the complex as weel as hybridization of the central metal ion and vice-verse.

Rack your Brain

Find the value of magnetic moment for $[CuCl_4]^{-2}$.

Previous Year's Questions

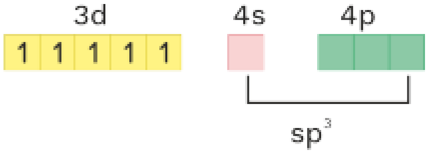
The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are

[NEET-2018]

(1) square planar geometry and diamagnetic
(2) tetrahedral geometry and diamagnetic
(3) square planar geometry and paramagnetic
(4) tetrahedral geometry and paramagnetic

(4) $\left[MnCl_4\right]^{-2}$ sp^3

O.S. = +2 C.N. =4 Ligand = WFL

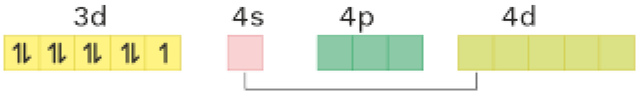


Tetrahedral
paramagnetic

$\mu = \sqrt{35}$

(5) $\left[CuCl_5\right]^{-3}$ sp^3d

O.S. = +2 C.N = 5 Ligand = WFL

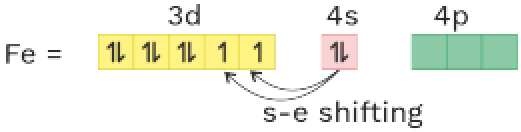


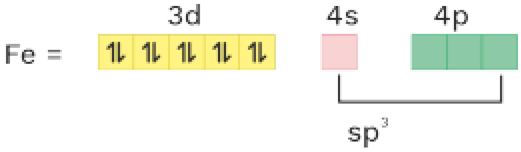
sp^3d, TBP
paramagnetic

$\mu = \sqrt{3}$

(6) $\left[Ni(CO)_4\right]$ or $\left[Ni(CN)_4\right]^{-4}$ sp^3

O.S = 0   C.N = 4   Ligand = SFL





Tetrahedral
diamagnetic

Concept Ladder

Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.

Rack your Brain

Find hybridization of $[Ni(CN)_5]^{-3}$ compound.

Previous Year's Questions

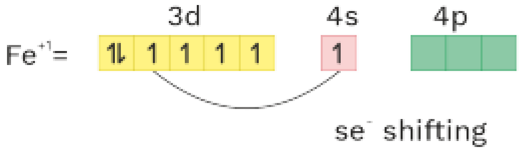
Aluminium chloride in acidified aqueous solution forms a complex 'A', in which hybridisation state of Al is 'B'. What are 'A' and 'B', respectively?

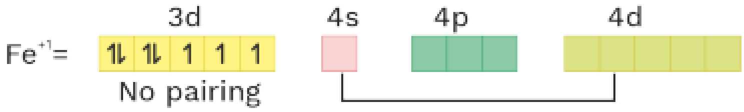
[NEET-2019]

(1) $[Al(H_2O)_6]^{3+}$, sp^3d^2
(2) $[Al(H_2O)_4]^{3+}$, sp^3
(3) $[Al(H_2O)_4]^{3+}$, dsp^2
(4) $[Al(H_2O)_6]^{3+}$, d^2sp^3

(7) $\left[Fe\left(H_2O\right)_5\left(NO\right)\right]SO_4$

O.S = +1 CN = 6 Ligand = WFL





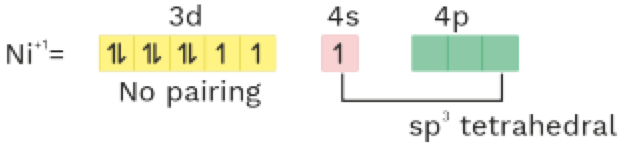
sp^3d^2, octahedral

paamag. $\mu = \sqrt{15}$

Octer orbital, low spin

(8) $\left[NiCl_2\left(PPh_3\right)_2\right]$ Paramagnetic

O.S = +2 CN = 4 Ligand = WFL = No pairing



(9) $\left[RhCl\left(PPh\right)_3\right], \left[PdCl_4\right]^{-2}, \left[AgF_4\right]^{-}$

$Rh^{+}, Pd^{+2}, Ag^{+3} = 4d^8 \xrightarrow[SFL]{C.N=4} dsp^2$

$$\boxed{\begin{array}{l} Co^{+}, Ni^{+2}, Cu^{+3} = 3d^8 \\ Rh^{+}, Pd^{+2}, Ag^{+3} = 4d^8 \\ Ir^{+}, Pt^{+2}, Au^{+3} = 5d^8 \end{array}}$$

$\downarrow$

CN = 4

dsp^2, square planar

diamag.

Previous Year's Questions

Pick out the correct statement with respect to $[Mn(CN)_6]^{3-}$

[NEET-2017]

(1) It is sp^3d^2 hybridised and tetrahedral

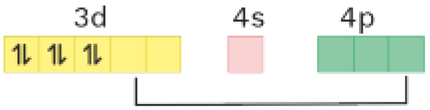
(2) It is d^2sp^3 hybridised and octahedral

(3) It is dsp^2 hybridised and square planarl

(4) It is sp^3d^2 hybridised and octahedral

(10) $\left[NiF_6\right]^{-2}$ $Ni^{+4} \to F^-$ act as SPL

O.S. = +4 CN = 6

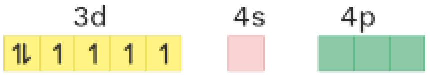


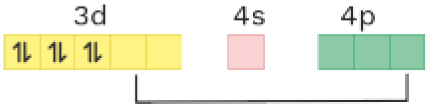
d^2sp^3 Octahedral

diamagnetic.

(11) $\left[Fe(CN)_5(O_2^-)\right]^{-4}$

O.S. = +2 CN = 6 Ligand = SFL



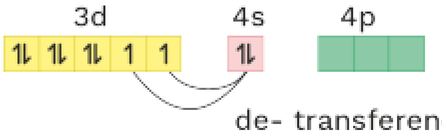


d^2sp^3 Paramagnetic

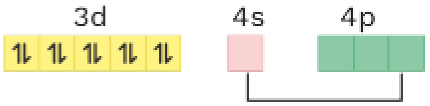
due to O_2^{-1}

(12) $\left[Fe(CO)_4\right]^{-2}$

O.S. = −2 CN = 4 Ligand = SPL



de- transference



sp^3, Tetrahedral

diamagnetic

Drawbacks of VBT

(1) It can't explain stability of complex compound

(2) It can't explain colour of complex compound

(3) It can't explain d e^- transference

(4) It can't explain pairing of (n-1)d e^-

(5) It doesn't give any criteria for classification of SFL and WFL.

Concept Ladder

Pt(II) and Au(III) always form square planar complexes irrespective of their ligands being strong or weak.

Rack your Brain

What is the shape of $[Co(NH_3)_6]^{+2}$ compound?

Previous Year's Questions

A magnetic moment at 1.73 BM will be shown by one among the following options

[NEET-2013]

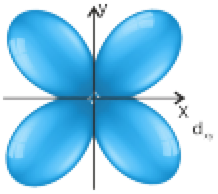
(1) $TiCl_4$ (2) $[CoCl_6]^{4-}$

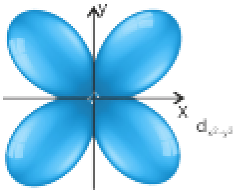
(3) $[Cu(NH_3)_4]^{2+}$ (4) $[Ni(CN)_4]^{2-}$

CFT for octahedral complex

$d_{xy}, d_{yz}, d_{zx} = t_{2g}$

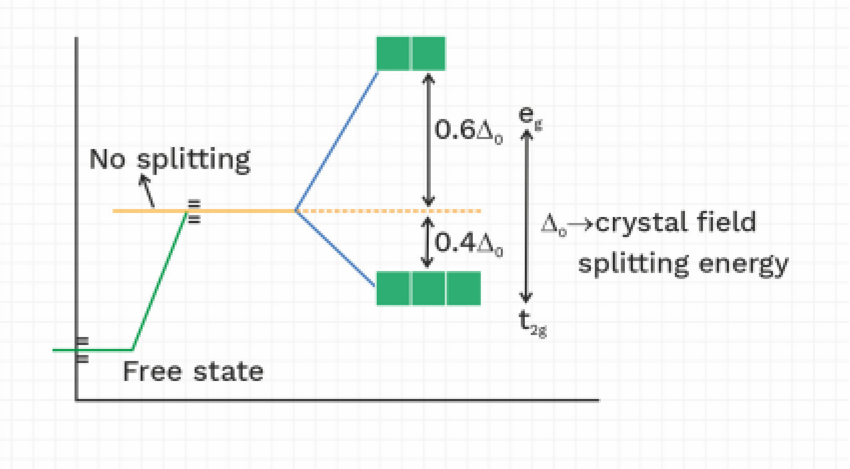
$d_{z^2}, d_{x^2-y^2} = e_g$





Concept Ladder

CFT is an electrostatic model which considers the metal ligand bond to be ionic occuring purely due to the electrostatic interaction between the metal ion and the ligand.



Q.7 Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$.

A.7 In a free transition metal ion, all the five d-orbitals are degenerate but when it is involved in a complex formation, the degeneracy is split into two sets of d-orbitals. This is called crystal field splitting.

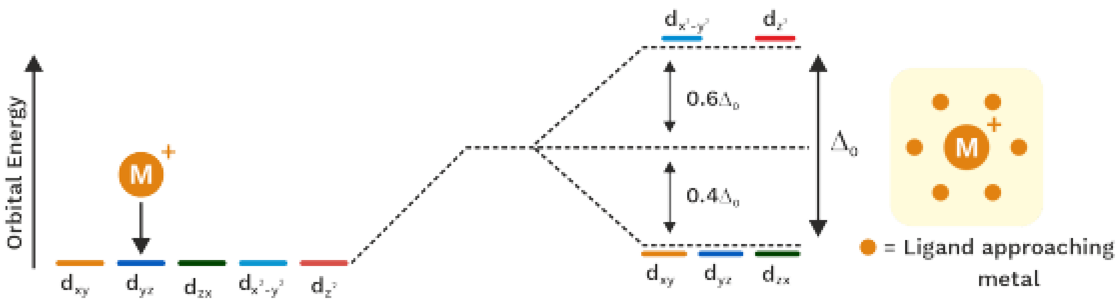
The difference of energy between the two sets of d-orbitals is called crystal field splitting energy (CFSE).

The lower energy set of three d-orbitals is called t_{2g} and the higher energy set of two d-orbitals is called e_g. The three electrons first enter into t_{2g}, one in each orbital. If $\Delta_o < P$, the 4th electron will enter e_g. Hence, the configuration will be $t^3_{2g}\ e^1_g$.

CRYSTAL FIELD THEORY

In crystal field theory bonding between metal and ligands is purely electrostatic.
Ligands are considered as negative point charges.

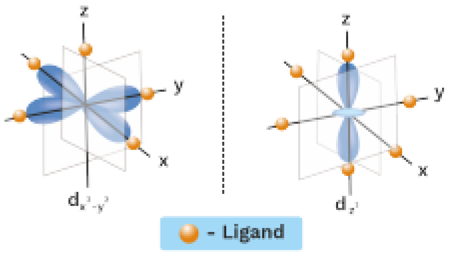
What Happens When Ligands Approach A Metal

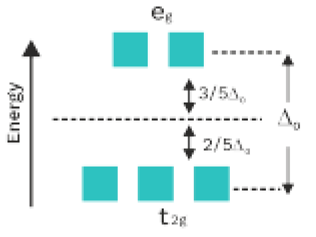


D-orbitals of metal ions when there are no-surrounding ligands

When Ligand approaches the metal ions, there will be a change in energy of electrons in d-orbitals of Metal ions.

Orbital Splitting In Octahedral Complexes

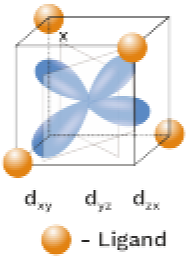


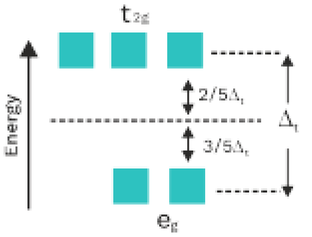


Δ_o -Energy gap between t_{2g} & e_g

In Octahedral complex, Ligands approach along x,y,z axis. $d_{x^2-y^2}$ and d_{z^2} orbitals align along the axis. So the repulsion between Orbitals and Ligands leads to increase in energy.

Orbital Splitting In Tetrahedral Complexes





Δ_{yt} -Energy gap between t_{2g} & e_g

In tetrahedral complexes, Ligands approach between the x,y and z axis ,therefore d_{xy}, d_{yz} and d_{zx} has more energy than $d_{x^2-y^2}$ and d_{z^2}

Strenght Of Ligands

$CO \approx CN^- > PPh_3 > NO_2^- > NH_3 >$ pyridine $> CH_3CH > NCG^- > H_2O \approx C_2O_4^{2-} > OH^- > NCO^- > F^-$
$> Cl^- > SCN^- > S^{2-} > Br^- > I^- > O_2^{2-}$

D^n system

Electronic configuration of (n–1) de^- of CMA (after splitting) depends upon 2 type of energies are :

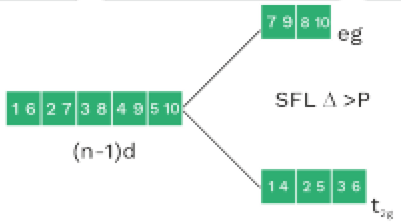
(1) $\Delta_{0(2)}$ Pairing energy (P)

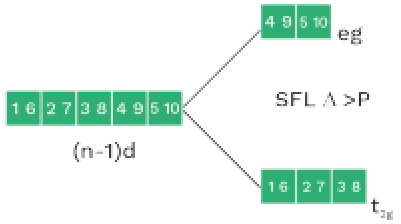
There are two conditions

(1) In presence of SFL $\Delta_0 > P$

(2) In presence of WFL $\Delta_0 < P$

D^n	Presence of SFL		Presence of WFL	
D^1	t_{2g}^1	eg^0	t_{2g}^1	eg^0
D^2	t_{2g}^2	eg^0	t_{2g}^2	eg^0
D^3	t_{2g}^3	eg^0	t_{2g}^3	eg^0
D^4	t_{2g}^4	eg^0	t_{2g}^3	eg^1
D^5	t_{2g}^5	eg^0	t_{2g}^3	eg^2
D^6	t_{2g}^6	eg^0	t_{2g}^4	eg^2
D^7	t_{2g}^6	eg^1	t_{2g}^5	eg^2
D^8	t_{2g}^6	eg^2	t_{2g}^6	eg^2
D^9	t_{2g}^6	eg^3	t_{2g}^6	eg^3
D^{10}	t_{2g}^6	eg^4	t_{2g}^6	eg^4





Concept Ladder

Complexes possessing d^0 or d^{10} configuration of a metal ion are always diamagnetic.

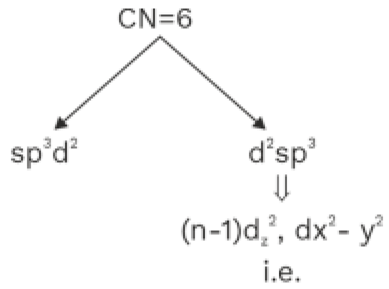
Rack your Brain

Explain how d-d transition is responsible for the colour of transition metal complexes?

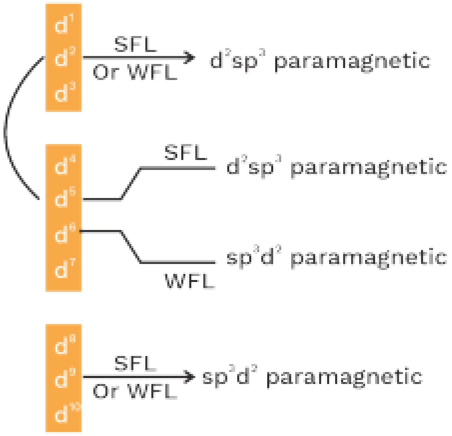
Concept Ladder

Complexes like CrO_4^{2-}, $Cr_2O_7^{2-}$ and MnO_4^- have d^0 configuration of the metal ion but still exhibit intense colour. Here the colour is caused by the charge transfer spectra (CT) and not by the d-d transition.

Hybridisation State and Magnetic Nature



Configuration of metal in



Factor affecting splitting energy

(1) $\Delta_0 \propto$ charges of central metal atom

(2) $\Delta_0 \propto Z_{eff}$ of central metal atom

$$3d \xrightarrow[30-50\%]{\Delta_0 \uparrow} 4d\text{ Series} \xrightarrow[30-50\%]{\Delta_0 \uparrow} 5d\text{ series}\Big] Z_{eff} \uparrow$$

(3) $\Delta_0 \propto$ strength of ligand

(4) Geometry of complex

$$\boxed{\Delta_{sp} > \Delta_0 > \Delta_t}$$

$$\boxed{\Delta_t = \frac{4\ \Delta_0}{9}}$$

Concept Ladder

It is observed that the higher the charge on the central metal atom (or oxidation state), higher is the value for CFSE.

Rack your Brain

Write the assumption made for Crystal Field theory?

Previous Year's Questions

The crystal field stabilisation energy (CFSE) for $[CoCl_6]^{4-}$ is 18000 cm^{-1}. The CFSE for $[CoCl_4]^{2-}$ will be **[NEET-2019]**

(1) 6000 cm^{-1} (2) 16000 cm^{-1}
(3) 18000 cm^{-1} (4) 8000 cm^{-1}

Examples,

(i) $\left[Co\left(H_2O\right)_6\right]^{+2} < \left[Co\left(H_2O\right)_6\right]^{+3}\ \Delta_0$

(I) (II)

H_2O acts as strong ligand with Co^{+3}, so splitting energy for (II) is higher than (I)

(ii) $\left[Fe\left(H_2O\right)_6\right]^{+3} < \left[Ru\left(H_2O\right)_6\right]^{+3} < \left[Os\left(H_2O\right)_6\right]^{+3}\ \Delta_0$

Fe is a 3d series element whereas Ru and Os are 4d and 5d transition elements, so H_2O is weaker ligand but it acts as strong ligand with higher d series transition element.

(iii) $\left[CrCl_6\right]^{-3} < \left[Cr\left(NH_3\right)_6\right]^{+3} < \left[Cr\left(CN\right)_6\right]^{-3}\ \Delta_0$

Ligand strength for $CN^- > NH_3 > Cl^-$

(iv) $\left[NiCl_4\right]^{-2} > \left[NiCl_6\right]^{-4}$

(I) (II)

(I) is tetrahedral and (II) is octahedral complex

$\Delta_t > \Delta_o$

Stability of complex compound

$$M^{+n} + xL^- \underset{}{\overset{K}{\rightleftharpoons}} [ML_x]$$

$$\left(\text{formation constant}\right)\ K = \frac{\left[ML_x\right]}{\left[M^{+n}\right]\left[L^-\right]^x}$$

K ↑, stability ↑

Stability $\propto$ charge of CMA

$\propto$ Z_{eff} of CMA

$\propto$ Strength of ligand

$\propto$ chelation effect

$\propto \dfrac{1}{\text{size of CMA}}$

Stability order :

(1) $\left[Fe\left(CN\right)_6\right]^{-4} < \left[Fe\left(CN\right)_6\right]^{-3}$

O.S = +2 O.S. = +3

Concept Ladder

Complexes normally exhibit two kinds of stabilities viz. thermodynamic and kinetic.

- Thermodynamic stability deals with the metal-ligand bond energy, stability constants etc that affect the equilibrium.
- Kinetic stability deals with the rates of reaction of complexes in a solution.

Previous Year's Questions

Crystal field splitting energy for high spin d^4 octahedral complex is **[NEET-2013]**

(1) $-1.2\ \Delta_0$ (2) $-0.6\ \Delta_0$

(3) $-0.8\ \Delta_0$ (4) $-1.6\ \Delta_0$

(2)

$\left[Co(H_2O)_6\right]^{+3} < \left[Rh(H_2O)_6\right]^{+3} < \left[Ir(H_2O)_6\right]^{+3}$ Zeff ↑

(3)

$\left[NiCl_6\right]^{-4} < \left[Ni(NH_3)_6\right]^{+2} < \left[Ni(CN)_6\right]^{-4}$ ligand strength

(4) $\left[Fe(NH_3)_6\right]^{+3} < \left[Fe(OX)_3\right]^{-3} < \left[Fe(EDTA)\right]^{-}$

No chelation   3 chelate   5 chelate rings

(5) $\left[Fe(Ox)_3\right]^{-3} < \left[Fe(CN)_6\right]^{-3}$

Chelation synergic bonding

(6) Irving williams series

$Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} \le Cu^{+2} > Zn^{+2}$

C.F.S.E. (Crystal field stabilisation energy)

Extra stabilisation (released energy) due to splitting in comparison to no splitting

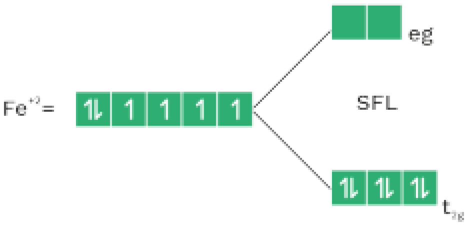
Concept Ladder

Weak ligands favor high spin complexes because they cannot pair up the electrons against Hund's rule while strong ligands favor low spin complexes.

Q.8 Calculate CFS for the given compound :

$\left[\mathbf{Fe(CN)_6}\right]^{-4}$

A.8 $\left[Fe(CN)_6\right]^{-4}$



Priority to 2P = N, New pairs

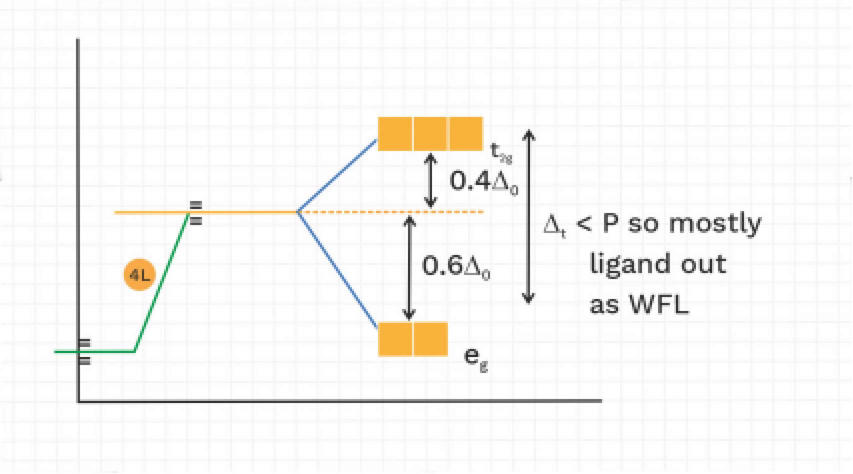
CFS = $-0.4\Delta_0 \times 6 + 0.6\Delta_0 \times 0$

= $-2.4\ \Delta_0$

Total pairs

CFSE = $0.4\Delta_0\, nt_{eg} + 0.6\, \Delta_0\, nt_{eg} + xp$ = new pairs

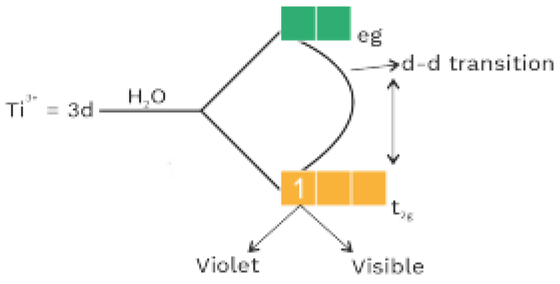
CFT for Tetrahedral complex



Colour

(a) d-d Transition

- Colour of complex compound is due to d-d transition
- Ag. Solution of Ti^{+3} is violet .



- Colour of complex compound depends upon spilitting energy.
- Complex become colourless in absence of ligand filled (no ligand, no splitting, no transition)
- Colour of f-block compounds is due to f-f transition.

Rack your Brain

What is the difference between inner and outer orbital complexes?

Examples,

(a) $[Ti(H_2O)_6]^+$ become colourless on heating due to removal of water molecules.

(b) Anhydrous $CuSO_4$ is colourless but hydrated $CuSO_4$ is blue (test of moisture)

$$\underset{\text{Colourless}}{\text{Anhyd. } CuSO_4} \xrightarrow{+5H_2O} \underset{\text{Blue vitriol}}{\left[Cu(H_2O)_4\right]SO_4H_2O}$$

(b) Charge transfer

Colour of some compound is due to charge transfer (e^- transition) from anion to metal ion.

$$\left[\begin{array}{ll} KM_nO_4 & \text{purple} \\ K_2Cr_2O_7 & \text{Orange} \\ Na_2CrO_4 & \text{Yellow} \\ CrO_2Cl_2 & \text{Blood Red} \end{array}\right] \begin{array}{l} Mn^{+3} \text{ or } Cr^{+6} = 3d^0 \\ (\text{no } d-d \text{ transition}) \end{array}$$

(c) Polarisation

- Colour of same compound can be explained on the basis of polarisation.
- Polarisation increase, possibility of finding colour increase

Examples,

(1) AgF coloulress but AgI yellow.

(2) PbF_2 colourless but PbI_2 yellow.

(3) HgF_2 colourless but HgI_2 Red.

(4) ZnS colourless but Cds yellow. HgS Black

Concept Ladder

In many complexes the d-orbital split takes place in the two sets t_{2g} and e_g, which possess diferent energies. the difference in energies of t_{2g} and e_g lies in the visible region of the spectrum and their helps tramsition metal complexes to absorbe color.

Rack your Brain

Why SnF_4 is colourless besides SnI_2 is red in colour?

Q.9 On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_0 > P$.

A.9 In this case, the 4th electron will enter into t_{2g}, i.e., pairing in one of the t_{2g} orbitals will take place. Hence, electronic configuration will be t_{2g}^4.

Colour of Co-ordination compounds

What is Colour Wheel ?

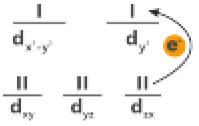
Generally white light is a mix of two opposite colors on colour wheel. These two colour are called component colours.

Why we are seeing Blue, Why Not Red or Green ?

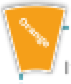
Let's see what happens inside the solution containing co-ordination compound when we cast a white light, on it

White light of energy E and wavelength λ is passed through the solution

In Presence of Ligands, d-orbitals Splits

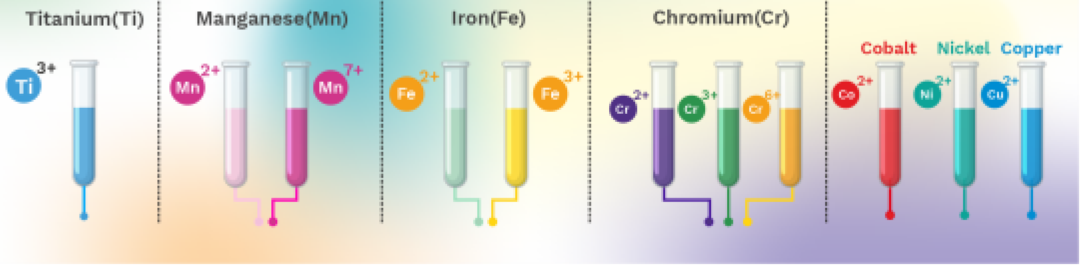


This electron absorbs the energy of wavelength λ and gets excited to d_{z^2}, to orbital.



If the wavelength, that got absorbed by solution represents the orange wheel, then colour, blue will be seen by viewer colour in colour its complimentary

Colours shown by metals in various oxidation states



Structural Isomerism

- Same molecular formula but different structural formula

(1) Coordination Isomerism

It arises due to exchange of ligands between complex cation and complex anion.

Q.10 How many Coordination isomers are there in the given compounds?

(a) $\left[Co(NH_3)_6\right]\left[Cu(NO_2)_6\right]$ (b) $\left[Pt(NH_3)_4\right]\left[PtCl_4\right]$

(c) $\left[Co(en)_3\right]\left[Cr(NO_2)_6\right]$ (d) $\left[Pt(NH_3)_4\right]\left[ZnCl_4\right]$

A.10 (a)

Co^{+3}		Cu^{+3}
$NH_3 : NO_2^-$		$NH^3 : NO_2^-$
6 : 0		0 : 6
5 : 1		1 : 5
4 : 2		2 : 4
~~3 : 3~~	Netural	~~3 : 3~~
2 : 4		4 : 2
1 : 5		5 : 1
0 : 6		6 : 0

Total no. of Coordination Isomers = 6

(b)

Pt^{+2}		Pt^{+2}
$NH_3 : Cl^-$		$NH_3 : Cl^-$
4 : 0		0 : 4
3 : 1		1 : 3
~~2 : 2~~	Netural	~~2 : 2~~
1 : 3		3 : 1
0 : 4		4 : 0

Total no. of Coordination Isomers = 2

(c)

Co	Cr^{+6}
en : NO_2	NO_2 : en
3 : 0	6 : 0
2 : 2	4 : 1
1 : 4	2 : 2
0 : 6	0 : 3

Total no. of Coordination Isomers = 4

(d)

Pt^{+2}	Zn
NH_3 : Cl	Cl : NH_3
4 : 0	4 : 0
3 : 1	3 : 1
2 : 2	2 : 2
1 : 3	1 : 3

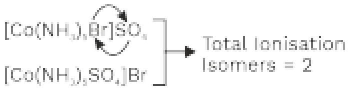
Total no. of Coordination Isomers = 4

(2) Ionisation Isomerism

- Structural isomer which give differ ions in aqueous solution
- Ionization isomerism is the result of the exchange of groups or ions between the coordinating sphere and the ionization sphere.

Examples,

(a)

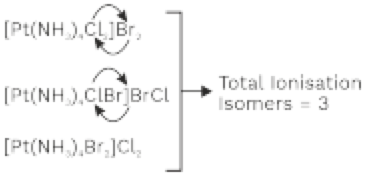


$[Co(NH_3)_5Br]SO_4$

$[Co(NH_3)_5SO_4]Br$

Total Ionisation Isomers = 2

(b)



$[Pt(NH_3)_4Cl_2]Br_2$

$[Pt(NH_3)_4ClBr]BrCl$

$[Pt(NH_3)_4Br_2]Cl_2$

Total Ionisation Isomers = 3

Previous Year's Questions

The type of isomerism shown by the complex $[CoCl_2(en)_2]$ is]

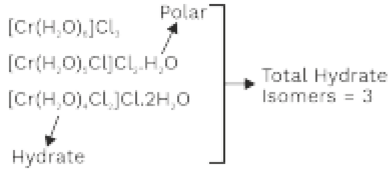
[NEET-2018]

(1) geometrical siomerism
(2) coordination isomerism
(3) ionization isomerism
(4) linkage isomerism

(3) Hydrate Isomerism

- It is a special type of ionisation isomerism in which number of water molecules differ in coordination sphere/outside region.

Examples,



(4) Linkage Isomerism

- It arise due to presence of ambidentate ligand.

Examples,

$[Co(NO_2)(NH_3)_5]Cl_2$

Pentaamminenitrocobalt (III) chloride

(5) Polymerisation Isomerism

- Complexes which have differ molecular formula but have same empirical formula. It is not a true isomerism.

Example,

$[PtCl_2(NH_3)_2]$ and $[Pt(NH_3)_4][PtCl_4]$

Geometrical Isomerism in square planar complexes

- Tetrahedral complexes don't show 'Geometrical Isomerism'.
- Square planar complexes can show 'Geometrical Isomerism'.
- Any two identical ligands at 180° show Trans.
- All identical ligands at 90° show Cis.

Examples,

(1) $\underset{[Ma_4]^{\pm}}{\left[Pt\left(NH_3\right)_4\right]}Cl_2\ Pt^{+2} = 5d^8 \xrightarrow{C.N=4} \underset{\text{sq. planar}}{dsp^2}$

(2) $\left[Pt\left(NH_3\right)_2\right]Cl = \left[Ma_3b\right]^{\pm}$

(aa) (ab) No G.I.

Concept Ladder

Complexes of formula MA_2B_2 and MA_2BC types have two geometrical isomers, where as MA_4, MA_3B and MAB_3 do not show geometrical isomerism when A & B are monodentate ligands.

Rack your Brain

Can in a complex compound water molecules behave in two ways? Explain in brief.

Previous Year's Questions

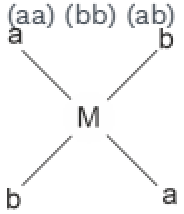
The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of which type of isomerism?

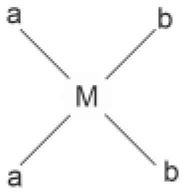
[NEET-2011]

(1) Linkage isomerism
(2) Ionization isomerism
(3) Coordination isomerism
(4) Geometrical isomerism

(3) $\left[Pt(NH_3)_2\,Cl_2\right] \Rightarrow \left[Ma_2b_2\right]$

(aa) (bb) (ab) (ab)





Is $[Pt(NH_3)_2Cl_2\ B]$ — it is used as anticancer agent.

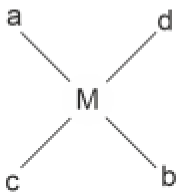
(4) $\left[Pt(NH_3)_2\,Cl\ Br\right] \Rightarrow \left[Ma_2bc\right]$2GI

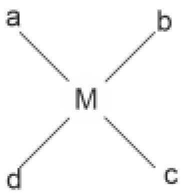
(aa) (bc) (bc) (ac)

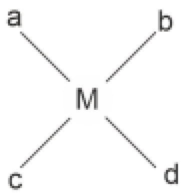
Trans cis

(5) $\left[Pt(NH_3)(H_2O)Cl\,Br\right] \Rightarrow \left[Mabed\right]$3GI

(ab) (cd), (ac) (bd), (ad)(bc) 2cis+1 trans







- **Geometrical and Optical Isomerism in octahedral complexes**

(1) $\left[Co(NH_3)_6\right]Cl_3$

$\left[Ma_6\right]^{\pm}$ optically inactive

(aa) (aa) (aa) No GI

(2) $\left[Co(NH_3)_5\,Cl\right]Cl_2$

$\left[Ma_5b\right]^{\pm}$

(aa) (aa) (ab) No GI

(3) $\left[Pt(NH_3)_4\,Cl\ Br\right]SO_4$

$\left[Ma_4bc\right]^{\pm}$ 2GI

(aa) (aa) (bc) (aa) (ab) (ac) O-inactive

Concept Ladder

Complexes of type MA_4R_2 exist in cis and trans forms and both forms are optically inactive due to plane of symmetry wherre as complexes of type MA_3B_3 exist infacial and meridonial form but both are optically inactive.

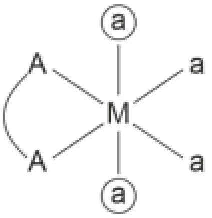
Previous Year's Questions

The complex, $[Pt(py)(NH_3)BrCl]$ will have how many geometrical isomers?

[NEET-2011]

(1) 3	(2) 4
(3) 0	(4) 2

(4) $\left[Pt(en)Cl_4\right] \Rightarrow \left[M(AA)a_4\right]^{\pm}$



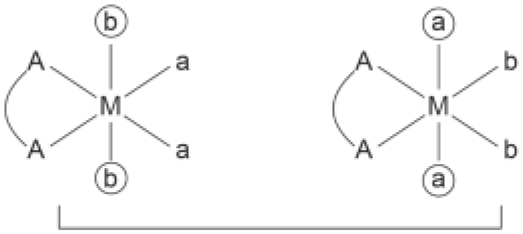
No GI

O-Inactive

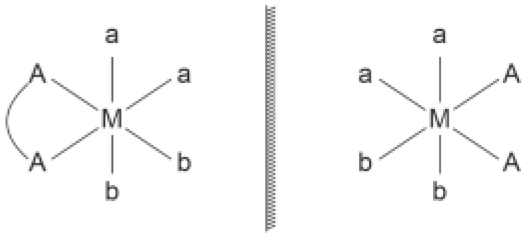
Rack your Brain

How many geometrical isomers are possible for the $[Ni(NH_3)_4]^{+2}$?

(5) $\left[Pt(en)Cl_2Br_2\right] = \left[M(AA)a_2b_2\right]$



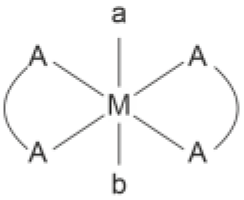
Trans, O-Inactive



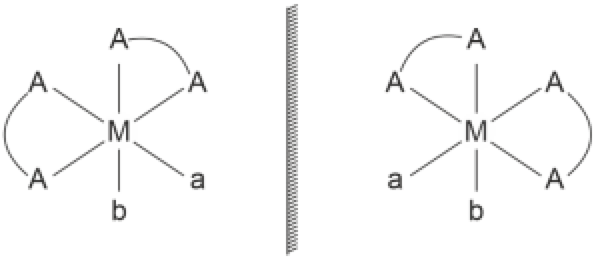
Cis, O-acitve
(Ab) (Aa) (ab)

GI = 3
O-active = 3
S.I = 4

(6) $\left[M(AA)_2\,ab\right]^{\pm}$



Trans



Cis, O-Inacitve

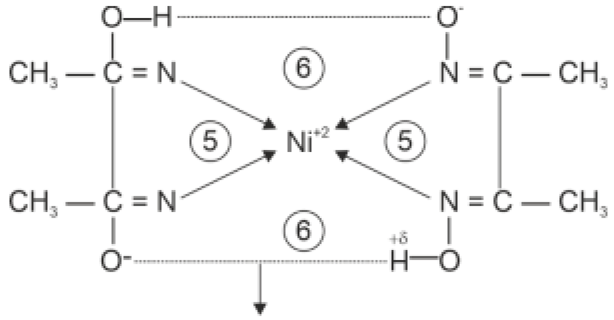
GI=2
O-Active = 2
$\boxed{SI = 3}$

Application of Complex compound

(1) Test of Ni^{+2}

$$Ni^{+2} + 2dmg \xrightarrow{NH_4OH} [Ni(dmg)_2]$$

$$Ni^{+2} = 3d^8 \xrightarrow[SFL]{CN=4} dsp^2, \text{square planar diamagnetic}$$



Symmetrical H-Bonding

Rack your Brain

Explain in brief how by forming complexes, silver and gold can be extracted from metals.

(2) Test of Fe^{+2}, Fe^{+3} and Cu^{+2}

$$\begin{tikzcd} \underset{\text{Salt}}{Fe^{+2}} \arrow[r, "K_3{[Fe(CN)_6]}", "\text{1-2 drops}"'] & \underset{\text{Blue}}{Fe_3[Fe(CN)_6]_2} \arrow[d, "K_3{[Fe(CN)_6]}"] \\ & \underset{\text{Colloidal blue solution}}{3K^+\,Fe^{+2}[Fe(CN)_6]^{-3}} \end{tikzcd}$$

$$\underset{\text{Salt}}{Fe^{+3}} \xrightarrow[\text{1-2 drops}]{+K_4[Fe(CN)_6]} \underset{\text{Blue}}{Fe_4[Fe(CN)_6]_3} \xrightarrow{K_4[Fe(CN)_6]} \underset{\text{Colloidal blue solution}}{4K^+Fe^{+3}[Fe(CN)_6]^{-4}}$$

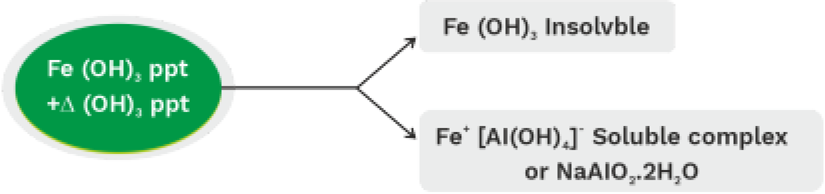
$$\underset{\text{Salt}}{Fe^{+3}Cl_3} + \underset{\text{Salt}}{3K^+SN^-} \longrightarrow \underset{\text{Red colour}}{3\,KCl + Fe\,(SCN)_3}$$

(3) Test of sulphide ion

$$Na_4S + \underset{\text{Sodium nitroprusside}}{Na_2\left[Fe(CN)_5\left(N^+O\right)\right]} \rightarrow \underset{\text{Voilet / Brown colour}}{Na_4\left[Fe(CN)_5(NOS)\right]}$$

$$S^{-2} + N^+O \rightarrow N\overline{O}S$$

(4) Separation of hydroxides or oxides



(5) If excess amount of KCN is added into $CuSO_4$ solution then insoluble CuCN is formed which later into soluble complex.

(6) AgCl or AgBr ppt (not AgI) are soluble in NH_3 or NH_4OH

$$\underset{\text{ppt}}{AgCl} + 2NH_3 \rightarrow \underset{\text{soluble complex}}{\left[Ag\left(NH_3\right)_2\right]^+} Cl^-$$

(7) $[EDTA]^{-4}$ is used for estimation and removal of hardness of H_2O.

$$Ca^{+2} + EDTA^{-4} \rightarrow \left[Ca\left(EDTA\right)\right]^{-2}$$

(8) Wilkinson catalyst $[RhCl(PPh)_3]$ is used for hydrogenation of alkene.

(9) Biological importance: -

(a) Chlorophyll → Mg
(b) Vit–B_{12} → Co
(c) Carboxypeptide → Zn
(d) Plastocynin → Cu
(e) Insolin → Zn
(f) Haemoglobin → Fe^{+2}
(g) Hyoglobin → Fe^{+2}

Concept Ladder

Light blue colour of aq. solution of $CuSO_4$ term into dark blue in presence of ammonia or NH_4OH but in presence of acid there is no colour change.

Q.11 Describe with an example of each, the role of coordination compounds in :
(i) Biological system (ii) Analytical chemicstry
(iii) Medicinal chemistry

A.11 (i) Vit. B-12, it is a antipernicious anemia factor.
(ii) Determining and estimation of metal
(iii) EDTA is used in lead poisoning.

Organometallic Compound

Compounds in which carbon atom of hydrocarbon part is directly bonded with metal or metalloid.

OMC	Not OMC
R-MgX	$Cu_3-COO^-Na^+$
R-Zn-R	$C_6H_5O^-Na^+$
Frankland reagent	$CaCO_3$
R–Cd–R	CaC_2
$(Cu_3)_3As$	NaCN
$(R_2SiO)_n$	$Ti(OC_6H_5)_4$
$[Ni-(CO)_4]$	

Types

(1) σ Bonded OMC

$(C_2H_5)_4Pb$ T.E.L used as anti knocking agent

$[TiCl_4 + (C_2H_5)_3 Al]$ Ziggler natta catalyst (Heterogenous catalyst) = used for polymerisation of alkene.

(2) π Bonded OMC

Presence of π donor ligand

$$\left[Cr\left(\eta^6 - C_6H_6\right)_2\right], \left[Fe\left(\eta^5 - C_5H_5\right)_2\right]$$

(3) σ and π bonded OMC

Presence of synergic bonding

$$\left[Ni\left(CO\right)_4\right].\left[Fe\left(CO\right)_5\right]$$

Trans effect

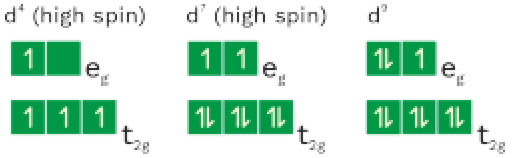
$$K\left[PtCl_3\left(\eta^2 - C_2H_4\right)\right]$$

$$Pt^{+2} = 5d^8 \xrightarrow{CN=4} dsp^2$$

square planar diamagnetic

John Taller effect

Distortion in octahedral geometry due to unsymmetrical e^- cloud in eg set of orbitals.



Definitions

The compounds in which carbon forms a bond with an atom (metal/non-metal) which is less electronegative than carbon, then the compound as organometallic compound.

Rack your Brain

Why compounds like alkoxides, carbides and cyanides are not termed as organometallic compounds?

Previous Year's Questions

An example of a sigma bonded organometallic compound is

[NEET-2017]

(1) Grignard's reagent
(2) ferrocene
(3) cobaltocene
(4) ruthenocene

Q.12 A coordination compound $CrCl_3.4H_2O$ precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write the structural formula of the compound and name it.

A.12 The structural formula will be [Cr(H2O)4Cl2]Cl.
Tetraaquadichlorido chromium(III) chloride is the name of this compound.

Q.13 Why are low spin tetrahedral complexes not formed?

A.13 The crystal field splitting energy of tetrahedral complexes is too low. It is lower than pairing energy so, the pairing of electrons is not favoured and therefore the complexes cannot form low spin complexes.

Q.14 Explain why $[Fe(H_2O)_6]^{3+}$ has a magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

A.14 H_2O is a weak field ligand for $[Fe(H_2O)_6]^{3+}$, won't cause pairing of electrons, therefore there are 5 unpaired electrons. CN^- is a strong field ligand for $[Fe(CN)_6]^{3-}$ so, Fe^{3+} has six unpaired electrons which will cause pairing of all the electrons. So, the electrons will start pairing leaving behind one unpaired electron.

Q.15 Name the type of isomerism when ambidentate ligands are attached to a central metal ion. Give two examples of ambidentate ligands.

A.15 Ambidendate ligands are those having different two binding sites.
Examples: Isothiocyanato Thiocyanato and Nitrite-N Nitrito-O
The type of isomerism when ambidentate ligands are attached to a central metal ion is called linkage isomerism because they only differ in the atom that is linked to the central metal ion.

Q.16 $CuSO_4.5H_2O$ is blue while $CuSO_4$ is colourless. Why?

A.16 In $CuSO_4.5H_2O$, H_2O molecule is a ligand. Whereas, in $CuSO_4$, there are no H_2O molecules to act as ligands, so no crystal field splitting happens and for $CuSO_4.5H_2O$ as electrons will excite to higher d-orbital and show colour.

Q.17 Why do compounds having similar geometry have a different magnetic moment?

A.17 They differ in the number of paired and unpaired electrons. A strong field ligand will cause pairing of electrons while a weak field ligand will not cause pairing. Pairing or not pairing will change the number of unpaired electrons, which affects the magnetic moment.

Q.18 Why are low spin tetrahedral complexes not formed?

A.18 For tetrahedral complexes, the crystal field splitting energy is too low. It is lower than pairing energy so, the pairing of electrons is not favoured and therefore the complexes cannot form low spin complexes.

Q.19 Based on crystal field theory explain why Co(III) forms a paramagnetic octahedral complex with weak field ligands whereas it forms a diamagnetic octahedral complex with strong field ligands.

A.19 The electronic configuration will be $t^{4}_{2g}\ e^{2}_{g}$. It has 4 unpaired electron and paramagnetic. With weal ligand $\Delta_0 < p$. The configuration with strong field ligand will be $t^{6}_{2g}\ e^{0}_{g}$. the $\Delta_0 > p$ and there won't be any unpaired electron therefore diamagnetic.

Summary

- In coordination compounds - central atom acts as lewis acid and ligands act as lewis base.
- Trans isomer does not show optical isomerism due to presence of symmetry. Only Cis isomer show optical isomerism due to presence of unsymmetry.
- Geometrical isomerism is not possible for complexes of type MA_4 and MA_3B.
- $MA_2X_2Y_2$ type of complexes show both optical and geometrical isomerism.
- (i) Octahdral complexes of type MA_3B_3 from 2 isomeric forms.
  (ii) Octahedral complexes of type MABCDEF from 15 isomeric forms.
- CO, CN^- and NO_2^- ligands cause passing of e^- in central metal atom.
- Zeisse's salt $K[PtCl_3(\eta^2-C_2H_4)]$
  Ferrocene $[Fe(\eta^2-C_2H_5)_2]$.
- Cis platin – cis $[PtCl_2(NH_3)_2]$ is used in treatment of cancer.
- (i) Zegler - Natta Catalyst is $(PH_3P)_3RhCl$ is use in hydrogenation of alkenes.
  (ii) Wilkinson's catalyst $(Ph_3P)_3RhCl$ is used in hydrogenation of alkenes.
- Bleaching powder is mixed salt – $CaOCl_2$ $Ca^{2+} + Cl^- + OCl^-$.
- Effectifve atomic no. (EAN rule) by Sidgwick :
  $EAN = Z - (O.N.) + 2 \times (C.N.)$
  where Z = At. no. of central atom.
  O.N. = Oxidation no. of central atom.
  C.N. = Co-ordination of central metal atom.
- EDTA is hexadentate ligand — It has six donar atoms; 2 nitrogen atoms and 4 oxygen atoms.
- CO is called π acid ligand due to back bonding present in it.
- In $CuSO_4.5H_2O$ (solid), Copper is co-ordinated to 4 water molecules.