28. CO-ORDINATION COMPOUNDS

1. INTRODUCTION

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

Molecular or Addition Compounds

When solutions of two or more simple stable compounds in molecular proportion are allowed to evaporate, crystals of new substances, called molecular or addition compounds, are obtained. Some common examples are given below:

$CuSO_4 + 4NH_3 \rightarrow CuSO_4 \cdot 4NH_3$

$AgCN + KCN \rightarrow KCN \cdot AgCN$

$4\,KCN + Fe\,(CN)_2 \rightarrow Fe\,(CN)_2.4KCN$

$$K_2SO_4 + Al_2\left(SO_4\right)_3 + 24H_2O \rightarrow \underset{\text{Alum}}{K_2SO_4.Al_2\left(SO_4\right)_3.24H_2O}$$

Simple stable	Addition or
Compounds	Molecular compounds

There are two types of molecular or addition compounds: (1) double salts or lattice compounds and (2) coordination or complex compounds.

Double Salts or Lattice Compounds

The addition compounds which are stable only in solid state but are broken down into their individual constituents when dissolved in water are called double salts or lattice compounds.

Nomenclature of Double Salts

(a) A hyphen (-) is used between the compounds while writing the names of double salts with the number of molecules appearing inside brackets at the end.

Example: $KCl \cdot MgCl_2 \cdot 6H_2O$ – potassium chloride-magnesium chloride-water (1/1/6)

$K_2SO_4 \cdot Cr_2\,(SO_4)_3 \cdot 24H_2O$ – potassium sulphate-chromium sulphate-water (1/1/24)

(a) Cations and anions with the same oxidation number are represented with English alphabets (cation first). If more than one type of cations are present, they are arranged in the increasing order (ascending order) of oxidation numbers. Anions of different oxidation numbers are arranged in the following order:

Oxide (O_2^-), hydroxide (OH^-), inorganic anion, organic anion, hydride (H^-).

The above rules are further clarified by following examples:

(i) $KNaCO_3$ – Potassium sodium carbonate (mixed salt)

(ii) $KHCO_3$ – Potassium hydrogen carbonate (mixed salt)

Note: Hydrogen is an exception and is written at the end.

(iii) $NH4\cdot MgPO_4\cdot 6H_2O$ — Ammonium magnesium phosphate-6-hydrate or water

(iv) $NaCl\cdot NaF\cdot 2Na_2SO_4$ — (Hexa) sodium chloride fluoride (bis) sulphate

Coordination or Complex Compounds: Those molecular compounds which retain their identity in solid as well as in solution, are known as coordination or complex compounds. A part (or whole compound) of these compounds is not dissociated in solution and its behavior is different from its constituents.

Example: $K_4\left[Fe\left(CN\right)_6\right]\rightarrow 4K^+ + \underbrace{\left[Fe\left(CN\right)_6\right]^{4-}}_{\text{Complex ion}}$

Illustration 1: Aqueous solution of potassium ferrocyanide does not give the test of Fe (II) and it is not poisonous like potassium cyanide. Why? **(JEE MAIN)**

Sol: Being a complex salt, it ionizes to K+ and $[Fe\ (CN)_6]^{4-}$ ions. Due to absence of Fe (II) it does not give the test of Fe (II). Absence of free CN^- makes it nonpoisonous.

Note: An imperfect complex compound may be too unstable to exist and may be completely dissociated in solution, and then becomes a double salt.

2. TYPES OF COORDINATION COMPOUNDS

(a) Based on the nature of cations and anions, coordination compounds are classified into four types:

- **(i)** Simple cation and complex anion: $K_4\ [Fe\ (CN)_6]$, $K_2\ [PtCl_6]$, etc.
- **(ii)** Complex cation and simple anion: $[Cu\ (NH_3)_4]\ SO_4$, $[Ni\ (NH_3)_6]\ Cl_2$, etc.
- **(iii)** Complex cation and complex anion: $[Pt\ (NH_3)_4]\ [PtCl_4]$, etc.
- **(iv)** Neutral complex compounds: $Ni\ (CO)_4$, $Fe\ (CO)_5$, etc.

(b) Based on stability, coordination compounds are of two types:

- **(i)** Perfect or penetrating complexes: These are compounds in which the complex ion is feebly dissociated in solution and is highly stable.

  E.g. $K_4\ [Fe\ (CN)_6] \rightarrow 4K^+ + [Fe\ (CN)_6]^{4-}$

  $[Fe\ (CN)_6]^{4-} \rightleftharpoons Fe^{2+} + 6CN^-$ (Feebly dissociated)

- **(ii)** Imperfect or normal complexes: These are compounds in which the complex ion is appreciably dissociated and is less stable.

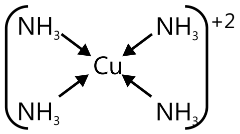
  E.g. $K_4\ [Cd\ (CN)_4] \rightarrow 2K^+ + [Cd\ (CN)_4]^{2-}$

  $[Cd\ (CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$ (Reversible dissociation)

3. TERMINOLOGIES IN COORDINATION COMPOUNDS

3.1 Central Metal Atom/Ion

Metal atom of complex ion which coordinates with atoms or group of atoms/ions by accepting their lone pair of electrons. Here Cu is the central metal atom. Some complex ions may also have more than one metal atom.



3.2 Ligands

The anions, cations or neutral molecules, which form coordinate bonds with the central metal atom by donating an electron pair (lone pair) are ligands. These electron pair donors are also known as Lewis bases. Thus, a complex ion is formed as: $M^{n+} + xL \rightarrow [ML_x]^{n+}$

In the above example, NH_3 is the ligand.

Classification of Ligands

Ligands are classified as follows:

(a) On the basis of the charge of ligand:

- **(i)** Anionic ligands: These are negatively charged and are the most common type of ligand, such as, F^-, Cl^-, Br^-, OH^-, CN^-, SO_3^{2-} , S^{2-}, SO_4^{2-}, etc.
- **(ii)** Neutral ligands: These are uncharged and are the electron pair donor species such as $H_2\ddot{\underset{..}{O}}$,$R\ddot{\underset{..}{O}}H$, $\ddot{N}H_3$ $R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$ etc.
- **(iii)** Cationic ligands: They are positively charged and are rare such as NO^+, etc.

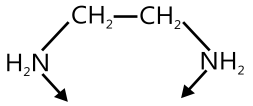
(b) On the basis of denticity: The number of donations accepted by a central atom from a particular ligand is known as the denticity of the ligand. Based on this, ligands are classified as follows:

- **(i)** Monodentate: when only one donation is accepted from the ligand. For example,

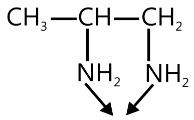
  H_2O, NO, CO, NH_3, CO^{2-}, Cl^-, etc.

- **(ii)** **Bidentate:** when two donations are accepted from the ligand. For example,

(1) En: Ethylenediamine

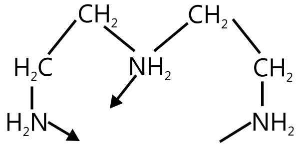


(2) Pn: Propylenediamine

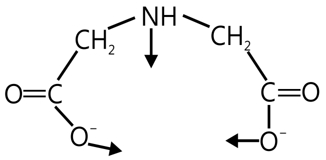


- **(iii)** **Tridentate:** when three donations are accepted from the ligand. For example,

(1) Dien: Diethylenetriamine

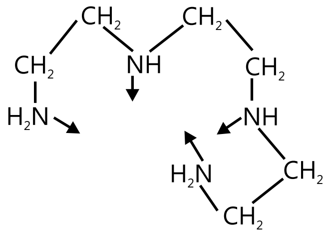


(2) Imda: Iminodiacetate

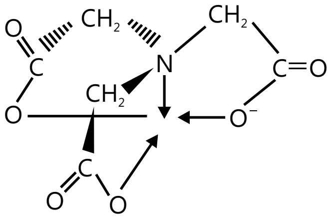


- **(iv)** **Tetradentate:** when four donations are accepted from the ligand. For example,

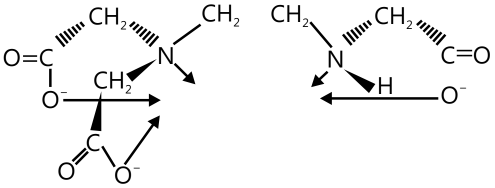
(1) Trien: Trie thylenetetraamine



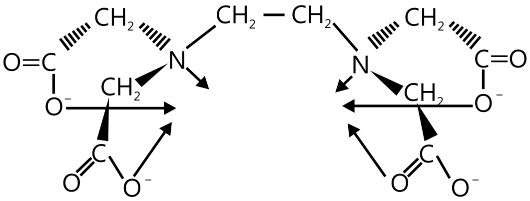
(2) NTA: Nitrilotriacetate



(v) Pentadentate: when five donations are accepted from the ligand. For example, EDTA: ethylenediamine triacetate



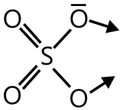
(vi) Hexadentate: when six donations are accepted from the ligand. For example, EDTA: Ethylenediamine tetraacetate



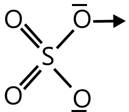
Some other types of ligands:

(a) Flexidentate: Some ligands exhibit variable denticity and are called flexidentate ligands. For example,

(i)



and



Bidentate ion Monodentate ion

(ii) [Co $(NH_3)_4CO_3$] Br and [Co $(NH_3)_4CO_3$] Br

CO_3^{2-} is bidentate CO_3^{2-} is monodentate

(b) Chelating: A ligand which forms a ring structure with the central atom is called a chelating ligand. All polydentate ligands are chelating ligands.

Chelated complex compounds are more stable than similar complexes with monodentate ligands because dissociation of the complex involves breaking down two bonds rather than one. However, it must be noted that NH_2NH_2 and $H_2N(–CH_2–CH_2–)NH_2$ cannot act as chelating ligands due to their three-member ring and locked structure, respectively.

(c) Ambidentate ligand: A ligand with more than one kind of donor sites but only one site is utilized at a time is called an ambidentate ligand. Ambidentate ligands are of two types:

(i) Monodentate and ambidentate:

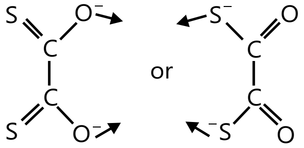
$\leftarrow\bar{C}\equiv N$ $\leftarrow\bar{O}-C\equiv N$ $\leftarrow S-C\equiv N$

or or or

$\bar{C}\equiv N\rightarrow$ $\bar{O}-C\equiv N\rightarrow$ $S-C\equiv N\rightarrow$

or

(ii) Bidentate and ambidentate:



dithicoxalate

(d) Classification of ligands on the basis of bonding interaction between the central metal atom and ligand:

(i) Classical or simple donor ligand: These ligands donate their lone pair of electrons to the central atom. For example, O_2^-, OH^-, F^-, NH_2^- , NH_3, N^{3-}, etc.

(ii) Nonclassical or π-acceptor ligand: These ligands donate the lone pair of electrons to the central atom and accept the electron cloud from the central atom in their low-lying vacant orbital. This kind of back donation is known as 'synergic effect' or 'synergic bonding'. For example, CO, CN^-, NO^+, PF_3, PR_3 (R = H, Et, Ph...), C_2H_4, C_2H_2, CO_2, etc.

- In the case of CO, the back donation to the π* orbital of the central atom can be depicted as:

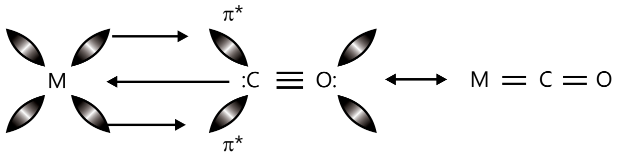


Figure 28.1: Back bonding in metal carbonyl

As per valence bond or molecular orbital theory, it is implicit that the bond order of C–O bond decreases but the C–O bond length increases due to synergic effect. Similarly, since CN^- and NO^+ are isoelectronic with CO, back donation takes place in these species also in the π* orbitals and the same conclusion can be drawn for the bond order and bond lengths.

- In PR_3, the back donation can be depicted as:

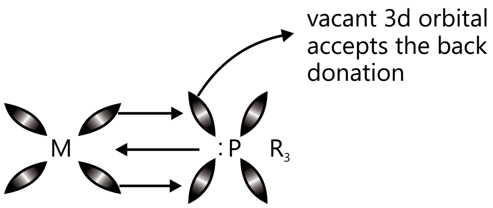


Figure 28.2: Back bonding in case of phosphine ligand

- In C_2H_4, the back donation is clearly depicted with the example of Zeise's salt.

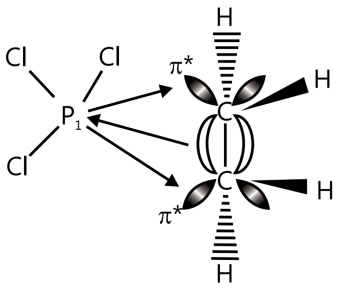


Figure 28.3: Back donation in case of ethylene ligand

Here, back donation is received in the p* orbital of the C–C bond. Hence, the bond order of C–C bond decreases and the bond length increases as compared to the free C_2H_4 molecule. Due to backbonding, the C_2H_4 molecule loses its planarity and likewise the C_2H_2 molecule loses its linearity.

Illustration 2: What is meant by the denticity of a ligand? Give examples of a unidentate and a bidentate ligand. **(JEE MAIN)**

Sol: Denticity indicates the number of donor sites in a ligand. It can be 1, 2, 3, 4 and 6 for unidentate, bidentate, terdentate, tetradentate and hexadentate ligands respectively. Unidentate ligands: Cl, H_2O, NH_3, Bidentate ligands: Ethylene diamine, Propylene, diamine.

Illustration 3: Although $NH_2{\cdot}NH_2$ possesses two electron pairs for donation, it does not act as a chelating agent. Why? **(JEE MAIN)**

Sol: The coordination by $NH_2{\cdot}NH_2$ leads to a three-member strained ring which is highly unstable and hence it does not act as chelating agent.

3.3 Coordination Number

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

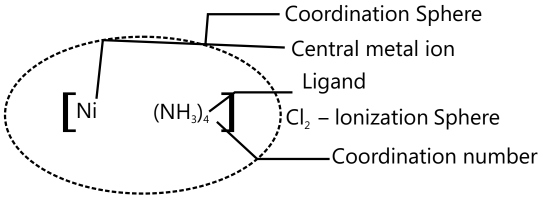
(b) In other words, it is the number of coordinate covalent bond which the ligands form with the central metal atom or ion.

(c) Some common coordination numbers exhibited by metal ions are 2, 4 and 6. The light transition metals exhibit 4 and 6 coordination numbers while heavy transition metals exhibit coordination numbers above 6.

(d) For example, the coordination number of Ni in the complex $[Ni\ (NH_3)_4]\ Cl_2$ is 4 and that of Pt in the complex $K_2\ [PtCl_6]$ is 6.

3.4 Coordination Sphere

The central metal atom/ion and the ligands directly attached to it are collectively termed as the coordination sphere. Coordination sphere is represented inside square brackets, e.g. $\left[Ni\left(NH_3\right)_4\right]^{2+}$



3.5 Oxidation Number

The actual charge that a metal atom experiences in a complex is known as its oxidation number. In other words, oxidation number of a metal atom will be equal to the total charge on this atom if all the ligands are removed without their electron pair.

Calculation of oxidation number: Algebraic sum of oxidation numbers of all the atoms of a molecule/ion is equal to the charge on it.

For example, for $M_a\ [M'_b\ (L)_x]$

[a× (O.N. of M)] + [b × O.N. of M′] + [x × (O.N. of L)] = 0

For ion $[M_a\ (L)_x]^{y+}$ a × (O.N. of M) + x × (O.N. of L) = y

e.g:- Oxidation number of Co (let it be x) in ion $[Co\ (CN)\ (H_2O)\ (en)_2]^{2+}$ can be calculated as:

x + (O.N. of CN) + (O.N. of H_2O) + 2 (O.N. of en) = +2

$x + (-1) + (0) + (2\times0) = +2 \qquad \therefore x = +3$

PLANCESS CONCEPTS

(a) Transition metals exhibit variable oxidation states.

(b) Oxidation number of different species:

  (i) Alkali metals (Li, Na, K, Rb, Cs) = +1

  (ii) Alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) = +2

  (iii) Oxidation number of ion = charge on ion

  (iv) Oxidation number of neutral molecule = 0

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Illustration 4: Specify the oxidation number of the central metals in the following coordination entities:

(a) $[Co\ (CN)\ (H_2O)\ (en)_2]^{2+}$ (b) $[PtCl_4]^{2-}$ (c) $[CrCl_3\ (NH_3)_3]$ (d) $[CoBr_2\ (en)_2]^+$

(e) $K_2\ [Fe\ (CN)_6]$ **(JEE MAIN)**

Sol:

(a) +3 (b) +2 (c) +3 (d) +3 (e) +3

3.6 Effective Atomic Number

(a) Effective atomic number was first proposed by Sidgwick in order to explain the stability of the complex.

(b) It can be defined as the resultant number of electrons present in the metal atom or ion after accepting electrons from the donor atoms of the ligands.

(c) In some cases, the effective atomic number coincides with the atomic number of the next noble gas.

(d) Effective atomic number is calculated as follows:

EAN = atomic number of the metal – number of electrons lost in ion formation + number of electrons gained from the donor atoms of the ligands.

PLANCESS CONCEPTS

Calculation of EAN: Effective atomic number = Atomic number (Z) – Electron donated (Equal to O.N.) + Electrons accepted from ligands (2 × No. of coordinate bonds formed)

Or $EAN = Z - O.N. + 2 \times (C.N.)$

Note: EAN and stability: An ion with central metal atom possessing EAN equal to next inert gas will be more stable.

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Illustration 5: Metal carbonyls having formula M $(CO)_x$ where the number of carbonyl units coordinated to metal M are formed by Fe, Cr and Ni. If effective atomic number of each metal is 36, write the formulas of these metal carbonyls. **(JEE MAIN)**

Sol: M $(CO)_x$, In Fe $(CO)_x$ EAN = At. No. of Fe + 2 × No. of ligands.

($\because$ O.N. of Metals in Metal carbonyls is zero as these compounds are neutral species formed by neutral ligand CO).

i.e. CO $\therefore$ 36 = 26+2x ; $\therefore$ x = 5

$\therefore$ Formula of iron carbonyl is Fe $(CO)_5$, Similarly, we get Cr $(CO)_6$ and Ni $(CO)_4$.

4. FORMULA AND IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

4.1 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^-
- **(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.

  E.g.

  - K_4 [Fe $(CN)_6$] — First cation and then anion [Rule 1 and 2]
  - [$CrCl_2$ $(H_2O)_4$] Br—Cl– (negative ligand) before H_2O (neutral ligand [Rule 3-(i)]

4.2 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 ligands are named in alphabetical order before the name of the central atom/ion. (This procedure is reversed in writing its formula).

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

Symbol	Name as ligand	Symbol	Name as ligand
N^{3-}	Azido	OH^-	Hydroxo
Cl^-	Chloro	CO_3^{2-}	Carbonato
O^-	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^-	Oxo	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) 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. For example, $[NiCl_2(PPh_3)_2]$ is named as dichlorobis (triphenylphosphine) nickel (II).

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

(h) 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.

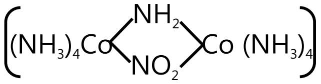
(i) Nomenclature of a neutral complex molecule is done in the similar way as that of a complex cation.

The following examples illustrate the nomenclature for coordination compounds:

- $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as: Triamminetriaquachromium (III) chloride
- $[Co(H_2NCH_2CH_2NH_2)_3]_2SO_4$ 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)

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

E.g.



$$\left[(NH_3)_4Co\begin{matrix}NH_2\\NO_2\end{matrix}Co(NH_3)_4\right](NO_3)_4$$

, in this complex

Here, NH_2 and NO_2 are bridge ligands and they are named μ-amido and μ-nitro, respectively.

Illustration 6: Write the formulas for the following coordination compounds: **(JEE MAIN)**

(A) Tetraammineaquachloridocobalt (III) chloride (B) Potassium tetrahydroxidozincate (II)

(C) Potassium trioxalatoaluminate (III) (D) Dichloridobis (ethane-1, 2-diamine) cobalt (III)

Sol: (A) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (B) $K_2[Zn(OH)_4]$ (C) $K_3[Al(C_2O_4)_3]$ (D) $[CoCl_2(en)_2]^+$

Illustration 7: Write the IUPAC names of the following coordination compounds: **(JEE MAIN)**

(A) $[Pt(NH_3)_2Cl(NO_2)]$ (B) $K_3[Cr(C_2O_4)_3]$ (C) $[CoCl_2(en)_2]Cl$

(D) $[Co(NH_3)_5(CO_3)]Cl$ (E) $Hg[Co(SCN)_4]$ (F) $[Ni(CO)_4]$

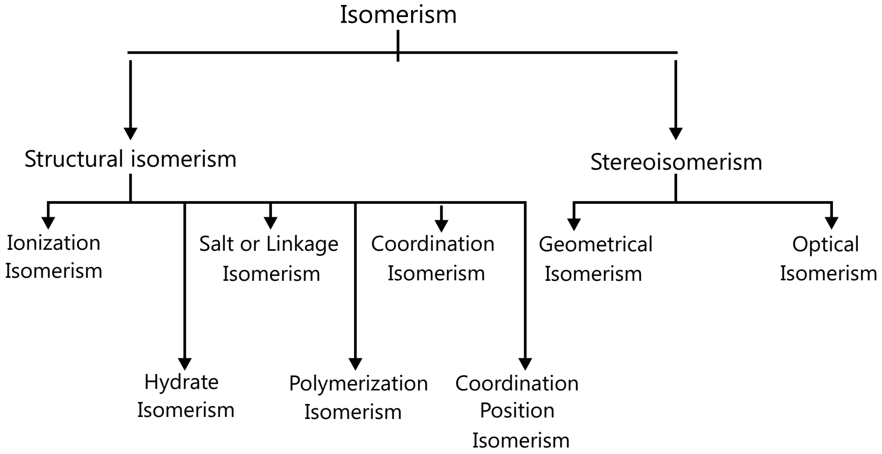
Sol: (A) Diamminechloridonitrito-N-platinum (II) (B) Potassium trioxalatochromate (III)

(C) Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride (D) Pentaamminecarbonatocobalt (III) chloride

(E) Mercury tetrathiocyanatocobaltate (III) (F) Tetracarbonylnickel (0)

5. ISOMERISM IN COORDINATION COMPOUNDS

Compounds having the same molecular formula but a different arrangement of atoms and different properties are called isomers and the phenomenon is called isomerism. Types of isomerism exhibited by complex compounds are summarized below:



5.1 Structural Isomerism

Structural isomerism occurs due to the difference in chemical linkages and distribution of ligands within and outside the coordination sphere. In Structural isomerism, isomers possess dissimilar bonding pattern. Different types of isomers are discussed below:

(a) Ionization Isomerism: Ionization isomerism is the result of the exchange of groups or ions between the coordinating sphere and the ionization sphere.

This isomerism occurs only in compounds where counter ions act as potential ligands. Ionization isomers exhibit different physical as well as chemical properties.

$$[CoBr(NH_3)_5]SO_4 \xrightarrow{\text{Ionisation}} [CoBr(NH_3)_5]^{2+} + SO_4^{2-}$$

(A) Red violet
Pentaamminebromocobalt (III) sulphate

$$[Co(SO_4)(NH_3)_5]Br \xrightarrow{\text{Ionisation}} [Co(SO_4)(NH_3)_5]^{+} + Br^{-}$$

(B) Red
Pentaamminesulphatocobalt (III) bromide

Here (A) and (B) are ionization isomers. (A) forms white precipitate ($BaSO_4$) with $BaCl_2$ whereas (B) does not react with $BaCl_2$. Similarly (B) gives yellowish white precipitate (AgBr) with $AgNO_3$ while (A) does not react with $AgNO_3$. Other examples of ionization isomers are:

(i) $[PtCl_2\ (NH_3)_4]\ SO_4$ and $[Pt\ (SO_4)\ (NH_3)_4]\ Cl_2$
(ii) $[CoCl_2\ (NH_3)_4]\ NO_2$ and $[CoCl\ (NO_2)\ (NH_3)_4]\ Cl$
(iii) $[Pt\ (OH)_2 \cdot (NH_3)_4]\ SO_4$ and $[Pt\ (SO_4)\ (NH_3)_4]\ (OH)_2$

(b) Hydrate Isomerism (Solvate Isomerism): In a complex compound, water molecules behave in two ways:

(i) Water molecules which behave as ligands are coordinated with the metal atom and are part of the complex ion, e.g. $[M\ (H_2O)_x]$.

(ii) Water molecules act as water of crystallization and these appear outside the coordination sphere, e.g. $[ML_x].nH_2O$.

Isomerism which occurs due to dissimilar number of water molecules as ligands (inside the sphere) and as water of crystallization (outside the sphere), is known as hydrate isomerism. This isomerism is analogous to ionization isomerism, in which water molecules inside and outside the sphere are exchanged.

For example,

$Cr\ (H_2O)_6Cl_3$ has three possible structures:

- $[Cr\ (H_2O)_6]\ Cl_3$ (violet)
- $[Cr\ (H_2O)_5Cl]\ Cl_2H_2O$ (green)
- $[Cr\ (H_2O)_4Cl_2]\ Cl._2H_2O$ (dark green)

These complex compounds differ from one another with respect to the number of water molecules acting as ligands.

Other hydrate isomers are:

- $[Co\ (NH_3)_4\ (H_2O)Cl]Cl_2$.
- $[Co\ (NH_3)_4Cl_2]\ Cl\ H_2O$

(c) Linkage or Salt Isomerism:

(i) Linkage isomerism occurs in complex compounds having ambidentate ligands like

—CN, —NC, —NO_2, —ONO, —CNO, —NCO, —CNS, —NCS, —SCN, etc.

(ii) In this isomerism, an ambidentate ligand coordinates with different atoms.

(iii) These isomers can be differentiated by IR spectroscopy.

For example,

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

(A) (B)

Pentaamminenitrocobalt (III) chloride Pentaammine nitritocobalt (II) chloride

(Yellow-red) (Red)

(A) is not decomposed by the action of acids whereas (B) liberates HNO3 by the action of acid. Other examples of linkage isomers are:

(i) $[Cr(SCN)(H_2O)_5]^{2+}$ and $[Cr(NCS)(H_2O)_5]^{2+}$

(ii) $[Co(NO_2)(py)_2(NH_3)_2]NO_3$ and $[Co(ONO)(py)_2(NH_3)_2]NO_3$

(d) Polymerization Isomerism: When two compounds possess stoichiometric composition but different molecular formulas, they are known as polymerization isomers of each other. Molecular formula of one isomer will be the integral multiple of the other one.

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

(e) Coordination Isomerism:

(i) This isomerism occurs only in those complexes in which both cation and anion are complex.

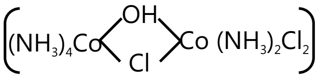
(ii) It occurs as a result of the exchange of ligands between the cation and anion.

(iii) It may occur in those complexes also in which both cation and anion have the same metal atoms.

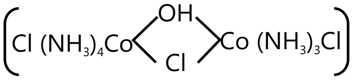
Example:

(i) $[Cr(NH_3)_6][Cr(SCN)_6]$ and $[Cr(SCN)_2(NH_3)_4][Cr(SCN)_4(NH_3)_2]$

(ii) $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$

(f) Coordination Position Isomerism: It occurs in complexes containing bridge ligands and is the result of dissimilar arrangement of metal atoms forming bridge, e.g. 

SO_4 and



SO_4

5.2 Stereoisomerism

Stereoisomerism occurs as a result of the different arrangements of ligands around the central metal atom. It may be of two types: (1) Geometrical isomerism and (2) Optical isomerism.

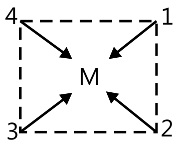
5.2.1 Geometrical Isomerism

Isomerism which occurs due to different relative arrangements of ligands around the central metal atom is known as geometrical isomerism. Geometrical isomers are of two types:

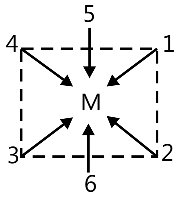
(a) **Cis-isomer:** In a disubstituted complex molecule/ion, when two similar ligands are at right angle (90º), the geometrical isomer is known as Cis-isomer.

(b) **Trans-isomer:** When two ligands are positioned in opposite directions, i.e. at 180º to each other, the isomer formed is trans-isomer.

Cis- and Trans- positions are indicated in figures:



Square planar



Octahedral

Cis- positions: (1, 2), (2, 3), (3, 4), (1, 4) (1, 2), (2, 3), (3, 4), (1, 4), (1, 5),

(4, 5), (3, 5), (2, 5), (1, 6), (2, 6),

(3, 6) and (4, 6)

Trans- positions: (1, 3) and (2, 4)

Geometrical Isomerism and Coordination Numbers

Geometrical Isomerism with Coordination Number 4:

Tetrahedral complexes do not show geometrical isomerism as all the four valences are identical.

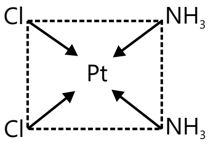
Square–planar complexes:

(a) Complexes of type MA_4, MA_3B and MAB_3 do not show geometrical isomerism, where A and B are monodentate ligands.

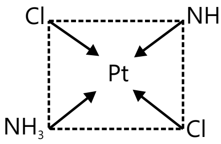
(b) Complexes of formula MA_2B_2 and MA_2BC types have two geometrical isomers, where A and B are monodentate ligands.

Example:

(i) $[PtCl_2 (NH_3)_2]$ resembles MA_2B_2 in formula and exists in two isomeric forms:

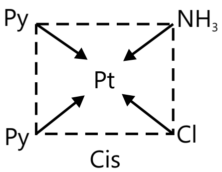


Cis-isomer
(light yellow)

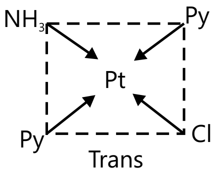


Trans-isomer
(Dark yellow)

(ii) $[PtCl (NH_3) (py)_2]$ resembles MA_2BC and exists in two isomeric forms:

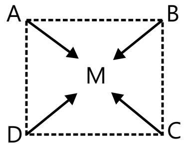


Cis

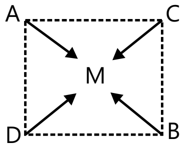


Trans

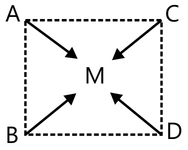
(c) Complexes of formula MABCD exist in three isomeric forms:



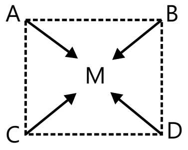
(I)



(II)



(III)



(IV)

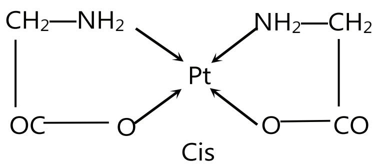
(III) and (IV) are similar.

e.g. [Pt (NO_2) (NH_2OH) (NH_3) (py)] + exists in 3 isomeric forms.

A = NO_2, B = NH_2OH, C = NH_3, D = py

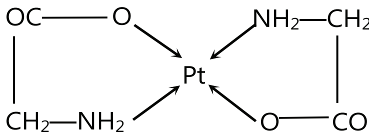
(d) If A is an unsymmetrical bidentate ligand, then compounds having formula MA_2 tend to exhibit geometrical isomerism, e.g.

$[Pt(gly)_2]$ gly = glycinate ($\ddot{N}H_2$—CH_2—COO–)



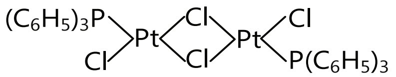
Cis

and



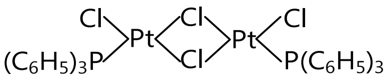
Trans

(e) Bridged dinuclear complexes of formula M2A2B4 also exhibit geometrical isomerism, e.g. $\left[PtCl_2\left(P\left(C_6H_5\right)_3\right)\right]_2$



Trans

and

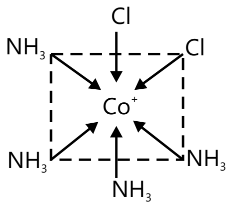


Cis

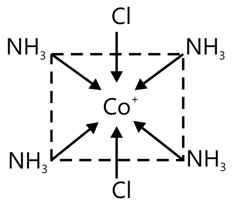
Geometrical Isomerism with Coordination Number 6:

(a) Complexes of type MA_6 and MA_5B type do not show geometrical isomerism.

(b) Complexes of type MA_4B_2 or MA_4BC exist in two isomeric forms, e.g. $[CoCl_2\cdot(NH_3)_4]^+$

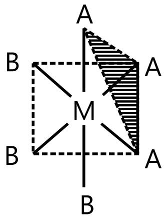


Cis

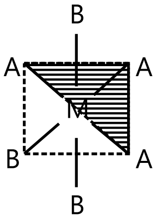


Trans

(c) Complexes of type MA_3B_3 exist in two geometrical forms which are named as facial (fac–) and meridonial (mer–) isomers. When three ligands of the same type are arranged in one triangular face, then isomer is facial. fac- and mer- isomers of complex MA_3B_3 are as follows:

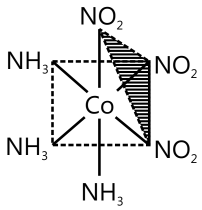


fac-isomer

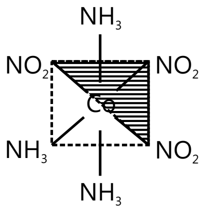


mer-isomer

E.g. [Co $(NO_2)_3$) $(NH_3)_3$] can be represented in fac- and mer- isomeric forms as follows:



fac-isomer

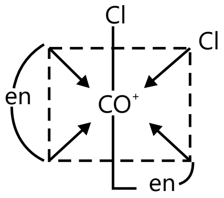


mer-isomer

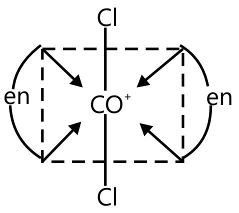
Similarly, [$RhCl_3$ $(py)_3$] also exists in fac- and mer- forms.

(d) Complex compound of formula MABCDEF may exist in 15 isomeric forms and only one compound of this type is identified so far [Pt (Br) (Cl) (I) (NO_2) (NH_3) (py)].

(e) Complexes of formula $M(AA)_2B_2$ and $M(AA)_2BC$ also exhibit geometrical isomerism, where A is the symmetrical bidentate ligand, e.g. ethylenediamine (en), oxalate (ox), etc. [$CoCl_2$ $(en)_2$]$^+$



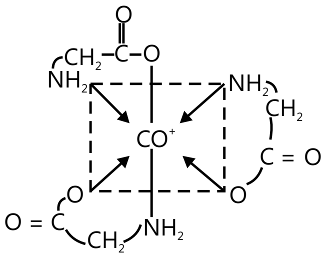
Cis-isomer



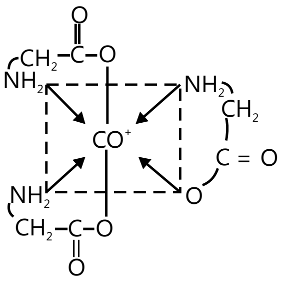
Trans-isomer

(f) Complex of type $M(AA')_3$ also exists in Cis- and Trans- forms. Where AA' is unsymmetrical bidentate ligand, e.g.

[Cr $(gly)_3$], gly: glycinate ($NH_2CH_2COO^-$)



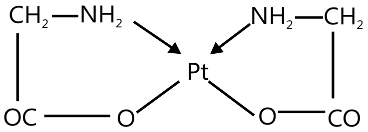
Cis-isomer



Trans-isomer

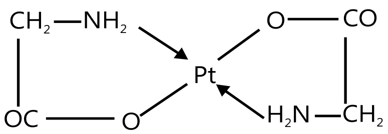
Illustration 8: Draw the structure of geometrical isomers of [Pt $(gly)_2$] where gly is $NH_2CH_2COO^-$. **(JEE ADVANCED)**

Sol:



Cis-isomer

and



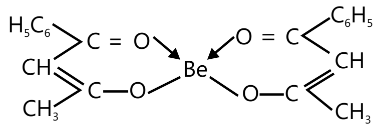
trans-isomer

5.2.2 Optical Isomerism

Optical activity: Compounds which rotate on the plane of polarized light are optically active. If the plane rotates clockwise, then the isomer is said to be dextro rotator (d or +) and if the plane rotates anticlockwise then the isomer is said to be laevo rotator (ℓ or -). Equimolar mixture of d– and isomer is optically inactive and is called racemic mixture. Optical isomers differ in optical properties.

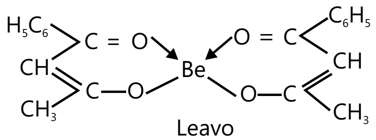
(a) Optical isomerism in complexes with coordination number 4:

(i) Tetrahedral complexes: Like carbon compounds, complex MABCD must be optically active but due to their labile nature, such complex cannot be resolved in d or ℓ form. However, tetrahedral complexes with unsymmetrical bidentate ligand are optically active. In optically active tetrahedral compounds, the ligand must be unsymmetrical. It is not necessary whether it is chiral (asymmetric) or not, e.g. bis (benzoyl acetonato) beryllium (II)



Dextro

and



Leavo

Another example of this type is $[Ni(CH_2NH_2COO)_2]$—bis (glycinato) nickel (II)

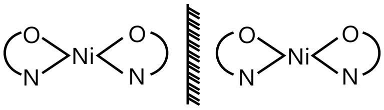
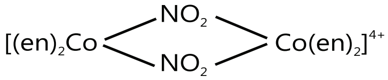
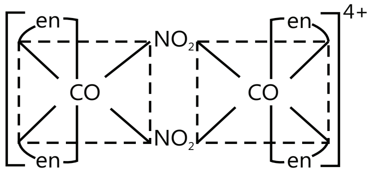


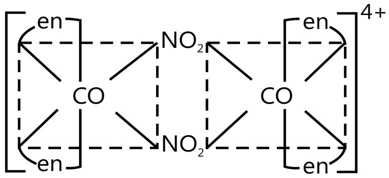
Illustration 9: Draw all the optical isomers for  $[(en)_2Co\begin{smallmatrix}NO_2\\NO_2\end{smallmatrix}Co(en)_2]^{4+}$ **(JEE MAIN)**

Sol: Complex compound shows optical isomerism and exists in d ℓ and meso forms.

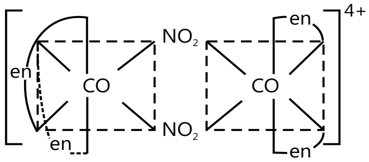
(1)



2)



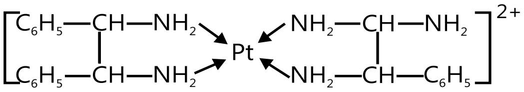
(3)



I and II d and ℓ form (mirror image of each other), III meso-form

(ii) Square planar complexes: Generally square planar complexes are not optically active as they have all the ligands and metal atoms in one plane. That is why there is a plane of symmetry.

Note: However some optically active square planar complexes are identified, e.g. isobutylenediaminemesostilbenediaminoplatinum (II) ion.

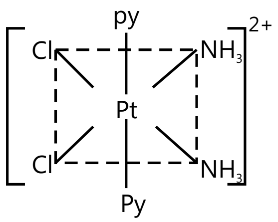


(a) Optical isomerism in compounds of coordination number 6 – Octahedral complexes:

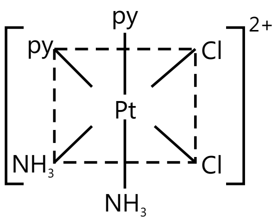
(i) Complexes of type MA_4R_2 exist in cis- and trans- forms and both forms are optically inactive due to plane of symmetry.

(ii) Complexes of type MA_3B_2 exist in facial and meridonial forms but both are optically inactive.

(iii) Complexes of type $MA_2B_2C_2$ are optically active, e.g. five geometrical isomers of $[PtCl_2(NH_3)_2(py)_2]^{2+}$ are possible. Out of these five possible isomers, three have been prepared. Their cis- form is optically active while trans- forms are optically inactive due to symmetry.



Cis-isomer



Trans-isomer

(iv) Complex MABCDEF has 15 geometrical isomers and each isomer exists as pair of enantiomers and hence total 30 optical isomers will be possible. Only one such compound has been identified so far – [Pt (Br) (Cl) (I) (NO_2) NH_2) (py)].

PLANCESS CONCEPTS

Number of Possible Isomers for Specific Complexes

Formula	Number of Stereoisomers	Pairs of Enantiomers
MA_6	1	0
MA_5B	1	0
MA_4B_2	2	0
MA_3B_3	2	0
MA_4BC	2	0
MA_3BCD	5	1
MA_2BCDE	15	6
MABCDEF	30	15
$MA_2B_2C_2$	6	1
MA_3B_2CD	8	2
MA_3B_2C	3	0
M (AA) BCDE	10	5
M $(AB)_2$ CD	11	5

Saurabh Gupta (JEE 2010, AIR 443)

PLANCESS CONCEPTS

Number of Possible Isomers for Specific Complexes

Formula	Number of Stereoisomers	Pairs of Enantiomers
M (AB) (CD)EF	20	10
M $(AB)_3$	4	2
M (ABA)CDE	9	3
M $(ABC)_2$	11	5
M (ABBA)CD	7	3
M (ABCBA)D	7	3

Saurabh Gupta (JEE 2010, AIR 443)

6. PREPARATION AND IDENTIFICATION OF COMPLEX COMPOUNDS

Preparation of Complex Compounds

(a) **By substitution reactions:** Ion of a salt can be substituted by a ligand to form a complex compound, e.g.

$$CuSO_4 + 4NH_3 \longrightarrow \underset{\text{tetraammine copper(II) sulphate}}{[Cu(NH_3)_4]SO_4}$$

(b) **By combination reaction:** Various complexes can be formed by combination reactions:

$$NiCl_2 + 6\ddot{N}H_3 \longrightarrow [Ni(NH_3)_6]Cl_2$$

$$AgCl + 2\ddot{N}H_3 \longrightarrow [Ag(NH_3)_2]Cl$$

(c) **By redox reactions:** Two important examples are:

$$2[Co(H_2O)_6](NO_3)_2 + 8\ddot{N}H_3 + 2NH_4NO_3 + H_2O_2 \longrightarrow 2[Co(NO_3)(NH_3)_5](NO_3)_2 + 14H_2O$$

$$2CoCl_2 + 2NH_4Cl + 10NH_3 + H_2O_2 \longrightarrow 2[Co(NO_3)_6]Cl_3 + 2H_2O + 9H_2$$

Identification of Complex Compound Formation

(a) **Change in solubility:** Solubility of a complex compound changes abnormally when complex is formed, e.g.

$$\underset{\text{Partialy soluble}}{AgCN + KCN} \longrightarrow \underset{\text{Soluble}}{K[Ag(CN)_2]} \qquad \text{(Solubility increases)}$$

$$\underset{\text{Insoluble}}{AgCl + 2NH_3} \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl} \qquad \text{(Solubility increases)}$$

$$\underset{\text{Soluble}}{Ni^{2+}} + 2dmg \longrightarrow \underset{\text{Insoluble}}{[Ni(dmg)_2]^{2+}} \qquad (\text{dmg} = \text{dimethylglyoxime})$$

(b) **Change in conductivity:** As complex formation changes the solubility, the number of ions in solution also changes and hence conductance changes suddenly.

(c) **Change in chemical properties:** Change in chemical properties of metal ion also indicates the formation of complex, e.g.

Ag^+ is precipitated by KCl solution but in the presence of $\ddot{N}H_3$, KCl does not precipitate Ag^+ due to formation of $[Ag\ (NH_3)_2]\ Cl$.

(d) **Change in color:** Change in color indicates complex formation, eg.

$$\underset{\text{Pink}}{Co^{2+}} + 4Cl^- \longrightarrow \underset{\text{Blue}}{[CoCl_4]^{2-}}$$

$$\underset{\text{Light blue}}{Cu^{2+}} + 4\ddot{N}H_3 \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}}$$

$$\underset{\text{Green}}{[Ni(H_2O)_6]^{2+}} + 6NH_3 \longrightarrow \underset{\text{Blue}}{[Ni(NH_3)_6]^{2+}} + 6H_2O$$

(e) Change in pH, EMF, Magnetic properties or colligative properties also indicate the complex formation.

7. THEORIES OF BONDING IN COORDINATION COMPOUNDS

7.1 Werner's Theory

In 1898, Werner propounded his theory of coordination compounds. Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Main postulates of his theory are:

(a) In coordination compounds metals show two types of linkages (valencies) – primary and secondary.

(b) The primary valencies are normally ionizable and are satisfied by negative ions.

(c) The secondary valencies are nonionizable. These are satisfied by the neutral molecules or negative ions (ligands). The secondary valency is equal to the coordination number and is constant for a metal.

(d) The ion groups bounded by the secondary linkages to the metal have a characteristic spatial arrangement corresponding to their different numbers.

Illustration 10: $PtCl_4$ and NH_3 may form five complexes, A ($PtCl_4{\cdot}6NH_3$), B ($PtCl_4{\cdot}5NH_3$), C ($PtCl_4{\cdot}4NH_3$), D $PtCl_4{\cdot}3NH_3$ and E ($PtCl_4{\cdot}2NH_3$). One mole of each A, B, C, D and E reacts with excess of $AgNO_3$ to yield 4, 3, 2 and 1 mole AgCl respectively, while E gives no AgCl. The conductances of their solutions are in the order A > B > C > D > E. On the basis of Werner's theory, write their structure and give the total number of ions given by one complex.

(JEE ADVANCED)

Sol:

Formula	Structural formula	Ionization	No. of ions
(A) $PtCl_4{\cdot}6NH_3$	$[Pt\ (NH_3)_6]\ Cl_4$	$\rightleftharpoons$ $[Pt\ (NH_3)_6]^{4+} + 4Cl^-$	5
(B) $PtCl_4{\cdot}5NH_3$	$[PtCl\ (NH_3)_5]\ Cl_3$	$\rightleftharpoons$ $[PtCl\ (NH_3)_5]^{3+} + 3Cl^-$	4
(C) $PtCl_4{\cdot}4NH_3$	$[PtCl_2\ (NH_3)_4]\ Cl_2$	$\rightleftharpoons$ $[PtCl_2\ (NH_3)_4]^{2+} + 2Cl^-$	3
(D) $PtCl_4{\cdot}3NH_3$	$[PtCl_3\ (NH_3)_3]\ Cl$	$\rightleftharpoons$ $[PtCl_3\ (NH_3)_3]^{+} + Cl^-$	2
(E) $PtCl_4{\cdot}2NH_3$	$[PtCl_4\ (NH_3)_2]$	No isonisation possible	0

7.2 Valence Bond Theory

The salient features of the valence bond theory are summarized below:

(a) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.

(b) The atomic orbitals (s, p or d) of the metal ion hybridize to form hybrid with definite directional properties. These hybrid orbitals tend to form strong chemical bonds with the ligand orbitals.

(c) The d-orbitals involved in the hybridization may be either inner (n – 1) d orbitals or outer n d-orbitals. The complexes formed in these two ways are referred to as low spin and high spin complexes, respectively.

(d) Each ligand possesses a lone pair of electrons.

(e) A covalent bond is formed when a vacant hybridized metal orbital and a filled orbital of the ligand overlap. The bond is also known as a coordinate bond or dative bond.

(f) When a complex contains unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons, it is diamagnetic in nature.

(g) The number of unpaired electrons in the complex, determines the geometry of the complex as well as hybridization of the central metal ion and vice-versa. In practice, the number of unpaired electrons in a complex is found from magnetic moment measurements as illustrated below. $\mu = \sqrt{n(n+2)}$ where n = no. of lone pair.

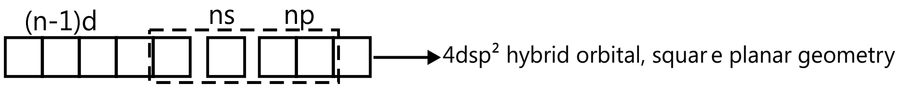
(h) Thus the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.

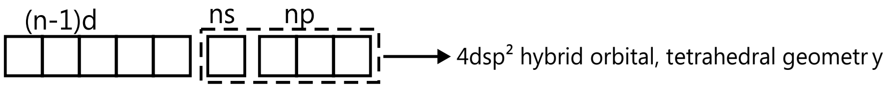
(i) Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.

Coordination Number	Type of Hybridization	Distribution of hybrid orbital in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

Application of Valence Bond Theory on Coordination Complexes

(a) **Complex with Coordination Number 4:** Tetra coordinated complexes have either tetrahedral or square planar geometry depending on the nature of orbitals involved in hybridization. If one ns and three np orbitals are involved in bonding, geometry will be tetrahedral and hybridization sp^3. If (n – 1) d, ns and two np are involved in bonding, geometry will be square planar and hybridization dsp^2. Tetra coordinated complexes are common with Ni (II), Cu (II), Pt (II), Pd (II), etc.



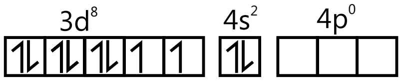


Some examples of tetra coordinated complexes are given below:

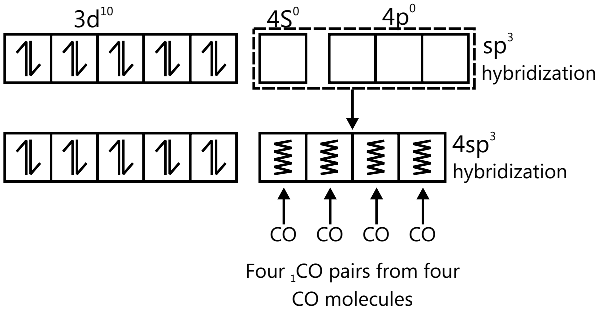
(i) Tetrahedral Complexes:

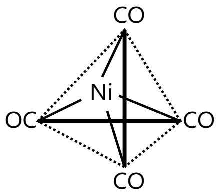
- **Ni $(CO)_4$:** In Ni $(CO)_4$, Ni has zero oxidation state and exists as Ni (0). Four ligands (CO) are attached to central metal atom Ni and require four orbitals. The electronic configuration in Ni $(CO)_4$ can be written as:

$_{28}$Ni atom = $3d^8$, $4s^2$



When four CO ligands are present, it is a strong ligand and the electrons pair up against "Hund's rule for maximum multiplicity".





Explanation: Four sp^3 hybrid orbitals are arranged tetrahedrally making it a tetrahedral complex. Since all the electrons are paired, it is diamagnetic.

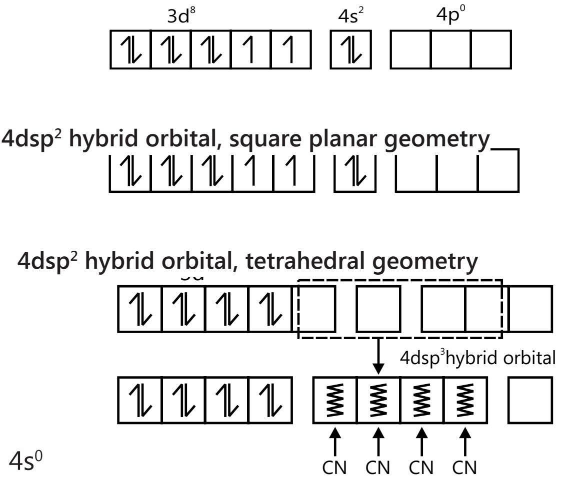
(ii) Square planar complexes:

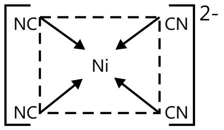
- **$[Ni (CN)_4]^{2-}$:** Here, Ni is in (II) oxidation state and the electronic arrangement is as follows:

Ni-[Ar]: $3d^8$. $4s^2$

Ni^{2+} ion [Ar] $3d^8$, $4s^0$

Ni^{2+} ion in [Ni (CN) 4]$^{2-}$ $3d^8$, $4s^0$



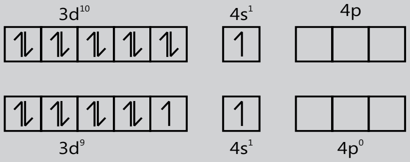


Explanation:

- CN– is a strong ligand and so it pairs up 3d-electrons against Hund's rule. The d-orbital thus made vacant, takes part in hybridization.
- Four dsp^2 hybrid orbitals are arranged in this manner and hence the geometry is square planar.
- Complex compounds are diamagnetic because all the electrons are paired.
- The complex makes use of the inner d-orbital, and so it is known as inner orbital or low spin or hyper ligand or spin paired complex.

PLANCESS CONCEPTS

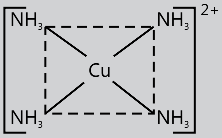
Exception: Structure of [Cu $(NH_3)_4]^{2+}$ ion: It is an exceptional case which involves sp^2 d hybridization. Here, Cu is tetra coordinated and may exist as square planar or tetrahedral complex. Physical measurement have indicated that tetrahedral geometry for [Cu $(NH_3)_4]^{2+}$ is not possible. If square planar geometry is supposed to be correct, then the following electronic arrangement must be followed:



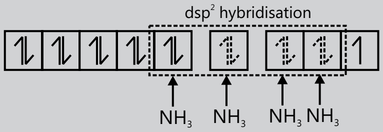
Cu [Ar]: $3d^{10}$, $4s^1$

Cu^{2-} ion: → [Ar]$3d^9$, $4s^0$

For dsp^2 hyb.3d-electron must be excited to 4-p with the following configuration.

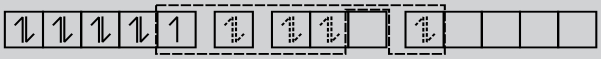


Cu^{2+} ion in [Cu $(NH_3)_4]^{2+}$:



Now if the above configuration is correct, the unpaired electrons present in higher energy, 4-p orbital should be expected to be easily lost and Cu^{2+} must be easily oxidized to Cu^{3+}, but it never occurs, so the configuration is not satisfactory. To explain it Huggin suggested sp^2d hybridization.

Cu^{2+} ion in [Cu $(NH_3)_4]^{2+}$:



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

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(b) Complexes with Coordination Number 6: Hexacoordinated complexes are of two types, inner orbital complexes and outer orbital complexes. They possess octahedral geometry.

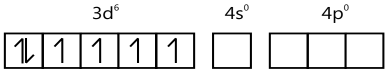
(i) Inner orbital complexes: In this type of complexes the d-orbitals used are of lower quantum number, i.e. (n – 1). Some examples are given below:

- Complexes formed by using the inner orbitals are diamagnetic or have reduced paramagnetism.
- These are also known as low spin or spin paired complexes,

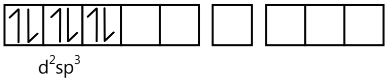
Example 1: [Fe $(CN)_6]^{4-}$

e^- configuration of Fe^{26} = [Ar] $3d^64s^2$

e^- configuration of Fe^{+2} = [Ar] $3d^6$ =



e^- configuration of Fe^{+2} after rearrangement =

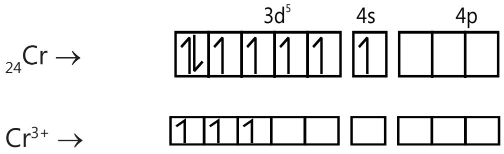


The above rearrangement is due to presence of the cyanide ligand.

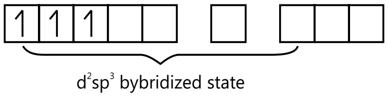
At this stage, Fe^{2+} undergoes d^2sp^3 hybridization to form six d^2sp^3 hybrid orbitals, each of which accepts an electron pair donated by CN^- ions. The complex is Diamagnetic as it has no unpaired electron.

Example 2: $[CO(NH_8)_6]^{3+}$

Example 3: $[Cr\ (NH_3)_6]^{3+}$



Cr^{3+} in d^2sp^3 hybridized state



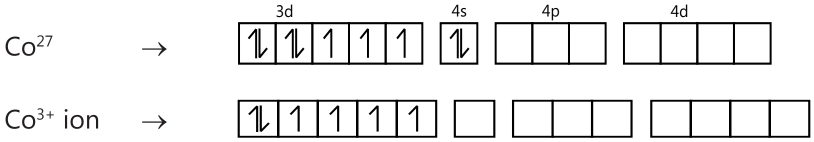
As this d^2sp^3 hybridization leads to octahedral geometry, the complex $[Cr\ (NH_3)_6]^{3+}$ will be octahedral in shape.

Since the complex ion has 3 unpaired electrons, it is paramagnetic.

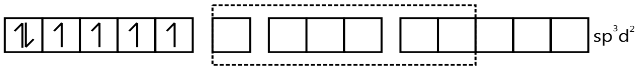
Other complexes of chromium with similar inner structure are $[Cr\ (CN)_6]^{3-}$ and $[Cr\ (H_2O)_6]^{3+}$.

(ii) Outer orbital complexes

- In these complexes s, p and d orbitals which are involved in hybridization, belong to the highest quantum number (n).
- Complex compound formed by the use of outer n and d orbitals will be paramagnetic.
- Outer orbital complexes are also known as high-spin or spin free complexes.
- The outer orbital complexes have a high number of unpaired electrons, E.g. $[CoF_6]^{3-}$



Co^{3+} ion in sp^3d^2 hybridized state



Owing to the octahedral orientation of six sp^3d^2 hybridized orbitals, shape of $[CoF_6]^{3-}$ complex ion is octahedral.

As it possesses four unpaired electrons in the 3d orbital, $[CoF_6]^{3-}$ ion is paramagnetic.

Some other examples are $[FeF_6]^{3-}$, $[Fe\ (NH_3)_6]^{2+}$, $[Ni\ (NH_3)_6]^{2+}$, $[Cu\ (NH_3)_6]^{2+}$, $[Cr\ (H_2O)_6]^{3+}$, etc.

Limitations of valence bond theory: Even though the valence bond theory explains the formation, structures and magnetic behavior of coordination compounds to a larger extent, it suffers from the following short comings:

- It includes a number of assumptions.
- It fails to provide quantitative interpretation of magnetic data.
- It lacks explanation to the color exhibited by coordination compounds.
- It does not provide a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- It is unable to predict the tetrahedral and planar structures of 4-coordinate complexes accurately.
- This theory does not distinguish between weak and strong ligands in compounds.

7.3 Crystal Field Splitting Theory

The important terms in Crystal Field Splitting theory are as follows:

(a) Degenerate orbitals: in free state, all the d-orbitals (viz., d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}) will possess the same energy and are said to be degenerate.

(b) t_{2g} and e_g set of orbitals: In a d-subshell, there are five d-orbitals and on the basis of orientation of lobes of these five d-orbitals with respect to coordinates, they have been grouped into two sets.

- **(i) e_g set of orbital:** $d_{x^2-y^2}$, and orbitals have their lobes arranged along the axes and they constitute e_g set. These orbitals are also called axial orbital. Term e_g refers to 'doubly Degenerate', according to group theory (e = doubly degenerate set)
- **(ii) t_{2g} set of orbital:** This set includes orbitals whose lobes lie between the axes and this set includes d_{xy}, d_{yz} and d_{xz} orbitals. These orbitals are also known nonaxial orbitals. Group theory called these orbital t_{2g} where 't' refers to 'triply degenerate'.

Crystal Field Theory: The crystal field splitting theory (CFT) is an electrostatic model which considers the metal–ligand bond to be ionic occurring purely due to the electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions and dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have the same energy, i.e. they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is resulted by the ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbital is lifted. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us discuss this splitting in different crystal fields in detail.

(a) Crystal field splitting in octahedral field: The orientation of d-orbital in octahedral field is represented in the diagram.

The lobes of t_{2g}, set of orbital (d_{xy}, d_{yz} and d_{xz}) point in between x, y and z axes while lobes of eg set (d_{z^2} and $d_{x^2-y^2}$) point along the x, y and z axes. Thus, energy of the eg set increases higher than that of the t_{2g} set. The splitting of orbital can be represented by Fig. 4:

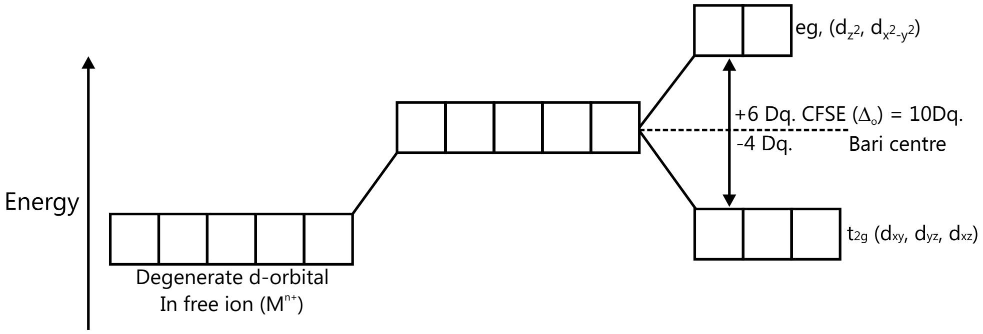


Figure 28.4: Splitting of d-orbital is a octahedral crystal field

The difference in energy of t_{2g} and e_g set is known as crystal field splitting energy or crystal field stabilization energy (CFSE), which is represented by Δ_o (o stands for octahedral) or 10 Dq. The value of 10 Dq or Δ_o can be measured by UV-visible spectrum.

The crystal field splitting, Δ_o, depends upon the field produced by the ligand and the charge on the metal ion. Some ligands are able to produce strong fields, and correspondingly, the splitting will be large whereas others produce weak fields and these consequently result in small splitting of d orbital. Ligands can be arranged according to their order of increasing field strength as follows:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCH^- < edta^{4-} < NH_3 < en < CN^- < CO$

This series is known as the spectrochemical series. It is an experimentally determined series based on the absorption of light by complex compounds with various ligands. Let us assign electrons in the d orbital of the metal ion in octahedral coordination entities. Obviously, the single d electron occupies one of the lower energy t_{2g} orbital. In d^2 and d^3 coordination compounds, the d electrons occupy the t_{2g} orbital singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise:

(a) The fourth electron could either enter the t_{2g} level and pair with an existing electron, or

(b) It could avoid paying the price of the pairing energy by occupying the eg level.

Either of these two possibilities depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (presents the energy required for electron pairing in a single orbital). The two options are:

(i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbital exhibiting the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands, form high spin complexes.

(ii) If $\Delta_o > P$, it becomes more energetically favorable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Such ligands are known as strong field ligands and they form low spin complexes. It is observed from calculations that d^4 to d^2 coordination entities are more stable for strong field cases compared to their weak counterparts.

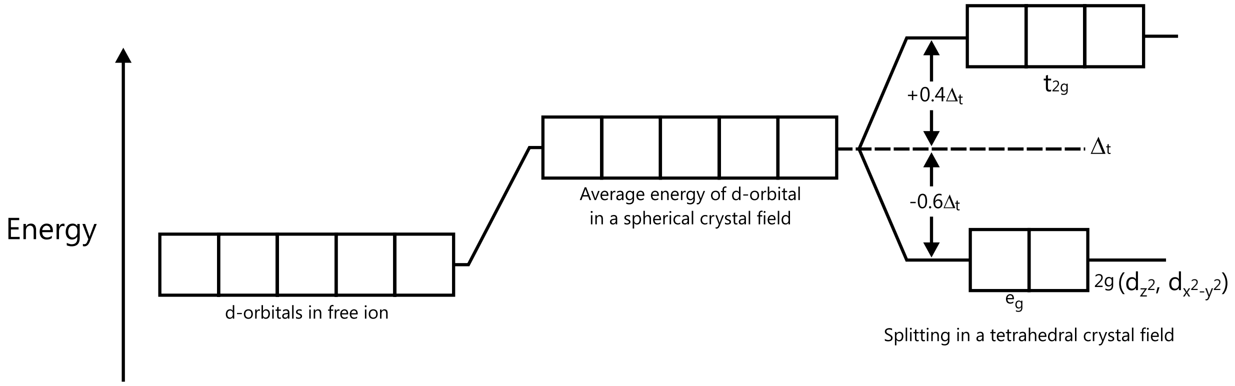


Figure 28.5: Splitting of d-orbital is a octahedral crystal field

(b) **Crystal field splitting in tetrahedral complexes:** The orientation of ligands in a tetrahedral complex is given in fig. 5. Although none of the d-orbitals point towards axes, the t_{2g} set is close to the direction in which ligands are approaching so their energy is higher.

The magnitude of Δ_t is considerably less than that in the octahedral field, which is mainly due to two reasons:

(i) In tetrahedral complex, number of the ligands is only four instead of six.

(ii) In tetrahedral complexes, the direction of the orbitals does not coincide with the direction of the ligands, both the factors reduce the CFSE by 2/3 and so Δ_t is roughly 4/9 times to Δ_o.

(c) **Crystal Field Splitting in Square Planar Complexes:** The square planar geometry can be considered to be derived from the octahedral by removing negative charges from the z-axis. As these negative charges are removed, d_{xy}, d_{xz} and d_{yz} orbital, all of which have a Z-component become more stable as shown in Fig. below.

This type of splitting can be further explained as follows:

As the lobes of point towards the ligands, this orbital has the highest energy. The lobes of dxy orbital lie between the ligands but are coplanar with them, hence this orbital has the second highest energy. The lobes of d_{x^2} orbital point out of the plane of the complex but the belt around the center of the orbital (which contains about 1/3rd of the electron density) lies in the plane. Therefore, d_{z^2} orbital is next highest in energy. The lobes of dxz and dyz orbital point out of the plane of the complex, and so they are least affected by the electrostatic field of the ligands, they degenerate and have the lowest in energy.

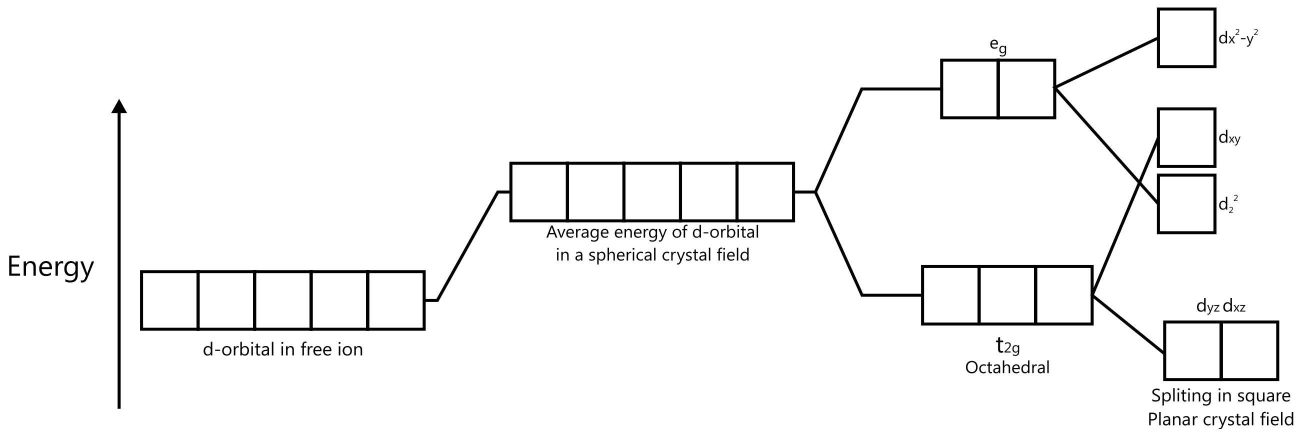


Figure 28.6: Splitting of d-orbital in a square planar crystal

PLANCESS CONCEPTS

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

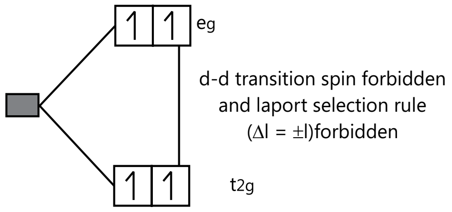
Vaibhav Krishnan (JEE 2009, AIR 22)

Illustration 11: $Mn^{2+}_{(aq.)}$ ion is light pink colored while $[Mn\ (CN)_6]^{4-}$ is blue in color. Explain. **(JEE ADVANCED)**

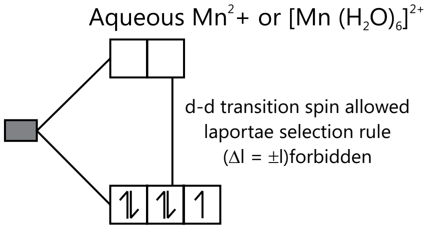
Sol: In complexes, where Mn (II) is present, configuration of a metal ion is d^5. There may be two types of spin arrangements in the presence of different kinds of ligands.

(A) High spin complex (with weak field ligands) and (B) Low spin complex (with strong field ligands)

The arrangement of electrons in these complexes can be depicted as:



High spin complex



Low spin complex

$[Mn\ (CN)_6]^{4-}$

In high spin complex compounds, it is observed that d–d transition requires reversion of spin which is against the spin selection rules and this makes them spin forbidden and the intensity of color is of only about 1/100 when the transition is allowed.

In $[Mn\ (CN)_6]^{4-}$ on the other hand, d–d transitions do not have any such restrictions and are spin allowed. Intense color also is observed when transition takes place.

7.3.1 Factors Affecting CFSE

(a) Nature of ligand: The value of Δ depends upon the nature of ligands. Ligands with a small degree of crystal field splitting capacity are termed as weak field ligands and those ligands which cause large splitting are called strong field ligands. In general, ligands can be arranged in the ascending order of CFSE caused by them. This series remains practically constant for different metals and is known as spectrochemical series. It is an experimentally determined series. The order is difficult to explain due to involvement of both σ and π bonding. Some ligands in spectrochemical series are given below:

$I^- < Br^- < S^{2-} < Cl^- < N_3^-$, $F^- <$ Urea, $OH^- <$ Oxalate, $O^{2-} < H_2O < NCS^- <$ EDTA $<$ py, $NH_3 <$ en $= SO_3^{2-} <$ bipy, phen $< NO_2^- < CH_3^- < C_6H_5^- < CN^- < CO$. For strong field ligands, the order depends on the donor atom and is in the following order:

C-donor > N-donor > O-donor > Halogen donor

(b) Geometry of the Complex: Δ_t is approximately 4/9 times of Δ^o. The lower value of Δ_t is due to lesser number of ligands in tetrahedral complex. Also, in tetrahedral complexes the orbital does not point toward the axes, resulting in less interaction.

(c) Oxidation state of metal ion: It is observed that the higher the charge on the central metal atom (or oxidation state), the higher the CFSE.

E.g., Δ_o for $[Fe\,(H_2O)_6]^{3+}$ is greater than $[Fe\,(H_2O)_6]^{2+}$, Δ_o for $[Co\,(H_2O)_6]^{3+}$ is greater than $[Co\,(H_2O)_6]^{2+}$ and Δ_o for $[V\,(H_2O)_6]^{2+}$ is greater than $[Cr\,(H_2O)_6]^{3+}$.

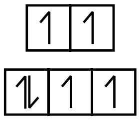
(d) Nature of metal ion: The value of CFSE is also determined by the transition series to which the metal belongs and the order for this is observed to be 3d < 4d < 5d. The value of Δ increases by 30% to 50% for 3d to 4d series and from 4d to 5d series. Hence, metals of 4d and 5d series have more tendency to form low spin complexes, e.g. CFSE for the given complexes follow the order:

$[Co\,(NH_3)_6]^{3+} < [Rh\,(NH_3)_6]^{3+} < [Ir\,(NH_3)_6]^{3+}]$

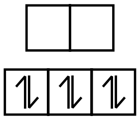
When two metal ions possess the same charge but different number of d-electrons, the magnitude of Δ_o decreases with increase in the number of d-electrons in the central metal atom. E.g. Δ_o for $[Co\,(H_2O)_6]^{2+}$ is greater than Δ_o for $[Ni\,(H_2O)_6]^{2+}$ because Co^{2+} possesses $3d^7$ configuration while Ni^{2+} has $3d^8$ configuration.

7.3.2 Applications of CFSE

(a) Magnetic character of complexes: Complexes containing unpaired electrons tend to be attracted by magnetic fields and hence known as paramagnetic. In contrast, when all the electrons are paired, the complex is slightly repelled by a magnetic field and is said to be diamagnetic. The magnetic moment of a transition metal wholly depends on the number of unpaired electrons and is equal to $\sqrt{n(n+2)}$ B.M., where n is number of unpaired electrons. For diamagnetic substance, the magnetic moment will be zero.



Weak field
$Fe^{2+}(3d^6)$ ion in
$[Fe(H_2O)_6]^{2+}$
(paramagnetic)



Strong field
$Fe^{2+}(3d^6)$ ion in
$[Fe(CN)_6]^{4-}$
(diamagnetic)

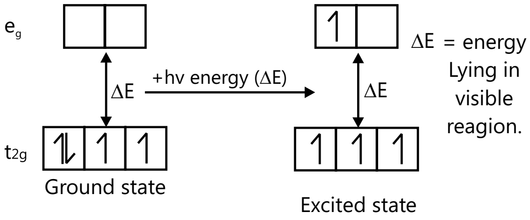
Magnetic moments of coordination compounds can be experimentally determined and this data provide information to examine the nature of coordination entities further. These measurements are termed as magnetic susceptibility measurements. For example, $[Fe\,(H_2O)_6]^{2+}$ is paramagnetic while $[Fe\,(CN)_6]^{4-}$ is diamagnetic. This observation can be explained on the basis of the electronic configurations of Fe^{2+} in $[Fe\,(H_2O)_6]^{2+}$ and $[Fe\,(CN)_6]^{4-}$. H_2O is a weak field ligand while CN^- is a strong field ligand. So $[Fe\,(CN)_6]^{4-}$ is the inner orbital low spin complex whereas $[Fe\,(H_2O)_6]^{2+}$ is an outer-orbital high spin complex. The configurations of Fe^{2+} in both the compounds are further explained in the diagram here.

PLANCESS CONCEPTS

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

Nikhil Khandelwal (JEE 2009, AIR 94)

(b) Colour of complexes: In many complexes the d-orbital split takes place in the two sets t_{2g} and e_g, which possess different energies. The difference in energies of t_{2g} and and e_g lies in the visible region of the spectrum and this helps transition metal complexes to absorb color. This makes them colored complementary to the color absorbed. This transition involves t_{2g} and e_g sets of d-orbital and is called as d–d transition. Thus d–d transition is responsible for the color of transition metal complexes. d–d transition can be represented diagrammatically as shown here.



PLANCESS CONCEPTS

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

Saurabh Gupta (JEE 2010, AIR 443)

7.3.3 Stability of Complexes

Complexes normally exhibit two kinds of stabilities: (i) Thermodynamic stability and (ii) Kinetic stability. Thermodynamic stability deals with the metal–ligand bond energy, stability constants, redox potentials, etc., that affect the equilibrium. On the basis of thermodynamic stability, Blitz classified the complexes into stable or penetration complexes and unstable or normal complexes.

Kinetic stability deals with the rates of reaction of complexes in a solution. On the basis of kinetic stability, Taube classified the complexes into labile and inert complexes. Ligands of labile complexes are easily replaceable while ligands of inert complexes cannot be replaced with easily.

Chelate effect: Complexes containing chelate rings are more stable, e.g. $[Ni\,(NH_3)_6]^{2+}$ and so is less stable than $[Ni\,(en)_3]^{2+}$.

Macrocylic effect: When a multidentate ligand is cyclic without any considerable steric effect, then the complex formed is more stable than acyclic ligand. This phenomenon is called the macrocyclic effect.

Illustration 12: $[Cu\,(CN)_4]^{2-}$ is a more stable complex than $[Cu\,(NH_3)_4]^{2+}$. Why? **(JEE MAIN)**

Sol: The higher stability constant $K = 2 \times 10^{27}$ for $Cu^{2+} + 4CN^- \rightarrow [Cu\,(CN)_4]^{2-}$ than for $[Cu\,(NH_3)_4]^{2+}$ (which is 4.5×10^{11}) explains stability. Also CN^- is stronger ligand than NH_3.

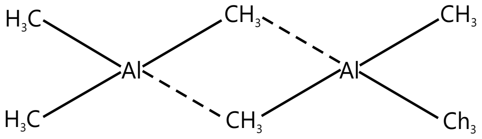
8. ORGANOMETALLIC COMPOUNDS

Organometallic compounds are defined as compounds in which carbon forms a bond with an atom (metal/non-metal) which is less electronegative than carbon.

These compounds are classified into two – covalently bonded compounds and ionic organometallic compounds.

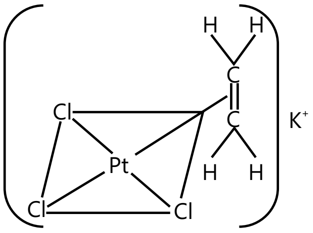
Covalently bonded compounds: In covalently bonded compounds, the metal and carbon atoms are attached to each other by a covalent bond. They can be further classified into: three groups:

(i) σ **(sigma) bonded complexes:** A σ-bonded complex consists of a metal atom and a carbon atom of the ligand joined together with a σ bond. In another words, the ligand contributes one electron and is called one electron donor. Tetramethyltin, $(CH_3)_4Sn$ and trimethyl aluminum, $(CH_3)_3$ Al are examples of σ-bonded organometallic compounds. The latter exists as dimmer and has a structure analogous to diborane. In this, two methyl groups bridge between two aluminum atoms.

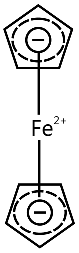


Trimethyl aluminium

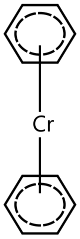
(ii) π **complexes:** Organometallic compounds with π-bonds present in them are called π-complexes. Zeise's salt, ferrocene and dibenzene chromium are π-complexes. In these compounds, the π electrons interact with the metal ion and occupy one of the coordination sites. For example, in ferrocene and dibenzene chromium, the iron and chromium atoms are sandwiched between two aromatic rings.



Zeise's salt
$K[PtCl_3(\eta^2\text{-}C_2H_4)]$



Ferrocene
$Fe[\eta^2\text{-}C_5H_5)]_2$



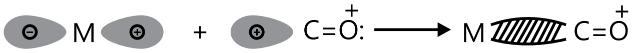
Dibenzene chromium
$Cr[\eta^6\text{-}C_6H_6)]_2$

The number of carbon atoms taking part in the formation of π-complexes is indicated by the power of η^x (pronounced as eta). For example, ferrocene is represented as $[Fe\eta^5–C_5H_5)_2]$ indicating that five carbon atoms or cyclopentadienyl anion are involved in the π- complication with the metal. Similarly, one can write dibenzene chromium as $[Cr\ (\eta^6–C_6H_6)_2]$ indicating that all the six carbons of benzene are involved in π-complexation with chromium.

8.1 Bonding in Organometallic Compounds

Bonding in Metal Carbonyls: The metal–carbon bond in metal carbonyls exhibits σ as well as π characteristics.

(i) σ-overlap: The lone pair of electron is present on the bonding orbital of carbon monoxide in a σ bonded complex and it interacts with the empty d-orbital of the metal to form a metal–carbon bond.



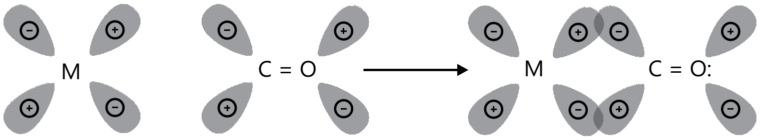
Metal orbital

Bonding orbiital

Bonding in metal carbon

(ii) π-overlap: Besides, the antibonding orbitals of CO also overlaps with the filled d-orbital of the metal resulting in back bonding as previously explained. Thus metal carbonyls become much more stable due to this multiple bonding.

It is important to note that the σ-bond is positioned in the nodal plane of the σ-electrons whereas π-overlap is perpendicular to the nodal plane.

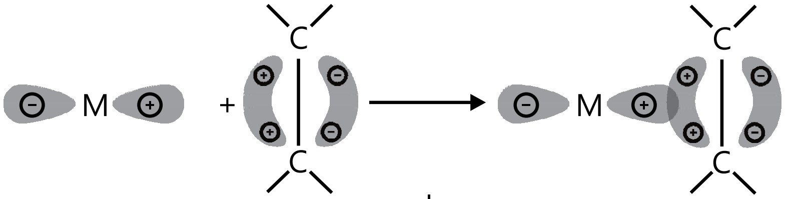


Metal orbital

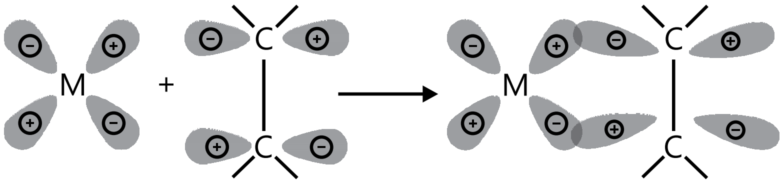
Anibonding orbital of carbon mono-oxide

Backbonding metal corbonyl

Bonding of Alkenes to a Transition Metal: There are two components in the bonding of alkenes to a transition metal to form complexes. First, the σ-electron density of the alkene overlaps with a π-type vacant orbital of the metal atom. Second is the backbonding resulting from the flow of electron density from a filled d-orbital on the metal into the vacant σ-antibonding molecular orbital on the carbon atom as depicted in the following diagram:



p overlap



PLANCESS CONCEPTS

As the electron density on metal atom increases, strength of backbonding from the metal to carbon increases and the metal–carbon bond length decreases. Likewise, when C–O bond order decreases, C–O bond length increases and vice versa.

Neeraj Toshniwal (JEE 2009, AIR 21)

8.2 Synthesis of Organometallic Compounds

Some important methods to generate metal–carbon bond as follows:

By the direct reaction of metals:

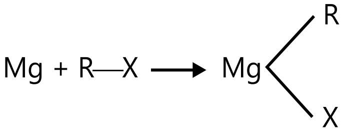
(a) n-Butyl lithium is prepared by the reaction of n-butyl bromide with lithium in ether.

$$\underset{\text{n-Butyl bromide}}{n-C_4H_9Br} + 2Li \xrightarrow{\text{Ether}} \underset{\text{n-Buthyl lithium}}{n-C_4H_9Li} + 2LiBr$$

(b) Likewise, tetra ethyl lead can be prepared as follows:

$$4C_2H_5Cl + \underset{\substack{\text{Sodium-lead}\\ \text{alloy}}}{4NaPb} \longrightarrow \underset{\text{Tetra-ethyl lead}}{(C_2H_5)_4Pb} + 4NaCl + 3Pb$$

(c) Grignard reagents are obtained by the reaction of alkyl halide (in ether) with magnesium:



Grignard reagent

By using an alkylating agent: Grignard reagent and alkyl lithium or reaction with most of the metal and non-metal halides in the presence of ether as solvent yield other organometallic compounds.

$$PCl_3 + 3C_6H_5MgCl \xrightarrow{Ether} \underset{\text{Triphenyl phosphine}}{P(C_6H_5)_3} + 3MgCl_2$$

$$SnCl_4 + 4n - C_4H_9Li \longrightarrow \underset{\text{Tetrabutyl tin}}{(n - C_4H_9)Sn} + 4LiCl$$

Preparation of Metal Carbonyls:

(a) Nickel carbonyl is obtained when finely divided nickel reacts with CO at room temperature.

$$Ni + 4CO \longrightarrow Ni(CO)_{4(g)} \xrightarrow{\Delta} Ni + 4CO$$

The nickel carbonyl so formed is in gaseous state and its subsequent thermal decomposition gives Ni and CO. This principle is used in the purification of Ni via Mond's process.

(b) Iron carbonyl is formed when iron reacts with CO at high pressure and temperature.

$$Fe + 5CO \longrightarrow [Fe\ (CO)_5]$$

PLANCESS CONCEPTS

Carbonyls containing only metal and CO are known as homoleptic carbonyls.

Nikhil Khandelwal (JEE 2009, AIR 94)

POINTS TO REMBEMBER

Coordination compound	A compound containing central metal atom or ion bonded to a fixed number of ions or molecules (called ligands).
Ligands	The ions or molecules which donate a pair of electrons to the central metal atom or ion and form coordinate bonds.
Coordination sphere	The central metals atom or ion and the ligands attached to it is collectively called coordination sphere.
Coordination number	The number of coordinate bonds formed by the ligands with the metal atom i.e. number of unidentate ligands or double the number of bidentate ligands, etc.
Denticity	The number of coordinating or ligating atoms preset in a ligand
Chelation	When a bidentate or a polydentate ligand uses it two or more donor atoms to bind to the central metal atom or ion forming ring structure, it is called chelation
Coordination polyhedron	The spatial arrangement of the ligands which are directly attached to the central metal atom.
Homoleptic complexes	The complexes which contain only one type of ligands.
Structural isomers	The isomers having same molecular formula but different structural arrangement of atoms or group of atoms around the central metal ion.
Stereiosomers	The isomers which have the same position of atom or group of atoms but they differ in the spatial arrangement around the central metal atom.
Crystal field splitting	The conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having different energies in the presence of electrical field of ligands is called crystal field splitting.
Spectrochemical series	The arrangement of ligands in the increasing order of crystal field splitting

Solved Examples

JEE Main/Boards

Example 1: Which of the following will give white precipitate with $AgNO_3$ solution?

(A) $[Co(py)_2(H_2O)_2Cl_2]Cl$

(B) $[Co(py)_2H_2OCl_3]H_2O$

Sol: (a) will give white precipitate

$[Co(py)_2(H_2O)_2Cl_2]Cl \longrightarrow Co(py)_2(H_2O)_2Cl_2]^+ + Cl^-$

$AgNO_3 + Cl^- \longrightarrow AgCl + NO^-_3$

Example 2: Specify the oxidation numbers of the metals in the following coordination entities:

(A) $[Co(CN)(H_2O)(en)_2]^{2+}$

(B) $[PtCl_4]^{2-}$

(C) $[CrCl_3(NH_3)_3]$

(D) $[CoBr_2(en)_2]$ + (d) $K_3[Fe(CN)_6]$

Sol: (A) +3, (B) +2, (C) +3, (D) +3, (E) +3]

Example 3: Using IUPAC rules, write the formula for the following:

(A) Tetrahydroxozincate (II) ion

(B) Hexaamminecobalt (III) sulphate

(C) Potassium tetrachloropalladate (II)

(D) Potassium tri (oxalato) chromate (III)

(E) Diamminedichloroplatinum (II)

Sol: (A) $[Zn(OH)_4]^{2-}$

(B) $[Co(NH_3)_6]_2(SO_4)_3$ (C) $K_2[PdCl_4]$

(D) $K_3[Cr(C_2O_4)_3]$ (E) $[PtCl_2(NH_3)_2]$

Example 4: Using IUPAC norms write the systematic names of the following:

(A) $[Co(NH_3)_6]Cl_3$ (B) $[CoCl(NO_2)(NH_3)_4]Cl$

(C) $[Ni(NH_3)_6]Cl_2$ (D) $[PtCl(NH_2CH_3)(NH_3)_2]Cl$

(E) $[Mn(H_2O)_6]^{2+}$

Sol: (A) Hexaamminecobalt (III) chloride.

(B) Tetraamminechloronitrito-N-cobalt (III) chloride.

(C) Hexaamminenickel (II) chloride.

(D) Diamminechloro (methylamine) platinum (II) chloride.

(E) Hexaaquamanganese (II) ion.

Example 5: Write the correct formula for the following coordination compounds:

(A) $CrCl_3 \cdot 6H_2O$ (violet, with 3 chloride ions/unit formula)

(B) $CrCl_3 \cdot 6H_2O$ (light green, with 2 chloride ions/unit formula)

(C) $CrCl_3 \cdot 6H_2O$ (dark green, with I chloride ion/unit formula)

Sol: (A) $[Cr(H_2O)_6]Cl_3$

(B) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

(C) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O]$

Example 6: Draw the structure of:

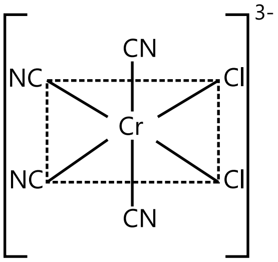
(A) Cis-dichlorotetracyanochromate (III) ion.

(B) Mer-triamminetrichlorocobalt (III).

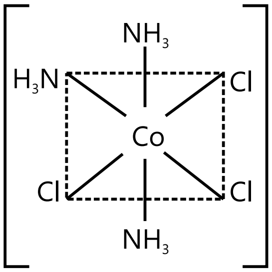
(C) Fac –triaquatrinitrito-N-cobalt (III).

Sol:

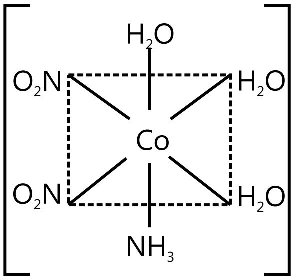
(A)



(B)



(C)



Example 7: Name the type of isomerism exhibited by

the following isomers:

(A) $[Cr(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_4(CN)_2]$ $[Cr(NH_3)_2(CN)_4]$

(B) $[Co(py)_2$ $(H_2O)_3Cl]Cl_2$ and $[Co(py)_2$ $(H_2O)_2Cl_2]$ $Cl{\cdot}H_2O$

(C) [Pt (NH_3)4Br_2] Cl_2 and [Pt $(NH_3)_4Cl_2$] Br_2

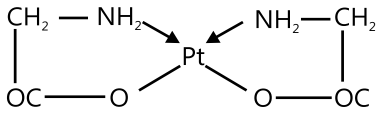
(D) [Co $(NH_3)_5NO_2$] Cl_2 and [Co $(NH_3)_5$ONO] Cl_2

Sol: (A) Coordination isomerism (B) Hydrate isomerism

(C) Ionization isomerism (D) Linkage isomerism

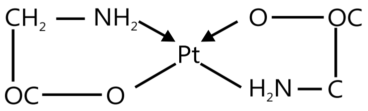
Example 8: Draw the structure of geometrical isomers of [Pt $(gly)_2$] where gly is $NH_2CH_2COO^-$.

Sol:



cis-isomer

and

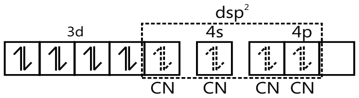


trans-isomer

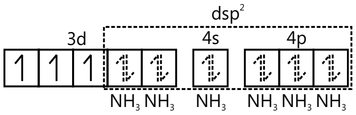
Example 9: $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Why?

Sol: Electronic structure of the two complexes may be written as

[Ni (CN) $_4]^{2-}$:



In $[Cr(NH_3)_6]^{3+}$, all the electrons are paired and hence it is diamagnetic.



Due to presence of three unpaired electrons in $[Ni(CN)_4]^{2-}$, it is paramagnetic.]

Example 10: $[Cu(CN)_4]^{2-}$ is more stable complex than $[Cu(NH_3)_4]^{2+}$. Why?

Sol: The higher stability constant K = 2×10^{27} for $Cu^{2+} + 4CN^- \rightarrow [Cu\ (CN)_4]^{2-}$ than for $[Cu(NH_3)_4]^{2+}$ (which is 4.5×10^{11}) explains stability. Also CN^- is stronger ligand than NH_3.]

JEE Advanced/Boards

Example 1: What is the coordination number of the central metal ions in the following complexes?

(A) $[Cu\ (NH_3)_4]^{2+}$
(B) $[Fe\ (C_2O_4)_3]^{3-}$
(C) $[Pt\ (en)_2Cl_2]$
(D) $[Mo\ (CN)_8]^{4-}$
(E) $[Fe\ (EDTA)]^-$
(F) $[Pd\ (H_2O)_2\ (ONO)_2I_2]$

Sol: (A) NH_3 is a monodentate ligand, Coordination number of Cu^{2+} = 4 × no. of electron pairs accepted = 4 × 1 = 4.

(B) $C_2O_4^{2-}$ is a bidentate ligand, coordination number of Fe^{3+} = 3 × 2 = 6.

(C) 'en' is a bidentate ligand and Cl^- is a monodentate ligand, coordination number of

(D) Mo^{4+} = 8 × 1 = 8.

(E) EDTA is a hexadentate ligand, coordination number of Fe^{3+} = 6 × 1 = 6.

(F) H_2O, ONO and I_2 are monodentate ligands, coordination number of Pd^{4+} = 2 × 1 + 2 × 1 + 2 × 1 = 6.

Example 2: A solution containing 2.665 g of $CrCl_3{\cdot}6H_2O$ is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 2.87 g of AgCl. Deduce the structure of compound.

Sol: Moles of Cl^- ions ionized from moles of $CrCl_3{\cdot}6H_2O$

$$= \frac{2.665}{2.665} = 0.01 \quad \text{Mol. Wt. of } CrCl_3{\cdot}6H_2O = 266.5$$

∴ Moles of AgCl obtained = Moles of Cl^- ionized

$$= \frac{2.87}{143.5} = 0.02$$

Thus, 0.01 mole of complex $CrCl_3{\cdot}6H_2O$ gives 0.02 moles of Cl^- on ionization.

Now, since the coordination number of Cr is 6 and only one Cl ion is attached to Cr by coordination bond or secondary valency, the compound is $[CrCl{\cdot}\ (H_2O)_5]$ $Cl_2{\cdot}H_2O$.

$$[CrCl{\cdot}(H_2O)_5]Cl_2{\cdot}H_2O \longrightarrow [CrCl{\cdot}(H_2O)_5]^{2+} + 2Cl^- + H_2O$$

$$2Cl^- + 2AgNO_3 \longrightarrow 2AgCl + 2NO^-_3$$

Example 3: Two compounds have empirical formula corresponding to $Cr(NH_3)_3(NO_2)_3$. In aqueous solution, one of these is a non-electrolyte while the other conducts electricity. What is the lowest possible formula weight of the conducting reagent? What is the highest possible formula weight for the non-conducting reagent?

Sol: For complex Cr $(NH_3)_3\cdot$ $(NO_2)_3$ $(H_2O)_2$, the two structures can be written as:

$$\underset{A}{\underline{\left[Cr\ (NO_2)_2\cdot\ (NH_3)_3\cdot\ (H_2O)\right]\cdot NO_2\cdot H_2O}}\ \text{and}$$

$$\underset{B}{\underline{\left[Cr\ (NO_2)_3\cdot\ (NH_3)_3\right]\cdot_2 H_2O}}$$

A will be a conducting reagent as it will give two ions on dissolving in water. B will be a non-conducting reagent as it will not be ionized in water.

Example 4: Write the IUPAC name of the compound $[Cr(NH_3)_5(NCS)][ZnCl_4]$. Is this compound colored?

Sol: Pentammineisothicyanatochromium (III) tetrachlorozincate (II). Compound will be colored because Cr (III) has d^3 configuration and so d–d transition is possible.

Example 5: On the basis of valence bond theory explain geometry, nature of hybridization, magnetic property and optical isomerism in:

(i) $[Co\ (Ox)_3]^{3-}$ (ii) $[CoF_6]^{3-}$

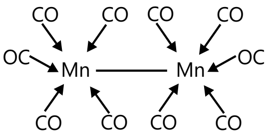
Sol: (i) $[Co\ (Ox)_3]^{3-}$ i.e., trioxalato cobaltate (III) ion has sp^3d^2 hybridization, having octahedral geometry and is paramagnetic in nature due to the presence of 4 unpaired electrons. It has 2 optical isomers.

(ii) $[CoF_6]^{3-}$ i.e., Hexafluoro cobaltate (III) ion has sp^3d^2 hybridization, having octahedral geometry and is paramagnetic in nature due to the presence of 4 unpaired electron. It does not show optical isomerism.

Example 6: The EAN of each Mn (Z = 25) in $Mn_2\ (CO)_{10}$ is 36. What is the structure of this complex?

Sol: EAN = 25 (electrons from Mn atom) + 10 (electrons from five CO ligand) + 1 (electron from Mn—Mn bond) = 36

Thus, structure will be,



Example 7: The magnetic moment of $[MnCl_4]^{2-}$ is 5.92 B.M. On the basis of its magnetic moment, write configuration of Mn^{2+} in this complex.

Sol: For an atom/ion

Magnetic moment (μ) = $\sqrt{n(n+2)}$

(n = No. of unpaired electrons)

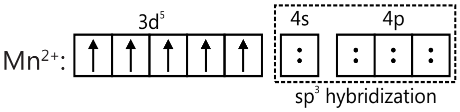
Given that μ = 5.92 B.M.

$\therefore$ $5.92 = \sqrt{n(n+2)}$ n = 5

Thus is this complex Mn contains 5 unpaired electrons and so its possible configuration may be

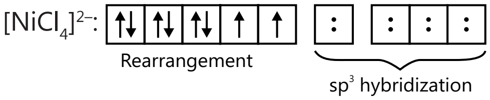
Mn^{2+} in $[MnCl_4]^{2-}$ = [Ar] $3d^5 4s^0$

So hybridization of Mn^{2+} in the given complex must be sp^3.



Example 8: $[Ni\ (CN)_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic, Why?

Sol: In $[Ni\ (CN)_4]^{2-}$ all orbitals are doubly occupied, hence it is diamagnetic whereas in $[NiCl_4)]^{2-}$, two orbitals are singly occupied, hence it is paramagnetic in nature.



Strong field ligands like CN^-, CO, en, NO^{-2} have very strong electron donating tendency, hence electrons of central metal ion pair up against Hund's rule (low spin complex). In $[Ni\ (CO)_4]$, Ni is sp^3 hybridized with no unpaired electron, and hence it is diamagnetic.

Example 9: What is the coordination entity formed when excess of KCN is added to an aqueous solution of $CuSO_4$? Why is that no precipitate of CuS is obtained when $H_2S(g)$ is passed through this solution?

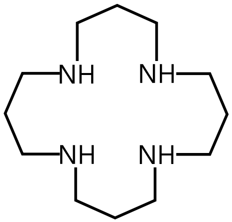
Sol: $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$

$[Cu\ (CN)_4]^{2-}$ is stable complex having

$K = 2 \times 10^{27}$ and so it does not provide sufficient Cu^{2+} ion to give precipitate of CuS.

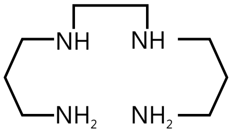
Example 10: What do you understand by macrocyclic effect?

Sol: It is the increased thermodynamic stability of a complex formed with a cyclic polydentate ligand when compared to the complex formed with a noncyclic ligand, e.g. Zn^{2+} complex with (I) is more stable than with (II).



(I) Cyclic

is



(II) Non-cyclic

JEE Main/Boards

Exercise 1

Q.1 Explain the bonding in coordination compounds in terms of Werner's postulates.

Q.2 $FeSO_4$ solution mixed with (NH_4) $2SO_4$ solution in 1: 1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1: 4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

Q.3 How many geometrical isomers are possible in the following coordination entities?

(i) $[Cr\ (C_2O_4)_3]^{3-}$ (ii) $[PtCl_2\ (en)_2]^{2+}$

(iii) $[Cr\ (NH_3)_2Cl_2\ (en)]$

Q.4 Draw the structures of optical isomer of:

(i) $[Cr\ (C_2O_4)_3]^{3-}$ (ii) $[PtCl_2\ (en)_2]^{2+}$

(iii) $[Cr\ (NH_3)_2Cl_2\ (en)]$

Q.5 Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2\ (en)_2]^{+}$ (ii) $[Co\ (NH_3)\ Cl\ (en)_2]^{2+}$

(iii) $[Co\ (NH_3)_2Cl_2\ (en)]$

Q.6 Aqueous copper sulphate solution (blue in color) gives:

(i) A green precipitate with aqueous potassium fluoride and

(ii) A bright green solution with aqueous potassium chloride. Explain these experimental results.

Q.7 What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when H_2S (g) is passed through this solution?

Q.8 $[Cr\ (NH_3)_6]^{3+}$ is paramagnetic while $[Ni\ (CN)_4]^{2-}$ is diamagnetic. Explain why?

Q.9 A solution of $[Ni\ (H_2O)_6]^{2+}$ is green but a solution of $[Ni\ (CN)_4]^{2-}$ is colorless. Explain.

Q.10 $[Fe\ (CN)_6]^{4-}$ and $[Fe\ (H_2O)_6]^{2+}$ are of different colors in dilute solutions. Why?

Q.11 Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes:

(i) $K_3\ [Co\ (C_2O_4)_3]$ (ii) $(NH_4)_2\ [CoF_4]$

(iii) cis- $[Cr\ (en)_2Cl_2]\ Cl$ (iv) $[Mn\ (H_2O)_6]\ SO_4$

Q.12 Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(i) $K\ [Cr\ (H_2O)_2\ (C_2O_4)_2].3H_2O$

(ii) $[Co\ (NH_3)_4Cl]\ Cl_2$

(iii) $CrCl_3\ (py)_3$

(iv) $Cs\ [FeCl_4]$

(v) $K_4\ [Mn\ (CN)_6]$

Q.13 What is meant by the chelate effect? Give an example.

Q.14 Amongst the following ions which one has the highest magnetic moment value?

(i) $[Cr\ (H_2O_6)]^{3+}$ (ii) $[Fe\ (H_2O)_6]^{2+}$

(iii) $[Zn\ (H_2O)_6]^{2+}$

Q.15 What will be the correct order for the wavelengths of absorption in the visible region for the following?

$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

Q.16 Why NH_4^+ ion does not form complexes?

Q.17 Write the formula of the following Complex.

Pentaamminechlorocobalt (III) ion

Exercise 2

Single Correct Choice Type

Q.1 Which of the following compound is not having synergic bonding?

(A) $Fe(CO)_5$ (B) $[Ni(CN)_4]^{2-}$

(C) $[Fe(\pi\text{–}C_5H_5)_2]$ (D) $[CoF_6]^{3-}$

Q.2 Which of the following is a low spin complex?

(A) $Ni(CO)_4$ (B) $[Ni(NH_3)_6]^{2+}$

(C) $[Cu(NH_3)_4]^{2+}$ (D) All of these

Q.3 Which of the following name is incorrect for the given complex. $K[Fe(H_2O)_2(NCS)_3(NO_3)]$

(A) Potassium diaquatrisothiocyanatonitrato ferrate (III)

(B) Potassium diaquanitratotrithiocyanato-N- ferrate (III)

(C) Potassium diaquatrithiocyanato-N-nitrito ferrate (III)

(D) Potassium diaquatrisothiocyanatonitrato ferrate (II)

Q.4 What is the hybridization of Fe in $[Fe(CO)_4]$?

(A) sp_3 (B) dsp^2 (C) sp (D) sp^3d^2

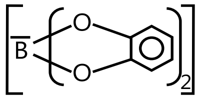
Q.5 Which of the following complex/molecule acts as a reducing agent?

(A) $[Co(NH_3)_6]^{2+}$ (B) $[Mn(CO)_6]$

(C) NO (D) All are acts as a Reducing

Q.6 Which of the following molecule is square planar.

(A) $K_4[Ni(CN)_4]$ (B) $[Be(acac)_2]$

(C) 

(D) $\left[Pd(NH_3)(H_2O)(Br)\ Cl\right]^o$

Q.7 Which type do d-electron configuration exhibit both low and high spin in octahedral complexes?

(A) d^1 (B) d^4 (C) d^3 (D) d^2

Q.8 Transition elements have the maximum tendency to form complexes because

(A) They are metals and all metal form complexes

(B) They contain incompletely filled d-orbitals

(C) Their charge/size ratio is quite large

(D) Both (B) and (C)

Q.9 $[(H_2O)_5Co-\underset{(A)}{O-O}-Co(H_2O)_5]^{4+}$

$$\downarrow$$

$$[(H_2O)_5Co-\underset{(B)}{O-O}-Co(H_2O)_5]^{5+}$$

What will be the bond length of O–O in complex A and B?

(A) A = B (B) A > B (C) B > A (D) None

Q.10 In the complex of [Ma3b3]n±, if two 'a' are replaced by AA type of ligand, then isomer of it, only one isomer of the product will be formed.

(A) Only Fac-isomer

(B) Only Mer-isomer

(C) Fac and Mer-isomer both

(D) None of these

Q.11 What is the hybridization of Fe in sodium thionitroprusside?

(A) sp^3d^2 (B) d^2sp^3

(C) sp^3d (D) No hybridization

Q.12 What is correct name of linkage isomer of $[Cr(H_2O)_5(NO_2)]Br_2$.

(A) Pentaaquanitro-'O' chromium (III) bromide

(B) Pentaaquanitro chromium (III) bromide

(C) Pentaaquonitro chromium (III) bromide

(D) Pentaaquanitrito-'O" chromium (II) bromide

Q.13 The effective atomic number of $Co(CO)_4$ is 35. It does not attain stability by

(A) Oxidation of $[Co(CO)_4]$

(B) Reduction of $[Co(CO)_4]$

(C) Dimerization of $[Co(CO)_4]$

(D) By both (B) and (C)

Q.14 Which one of the following ions is colored?

(A) Sc^{3+} (B) Ti^{4+} (C) Zn^{2+} (D) V^{2+}

Q.15 Which of the following statement is correct.

(A) The name of $[Fe(H_2O)_5NO]SO_4$ is pentaaquanitrosyliron (II) sulphate

(B) $[Co(C_2O_4)_3]^{3-}$ does not have any unpaired electron

(C) E.A.N. of $[Fe(CO)_2(NO)_2]$ is 34

(D) $[SnCl_3]^-$ acts as ligand where the Cl-atom as donor atom.

Q.16 How many stereoisomer are possible for complex $[Co(NH_3)_3Cl_3]$

(A) 1 (B) 2 (C) 3 (D) 4

Q.17 In the volumetric analysis, Mohr's salts is preferred to ferrous sulphate because

(A) It is more readily oxidizable than $FeSO_4$

(B) It is less easily oxidizable than $FeSO_4$

(C) It can undergo both oxidation and reduction

(D) It can be oxidized even in the absence of dilute H_2SO_4.

Q.18 $[RhF_6]^{5-}$ complex ion is a

(A) Outer orbital complex

(B) Inner orbital complex

(C) No outer or no inner orbital complex

(D) None of these

Q.19 Which of the following complex are tetrahedral in shape.

(A) $[FeCl_4]^-$ (B) $[BrF_4]^-$

(C) $[Cu(CN)_4]^{3-}$ (D) $[AuCl_4]^-$

Q.20 How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

(A) 6 (B) 4 (C) 3 (D) 2

Q.21 The oxidation number of cobalt in $K[Co(CO)_4]$ is

(A) +1 (B) +3 (C) –1 (D) –3

Q.22 Amongst the following the most stable complex is

(A) $[Fe(H_2O_6)]^{3+}$ (B) $[Fe(NH_3)_6]^{3+}$

(C) $[Fe(C_2O_4)_3]^{3-}$ (D) $[FeCl_6]^{3-}$

Previous Years' Questions

Q.1 The coordination number of a central metal atom in a complex is determined by ***(2004)***

(A) The number of ligands around a metal ion bonded by sigma and pi-bonds both.

(B) The number around a metal ion bonded by pi-bonds

(C) The number of ligands around a metal ion bonded by sigma bonds

(D) The number of only anionic ligands bonded to the metal ion

Q.2 Among the properties (i) reducing (ii) oxidizing (iii) complexing, the set of properties shown by CN– ion towards metal species is ***(2004)***

(A) iii, i (B) ii, iii (C) i, ii (D) i, ii, iii

Q.3 Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solution. What is the reason for it? ***(2003)***

(A) In acidic solutions hydration protects copper ions

(B) In acidic solutions protons coordinate with ammonia molecules forming NH^{4+} ions and NH3 molecules are not available

(C) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali

(D) Copper hydroxide is an amphoteric substance

Q.4 In the coordination compound, $K_4[Ni(CN)_4]$ oxidation state of nickel is ***(2003)***

(A) –1 (B) 0 (C) +1 (D) +2

Q.5 The coordination number and the oxidation state of the element 'E' in the complex $[E(en)_2(C_2O_4)]NO_2$ (where (en) is ethylene diamine) are, respectively ***(2008)***

(A) 4 and 2 (B) 4 and 3

(C) 6 and 3 (D) 6 and 2

Q.6 Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide ***(2012)***

(A) $[Cr(en)_3]Br_3$ (B) $[Cr(en)_2Br_2]Br$

(C) $[Cr(en)Br_4]^-$ (D) $[Cr(en)Br_2]Br$

Q.7 The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni = 28) ***(2006)***

(A) 2.83 (B) 4.90 (C) 0 (D) 1.73

Q.8 The pair in which both species have same magnetic moment (spin only value) is ***(2006)***

(A) $[Cr(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$ (B) $[Cr(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$

(C) $[Mn(H_2O_6)]^{2+}$, $[Cr(H_2O)_6]^{2+}$ (D) $[CoCl_4]^{2-}$, $[Fe(H_2O)_6]^{2+}$

Q.9 Which of the following has an optical isomer? ***(2009)***

(A) $[Co(NH_3)_3Cl]^+$ (B) $[Co(en)(NH_3)_2]^{2+}$

(C) $[Co(H_2O)_4(en)]^{3+}$ (D) $[Co(en)_2(NH_3)_2]^{3+}$

Q.10 Which of the following pairs represents linkage isomers ? ***(2009)***

(A) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(B) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$

(C) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(D) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

Q.11 Which one of the following has a square planner geometry? ***(2007)***

(A) $[CoCl_4]^{2-}$ (B) $[FeCl_4]^{2-}$ (C) $[NiCl_4]^{2-}$ (D) $[PtCl_4]^{2-}$

Q.12 Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong ***(2011)***

(A) The complex involves d^2sp^3 hybridization and is octahedral in shape

(B) The complex is paramagnetic

(C) The complex is an outer orbital complex

(D) The complex gives white precipitate with silver nitrate solution

Q.13 One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl (s). The structure of the complex is ***(2003)***

(A) $[Co(NH_3)_5Cl]Cl_2$ (B) $[Co(NH_3)_3Cl_3].2NH_3$

(C) $[Co(NH_3)_4Cl_2]Cl.NH_3$ (D) $[Co(NH_3)_4Cl]Cl_2.NH_3$

Q.14 How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with a Ca2+ion ***(2006)***

(A) Six (B) Three (C) One (D) Two

Q.15 In $Fe(CO)_5$, the Fe-C bond possesses ***(2006)***

(A) π-character only (B) Both σ and π characters

(C) Ionic character (D) σ-character only

Q.16 The coordination number and the oxidation state of the element 'E' in the complex $\left[E(en)_2(C_2O_4)\right]NO_2$ (where (en) is ethylene diamine) are respectively, ***(2008)***

(A) 6 and 2 (B) 4 and 2

(C) 4 and 3 (D) 6 and 3

Q.17 Being lesser energy difference between 5f and 6d than 4f and 5d orbitals. In which of the following octahedral complexes of Co (at no. 27), will the magnitude of be the highest? ***(2008)***

(A) $\left[Co(CN)_6\right]^{3-}$ (B) $\left[Co(C_2O_4)_3\right]^{3-}$

(C) $\left[Co(H_2O)_6\right]^{3+}$ (D) $\left[Co(NH_3)_6\right]^{3+}$

Q.18 Which of the following has an optical isomer? ***(2009)***

(A) $\left[Co(NH_3)_3Cl\right]^+$ (B) $\left[Co(en)(NH_3)_2Cl\right]^{2+}$

(C) $\left[Co(H_3O)_4(en)\right]^{3+}$ (D) $\left[Co(en)_2(NH_3)_2\right]^{3+}$

Q.19 Which of the following pairs represents linkage isomers? ***(2009)***

(A) $\left[(Cu(NH_3)_4)\right]\left[PtICl_4\right]$ and $\left[Pt(NH_3)\right]\left[CuCl_4\right]$

(B) $\left[Pd(PPh_3)(NCS)_2\right]$ and $\left[Pd(P\,Ph_2)_2(SCN_2)\right]$

(C) $\left[Co(NH_3)_5NO_3\right]SO_4$ and $\left[Co(NH_3)_5SO_4\right]NO_3$

(D) $\left[PtCl_2(NH_3)_4\right]Be_2$ and $\left[PtBr_2(NH_3)_4\right]Cl_2$

Q.20 A solution containing 2.675 g of $CoCl_3.6\ NH_3$ (molar mass = 267.5 g mol-1) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is (At. Mass of Ag = 108 u) ***(2010)***

(A) $\left[Co(NH_3)_6\right]Cl_3$ (B) $\left[CoCl_2(NH_3)_4\right]Cl$

(C) $\left[CoCl_3(NH_3)_3\right]$ (D) $\left[CoCl(NH_3)_5\right]Cl_2$

Q.21 Which one of the following has an optical isomer? ***(2010)***

(A) $\left[Zn(en)(NH_3)_2\right]^{2+}$ (B) $\left[Co(en)_3\right]^{3+}$

(C) $\left[Co(H_2O)_4(en)\right]^{3+}$ (D) $\left[Zn(en)_2\right]^{2+}$

Q.22 Which of the following facts about the complex $\left[Cr(NH_3)_6\right]Cl_3$ wrong? ***(2011)***

(A) The complex is paramagnetic

(B) The complex is an outer orbital complex

(C) The complex gives white precipitate with silver nitrate solution

(D) The complex involves $d^2\ sp^3$ hybridization and is octahedral in shape.

Q.23 The magnetic moment (spin only) of $\left[NiCl_4\right]^{2-}$ is ***(2011)***

(A) 5.46 BM (B) 2.83 BM (C) 1.41 BM (D) 1.82 BM

Q.24 Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide? ***(2012)***

(A) $\left[Cr(en)_3\right]Br_3$ (B) $\left[Cr(en)_2Br_2\right]Br$

(C) $\left[Cr(en)Br_4\right]^-$ (D) $\left[Cr(en)Br_2\right]Br$

Q.25 Which of the following complex species in not expected to exhibit option isomerism? ***(2013)***

(A) $\left[Co(en)_3\right]^{3+}$ (B) $\left[Co(en)_2Cl_2\right]^+$

(C) $\left[Co(NH_3)_3Cl_3\right]$ (D) $\left[Co(en)_2(NH_3)_2Cl_2\right]^+$

Q.26 The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is ***(2014)***

(A) $L_4 < L_3 < L_2 < L_1$ (B) $L_1 < L_3 < L_2 < L_4$

(C) $L_3 < L_2 < L_4 < L_1$ (D) $L_1 < L_2 < L_3 < L_4$

Q.27 The number of geometric isomers that can exist for square planar $\left[Pt(Cl)(py)(NH_3)(NH_2OH)\right]^+$ is (py = pyridine): ***(2015)***

(A) 2 (B) 3 (C) 4 (D) 6

Q.28 Which of the following compounds is not colored yellow? ***(2015)***

(A) $Zn_2\left[Fe(CN)_6\right]$ (B) $K_3\left[Co(NO_2)_6\right]$

(C) $(NH_4)_3\left[As(Mo_3O_{10})_4\right]$ (D) $BaCrO_4$

Q.29 The pair having the same magnetic moment is:

[At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27] ***(2016)***

(A) $\left[Cr(H_2O)_6\right]^{2+}$ and $\left[Fe(H_2O)_6\right]^{2+}$

(B) $\left[Mn(H_2O)_6\right]^{2+}$ and $\left[Cr(H_2O)_6\right]^{2+}$

(C) $\left[CoCl_4\right]^{2-}$ and $\left[Fe(H_2O)_6\right]^{2+}$

(D) $\left[Cr(H_2O)_6\right]^{2+}$ and $\left[CoCl_4\right]^{2-}$

Q.30 Which one of the following complexes shows optical isomerism? ***(2016)***

(A) cis $\left[Co(en)_2Cl_2\right]Cl$ (B) trans $\left[Co(en)_2Cl_2\right]Cl$

(C) $\left[Co(NH_3)_4Cl_2\right]Cl$ (D) $\left[Co(NH_3)_3Cl_3\right]$

JEE Advanced/Boards

Exercise 1

Q.1 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Q.2 What is meant by unidentate, bidentate and ambidentate ligands? Give two examples for each.

Q.3 (A) What is the basis of formation of spectrochemical series?

(B) Draw the structure of geometrical isomers of the following coordination complexes: $[Co(NH_3)_3Cl_3]$ and $[CoCl_2\ (en)_2]^+$

Q.4 Write all the geometrical isomers of $[Pt\ (NH_3)\ (Br)\ (Cl)\ (py)]$ and how many of these will exhibit optical isomers?

Q.5 What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

Q.6 Draw a sketch to show the splitting of d-orbitals in an octahedral crystal filed. State for a d^5 ion how the actual configuration of the split d-orbitals in an octahedral crystal field is decided by the relative values of D and P.

Q.7 Writ the IUPAC name of $[Co\ (en)_2Cl_2]\ Cl$ and draw the structures of all the isomers with this formula of complex.

Q.8 Draw diagram to show crystal field splitting in a tetrahedral crystal field

Q.9 Discuss briefly giving an example in each case the role of coordination compounds in:

(i) Biological systems

(ii) Medicinal chemistry

(iii) Analytical chemistry and

(iv) Extraction/metallurgy of metals.

Q.10 $NH_2.NH_2$ although possesses two electron pair for donation but not acts as chelating agent. Why?

Q.11 Square planar complexes with co-ordination number four exhibit geometrical isomerism whereas tetrahedral complexes does not. Why?

Q.12 Determine the oxidation state of metal in the complex ion, $[PtCl_6]^{2-}$?

Q.13 The color of Hg_2Cl_2 changes from white to black when treated with NH_3. Why?

Q.14 $[Fe\ (CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic, why?

Q.15 The magnetic moment of $[MnCl_4]^{2-}$ is 5.92 B.M. On the basic of its magnetic moment, write configuration of Mn^{2+} in this complex.

Q.16 List various types of isomerism possible for coordination compounds, giving an example of each.

Q.17 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory.

(A) $[Fe\ (CN)_6]^{4-}$ (B) $[FeF_6]^{3-}$

(C) $[Co\ (C_2O_4)_3]^{3-}$ (D) $[CoF_6]^{3-}$

Q.18 Draw figure to show the splitting of d orbital in an octahedral crystal field.

Q.19 What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

Q.20 What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of d orbital in a coordination entity?

Q.21 Discuss the nature of bonding in metal carbonyls.

Q.22 Specify the oxidation numbers of the metals in the following coordination entities and geometry of these compound?

(i) $[Co\ (H_2O)\ (CN)\ (en)_2]^{2+}$ (ii) $[CoBr_2(en)_2]^+$

(iii) $[PtCl_4]^{2-}$ (iv) $K_3\ [Fe\ (CN)_6]$

(v) $[Cr\ (NH_3)_3Cl_3]$

Q.23 Using IUPAC norms write the formulas for the following and explain all property according to VBT?

(1) Tetrahydroxozincate (II)
(2) Potassium tetrachloridopalladate(II)
(3) Diamminedichloridoplatinum (II)
(4) Potassium tetracyanonickelate (II)
(5) Pentaamminenitrito-O-cobalt (III)
(6) Hexaamminecobalt (III) sulphate
(7) Potassium tri (oxalate) chromate (III)
(8) Hexaammineplatinum (IV)
(9) Tetrabromideocuprate (II)
(10) Pentaamminenitrito-N-cobalt (III)

Q.24 Write the difference between VBT and CFT?

Q.25 Write the formulas for the following coordination compounds:

(i) Tetraaminequachloridocobalt (III) chloride
(ii) Potassium tetrahydroxozincate (II)
(iii) Potassium trioxalatoaluminate (III)
(iv) Dichloridobis (ethane-1, 2-diamine) cobalt (III)
(v) Tetracrabonylnickel (0).

Exercise 2

Single Correct Choice Type

Q.1 Select the correct order of C—O bond order in following complexes.

(A) $[M(CO_3(PCl_3)_2(PMe_3)] > [M(CO)_3(PCl_3)_3] > [M(CO)_3(PCl_3)(PMe_3)_2]$

(B) $[M(CO)_3(PCl_3)_2(PMe_3)_2] > [M(CO)_3(PCl_3)_3] > [M(CO)_3(PCl_3)_2(PMe_3)]$

(C) $[M(CO)_3(PCl_3)(PMe_3)_2] = [M(CO)_3(PCl_3)_3] < [M(CO)_3(PCl_3)_2(PMe_3)]$

(D) $[M(CO)_3(PCl_3)_3] > [M(CO_3(PCl_3)_2(PMe_3)] > [M(CO)_3(PCl_3)(PMe_3)_2]$

Q.2 What is the hybridization of Fe in $[Fe(CO)_4]$?

(A) sp^3 (B) dsp^2 (C) sp (D) sp^3d^2

Q.3 Which of the following complex/molecule acts as a reducing agent.

(A) $[Co(NH_3)_6]^{2+}$ (B) $[Mn(CO)_6]$
(C) NO (D) All act as a reducing agent

Q.4 The effective atomic number of $Co(CO)_4$ is 35. It does not attain stability by

(A) Oxidation of $[Co(CO)_4]$ (B) Reduction of $[Co(CO)_4]$
(C) Dimerization of $[Co(CO)_4]$ (D) By both (B) and (C)

Q.5 In the volumetric analysis, Mohr's salt is preferred to ferrous sulphate because

(A) It is more readily oxidizable than $FeSO_4$
(B) It is less easily oxidizable than $FeSO_4$
(C) It can undergo both oxidation and reduction
(D) It can be oxidized even in the absence of dilute H_2SO_4

Multiple Correct Choice Type

Q.6 Select the correct statement.

(A) CO bond order in bridging carbonyl group is found to be lower than in that terminal carbonyl group in $Fe_2(CO)_9$.
(B) Bond angle in NO_2 < Bond angle in NO_2^-
(C) CO is a σ donor as well as π acceptor ligand.
(D) NO is the only σ donor ligand.

Q.7 Which of the following complex is/are square planar as well as paramagnetic?

(A) $[AuCl_4]^-$ (B) $[CuCl_4]^-$
(C) $[Cu(NH_3)_4]^{2+}$ (D) $[Co(dmg)_2]^{o}$

Q.8 Which one of the following statements is incorrect about transition elements?

(A) The last electron enters in the d-orbital
(B) Their properties are in between those of s-block elements and p-block elements
(C) The transition element with smallest atomic number is scandium
(D) Lanthanum is not a transition element but is a lanthanide.

Q.9 Which of the following type of complex (s) is/are having six number of stereoisomers.

(A) $[MA_2B_2C_2]^{n\pm}$ (B) $[M(AB)A_2BC]^{n\pm}$
(C) $[M(AA)A_2B_2]^{n\pm}$ (D) $[M(AB)A_2B_2]^{n\pm}$

Q.10 Which of the following complex (s) is/are low spin

(A) K_4 [Fe $(CN)_6$] (B) $[PtCl_4]^{2-}$

(C) [Co $(C_2O_4)_3]^{3-}$ (D) [Ni $(NH_3)_6]^{2+}$

Q.11 Which of the following molecules have same number of unpaired electrons.

(A) [Cu $(NH_3)_6]^{2+}$ (B) [Ti $(H_2O)_6]^{3+}$

(C) K4 [Fe $(CN)_6O_2$] (D) [Cr $(NH_3)_6]^{3+}$

Q.12 Which of the following type of complex (s) do/does not produce optically active isomer (s).

(A) $MA_2B_2C_2$ (B) MA_4B_2

(C) MA_3B_2C (D) MA_2B_2CD

Q.13 For which of the complex, the E.A.N. of the central atom of the complex obeys Sidgwick E.A.N. rule.

(A) [Ti $(\sigma\text{–}C_5H_5)_5]_2$ (B) $[Fe(NO)_2(CO)_2]$

(C) $[Ag(CN)_2]^-$ (D)$[Hg(SCN)_4]^{2-}$

Q.14 Identify the ligands can cause the linkage isomerism.

(A) NO_3^- (B) NO_2^- (C) OCN^- (D) $S_2O_3^{2-}$

Assertion Reasoning Type

(A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I.

(B) Statement-I is true, statement-II is true and statement-II is not the correct explanation for statement-I.

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true.

Q.15 Statement-I: $[Cr(NH_3)_6]^{3+}$ has three unpaired electron in t_{2g} orbital

Statement-II: $[Cr(NH_3)_6]^{3+}$ does not show geometrical isomerism.

Q.16 Statement-I: The square planar complex, $[M_{abcd}]^{n+}$ type shows geometrical isomerism.

Statement-II: Restricted rotation around the single bond is present within the above complex.

Comprehension Type

Paragraph 1: Isomerism is a phenomenon where the molecules are having same formula but they have different structures.

Q.17 Which of the following ligand can show linkage isomerism?

(A) NMe_3 (B) $\bar{O}CN$ (C) SO_4^{2-} (D) None of these

Q.18 Which of the following ligand can show linkages isomerism?

(A) It increase the stability of complex.

(B) It increase the strength of metal–ligand bond.

(C) More negative charge on the central atom causes more extent of synergic bonding.

(D) All of these

Q.19 Choose the incorrect statement from the following options.

(A) C_2H_2 can acts as π-acid ligand

(B) $[MA_3B_2C]^{n\pm}$: All isomers are optically inactive.

(C) $[MABCDE_2]^{n\pm}$ complex has total 12 optically active isomer

(D) All statements are incorrect.

Paragraph 2: Metals from complexes with various lewis bases called ligands, more the basic character better is the complex. Electron donating tendency decreases with increase in electronegativity of donor atoms in a period. Higher the bond order of metal ligand bond more is the stability of complex. Geometry and symmetry also influence the stability of complex. More symmetricity of the complex, more is the stability.

Q.20 Little Mohr's salt was dissolved in a water sample containing CO_3^{2-}, Cl^-, CN^- and OH^- in minute amounts. Fe2+ prefers formation of complex with

(A) CO_3^{2-} (B) Cl^- (C) CN^- (D) OH^-

Q.21 Fe^{2+} forms diamagnetic complex with either of CO_3^{2-}, Cl^-, CN^- or OH^-. Geometry of the complex formed is supposed to be

(A) Tetrahedral (B) Triangular bipyramidal

(C) Octahedral (D) Square planar

Q.22 Least stable complex is

(A) Mn $(CO)_5$ (B) K [V $(CO)_5$]

(C) K [Fe $(NC)_6]^{4-}$ (D) [Fe $(NC)_6]^{4-}$

Match the Columns

Q.23

Column I	Column II
(A) Na $[Co(CO)_4]$ Pt	(p) Complex having only monodentate ligand
(B) (Trien) Cl_2	(q) Complex not following Sidgwick EAN rule.
(C) $[Fe(H_2O)_5NO]SO_4$	(r) Complex is having 3 or 5 member of ring within it.
(D) $[Fe(EDTA)]^-$	(s) Complex having positively charged ligand
	(t) Complex having chelating ligand

Q.24

Column I	Column II
(A) $[Co(CO)_4]^-$	(p) E.A.N $\neq 36$
(B) $[Zn(gly)_2]$	(q) Synergic bonding is involved
(C) $[Ag(CN)_2]^-$	(r) Two optically active isomer
	(s) The complex is diamagnetic

Q.25

Column I	Column II
(A) $[M(AA)_3]$	(p) Two pair of enantiomer
(B) $[M(AB)B_2C_2]$	(q) Four geometrical isomer
(C) $[M(AB)_3]$	(r) Two optically inactive isomer
(D) $[MA_3BCD]$	(s) Two optically active isomer
	(t) At least one stereoisomer is planar

Note: $\widehat{AA}$,$\widehat{AB}$, a, b, c, d are not having chiral center.

Q.26

Column I	Column II
(A) Zn $[Fe(CN)_5NO]$	(p) Blue color due to charge transfer
(B) $[Fe(H_2O)_5NO]SO_4$	(q) d^2sp^3 hybridization
(C) $Fe_4[Fe(CN)_6]_3$	(r) Paramagnetic compound
(D) $K_4[Fe(CN)_5O_2]$	(s) NO acts as positive ligand
	(t) Charge transfer metal to metal in complex.

Q.27

Column I	Column II
(A) $[Pt(NH_3)_5Cl]Cl_3$	(p) 229
(B) $[Pt(NH_3)_4Cl_2]Cl_2$	(q) 97
(C) $[Pt(NH_3)_3Cl_3]Cl$	(r) 404
(D) $[Pt(NH_3)_6]Cl_3$	(s) 523

Previous Years' Questions

Q.1 Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by ***(1988)***

(A) $MnSO_4{\cdot}4H_2O$ (B) $CuSO_4{\cdot}5H_2O$

(C) $FeSO_4{\cdot}6H_2O$ (D) $NiSO_4{\cdot}6H_2O$

Q.2 Which of the following is formed when excess of KCN is added to aqueous solution of copper sulphate? ***(1996)***

(A) $Cu(CN)_2$ (B) $K_2[Cu(CN)_4]$

(C) $K[Cu(CN)_2]$ (D) $K_3[Cu(CN)_4]$

Q.3 The complex ion which has no 'd' –electrons in the central metal atom is ***(2001)***

(A) $[MnO_4]^-$ (B) $[Co(NH_3)_6]^{3+}$

(C) $[Fe(CN)_6]^{3-}$ (D) $[Cr(H_2O)_6]^{3+}$

Q.4 The compound having tetrahedral geometry is ***(2004)***

(A) $[Ni(CN)_4]^{2-}$ (B) $[Pd(CN)_4]^{2-}$ (C) $[PdCl_4]^{2-}$ (D) $[NiCl_4]^{2-}$

Q.5 The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is ***(2008)***

(A) Tetrachloronickel (II)-tetraamminenickel (II)

(B) Tetraamminenickel (II)-tetrachloRonickel(II)

(C) Tetraamminenickel (II)-tetrachloronickelate (II)

(D) Tetrachloronickel (II)-tetraamminenickelate (0)

Q.6 Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O, respectively, are ***(2011)***

(A) Octahedral, tetrahedral and square planar

(B) Tetrahedral, square planar and octahedral

(C) Square planar, tetrahedral and octahedral

(D) Octahedral, square planar and octahedral

Q. 7 Among the following metal carbonyls, the C—O bond order is lowest in ***(2007)***

(A) $[Mn(CO)_6]^+$ (B) $[Fe(CO)_5]$ (C) $[Cr(CO)_6]$ (D) $[V(CO)_6]^-$

Q.8 Statement-I: The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.

Statement-II: Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry. ***(2008)***

(A) Statement-I is true, statement-II is true and statement- II is correct explanation for statement-I.

(B) Statement-I is true, statement-II is true and statement-II is not the correct explanation for statement-I.

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true

Q.9 Match the Columns ***(2007)***

Match the complexes in column I with their properties listed in column II.

Column-I	Column-II
(A) $[Co(NH_3)_4(H_2O)_2]Cl_2$	(p) Geometrical isomers
(B) $[Pt(NH_3)_2\,Cl_2]$	(q) Paramagnetic
(C) $[Co(H_2O)_5Cl_2]$	(r) Diamagnetic
(D) $[Ni(H_2O)_6]Cl_2$	(s) Metal ion with+2 oxidation state

Q.10 Total number of geometrical isomers for the complex $[RhCl\,(CO)\,(PPh_3)\,(NH_3)]$ is ***(2010)***

Q.11 The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr\,(H_2O)_5Cl]\,Cl_2$, as silver chloride is close to ......

Q.12 Identify the complexes which are expected to be colored. Explain ***(1994)***

(i) $[Ti\,(NO_3)_4]$ (ii) $[Cu\,(NCCH_3)] + BF_4$

(iii) $[Cr\,(NH_3)_6]\,Cl_3$ (iv) $K_3\,[VF_6]$

Q.13 Draw the structures of $[Co\,(NH_3)_6]^{3+}$, $[Ni\,(CN)_4]^{2-}$ and $[Ni\,(CO)_4]$. Write the hybridization of atomic orbitals of the transition metal in each case. ***(2000)***

Q.14 Write the IUPAC name of the compound $K_2\,[Cr\,(NO)(CN)_4(NH_3)]$. Spin magnetic moment of the complex $\mu = 1.73$ BM. Give the structure of anion. ***(2003)***

Q.15 $NiCl_2$ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH, giving a bright red color. ***(2004)***

(A) Draw its structure and show H-bonding

(B) Give oxidation state of Ni and its hybridization

(C) Predict whether it is paramagnetic or diamagnetic

Q.16 Statement-I: $\left[Fe\left(H_2O\right)_5NO\right]SO_4$ is paramagnetic

Statement-II: The Fe in $\left[Fe\left(H_2O\right)_5NO\right]SO_4$ has three unpaired electrons. ***(2008)***

(A) Statement-I is true, statement-II is true; statement-II is correct explanation for statement-I

(B) Statement-I is true, statement-II is true; statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, statement-II is false

(D) Statement-I is false, statement-II is true

Q.17 As per IUPAC nomenclature, the name of the complex is $\left[Co\left(H_2O\right)_4\left(NH_3\right)_2Cl_3\right]$ ***(2012)***

(A) Tetraaquadiaminecobalt (III) chloride

(B) Tetraaquadiamminecobalt (III) chloride

(C) Diaminetetraaquacobalt (III) chloride

(D) Diamminetetraaquacobalt (III) chloride

Q.18 Consider the following complex ions, P, Q and R

$$P = \left[FeF_6\right]^{3-}, Q = \left[V\left(H_2O\right)_6\right]^{2+} \text{ and } R = \left[Fe\left(H_2O\right)_6\right]^{2+}$$

The correct order of the complex ions, according to their spin–only magnetic moment values (in B.M.) is ***(2013)***

(A) R < Q < P (B) Q < R < P

(C) R < P < Q (D) Q < P < R

Q.19 The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) ***(2013)***

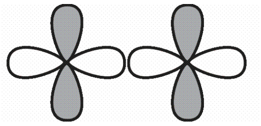
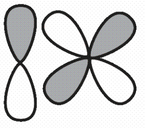
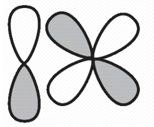
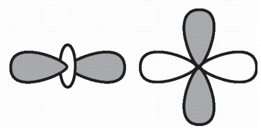
(A) $\left[Cr\left(NH_3\right)_5Cl\right]Cl_2$ and $\left[Cr\left(NH_3\right)_4Cl\right]Cl$

(B) $\left[Co\left(NH_3\right)_4Cl_2\right]^+$ and $\left[Pt\left(NH_3\right)_2\left(H_2O\right)Cl\right]^+$

(C) $\left[CoBr_2Cl_2\right]^{2-}$ and $\left[PtBr_2Cl_2\right]^{2-}$

(D) $\left[Pt\left(NH_3\right)_3\left(NO_3\right)\right]Cl$ and $\left[Pt\left(NH_3\right)_3Cl\right]Br$

Q.20 Match the orbital overlap figures shown in list-I with the description given in list-II and select the correct answer using the code given below the lists. ***(2014)***

List-I	List-II
(A) 	(p) $p-d\pi$ anticoding
(B) 	(q) $d-d\sigma$ bonding
(C) 	(r) $p-d\pi$ bonding
(D) 	(s) $d-d\sigma$

Code:

	p	Q	r	Ss
(A)	2	1	3	4
(B)	4	3	1	2
(C)	2	3	1	4
(D)	4	1	3	2

Q.21 For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (When approximated to the nearest integer) is

[Atomic number of Fe = 26] ***(2015)***

Q.22 Among the complex ions,

$$\left[Co\left(NH_2-CH_2-CH_2-NH_2\right)Cl_2\right]^+,\left[CrI_2\left(C_2O_4\right)_2\right]^{3-},$$

$$\left[Fe\left(H_2O\right)_4\left(OH\right)_2\right]^+,\left[Fe\left(NH_3\left(CN_4\right)\right)\right]^{-.}$$

$$\left[Co\left(NH_2-CH_2-CH_2-NH_2\right)Cl\right]^{2+}$$

and $\left[Co\left(NH_3\right)_4\left(H_2O\right)Cl_2\right]^{2+}$

the number of complex ion(s) that show(s) cis-trans isomerism is ***(2015)***

Q.23 In the complex acetylbromidodicarbonylbis (triethylphosphine) iron(II), the number of Fe–C bond(s) is ***(2015)***

Q.24 Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4\ Cl_2]Cl$, $Na_3[CoFe_6]$, Na_2O_2 and CsO_2 the total number of paramagnetic is ***(2016)***

(A) 2 (B) 3 (C) 4 (D) 5

Q.25 The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$) is ***(2016)***

Q.26 The geometries of the ammonia complexes of respectively, are ***(2016)***

(A) Octahedral, square planar and tetrahedral

(B) Square planar, octahedral and tetrahedral

(C) Tetrahedral, square planar and octahedral

(D) Octahedral, tetrahedral and square planar

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.2 Q.5 Q.12

Exercise 2

Q.6 Q.8 Q.13
Q.18 Q.22

Previous Years' Questions

Q.2 Q.5 Q.8
Q.10 Q.11 Q.14

JEE Advanced/Boards

Exercise 1

Q.6 Q.13 Q.19
Q.23 (iii, v, vii, ix) Q.25

Exercise 2

Q.4 Q.11 Q.15
Q.18 Q.29

Previous Years' Questions

Q.1 Q.6 Q.12

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 D **Q.2** D **Q.3** D **Q.4** B **Q.5** D **Q.6** D **Q.7** B
Q.8 D **Q.9** B **Q.10** C **Q.11** B **Q.12** A **Q.13** B **Q.14** D
Q.15 B **Q.16** B **Q.17** B **Q.18** B **Q.19** A **Q.20** C **Q.21** C
Q.22 C

Previous Years’ Questions

Q.1 C **Q.2** A **Q.3** B **Q.4** B **Q.5** C **Q. 6** B **Q.7** A
Q.8 B **Q.9** D **Q.10** B **Q.11** D **Q.12** C **Q.13** A **Q.14** C
Q.15 B **Q.16** D **Q.17** A **Q.18** D **Q.19** B **Q.20** A **Q.21** B
Q.22 B **Q.23** B **Q.24** B **Q.25** C **Q.26** B **Q.27** B **Q.28** A
Q.29 A **Q.30** A

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 D **Q.2** B **Q.3** D **Q.4** A **Q.5** B

Multiple Correct Choice Type

Q. 6 A, C **Q.7** C, D **Q.8** C, D **Q.9** A, D **Q.10** A, B, C **Q.11** A, B, C
Q.12 A, B, C, D **Q.13** A, C, D **Q.14** B, C, D

Assertion Reasoning Type

Q.15 B **Q.16** C

Comprehension Type

Paragraph 1: Q.17 B **Q.18** D **Q.19** C **Paragraph 2: Q.20** C **Q.21** C **Q.22** B

Match the Colulmns

Q.23 A → p; B → q, r, t; C → p, q, s; D → q, r, t

Q.24 A → q, s; B → r, s; C → p, q, s

Q.25 A → s; B → p, q, r; C → p; D → q, s

Q.26 A → q, s; B → r, s; C → p, q, r, t; D → q, r

Q.27 A → r; B → p; C → q; D → s

Previous Years' Questions

Q.1 B **Q.2** D **Q.3** A **Q.4** D **Q.5** C **Q.6** B **Q.7** B

Q.8 B **Q.9** A → p, q; B → p, r; C → q; D → q, s **Q.10** 3 **Q.11** 6 mL **Q.12** (iii) (iv)

Q.16 A → p, q, s; B → p, r, s; C → q, s; D → q, s **Q.17** B **Q.18** C **Q.19** B

Q.20 A **Q.21** D **Q.22** 5 **Q.23** D **Q.24** B **Q.25** 5 **Q.26** A

Solutions

JEE Main/Boards

Exercise 1

Sol 1: According to Werner Metal show two types of linkages /valences namely primary and secondary. Primary are ionisable and exhibit negative charge. Secondary are non-ionisable. Secondary valency is the coordination no. of central metal atom and is fixed.

Sol 2: 1: 1 ratio, $FeSO_4.(NH_2)_2SO_4$ is a double salt. So, we can detect all the ions.

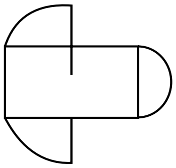
In 2nd case, we get $[Cu(NH_3)_4]^{2+}$, so we cannot get positive test for Cu^{2+}

Sol 3: (i) $[Cr(C_2O_4)_3]^{3-}$ doesn't exhibit geometric isomerism.

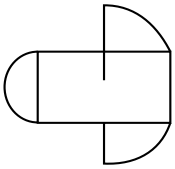
(ii) $[PtCl_2(en)_2]^{2+}$ has 2 geometrical isomers.

(iii) $[Cr(NH_3)_2\ Cl_2(en)]$ has 2 geometrical isomers.

Sol 4: (i)

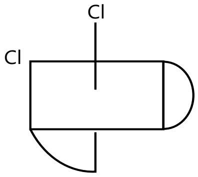


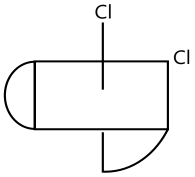
Leavo



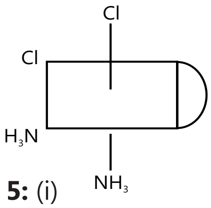
Dextro

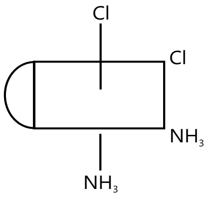
(ii)



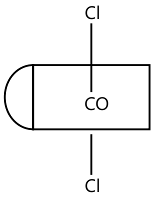


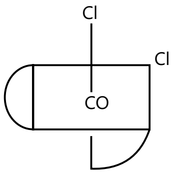
(iii)

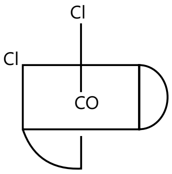




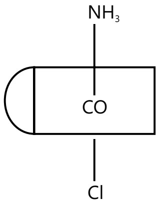
Sol 5: (i)

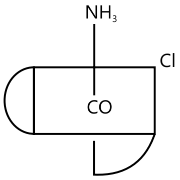


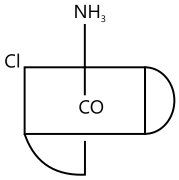




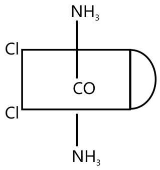
(ii)

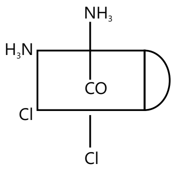


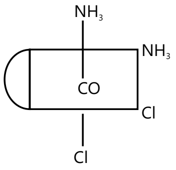




(iii)





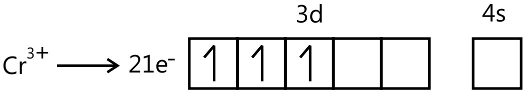


Sol 6: (i) We get a precipitate of CuF_2.

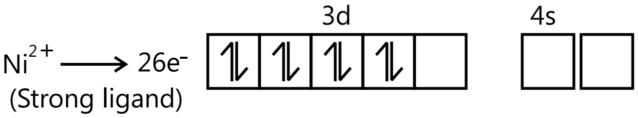
(ii) We get a complex $K_2[CuCl_4]$.

Sol 7: $K_3[Cu(CN)_4]$ is formed. No precipitate is obtained because of the lack of Cu^{2+} ions in the solutions. All the copper is in complex form.

Sol 8:



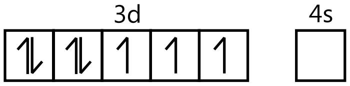
3 unpaired e^- which do not pair up after hybridisation as is a weak field ligand.



Present even after hybridisation as CN^- is a strong field ligand.

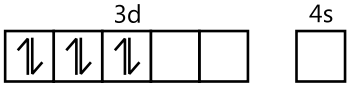
Sol 9: Ni^{2+} is present in both cases but H_2O is present weak ligand

∴ Configuration in 1st Case



2 unpaired e⁻

Configuration in 2nd Case

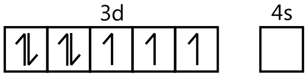


no unpaired e⁻

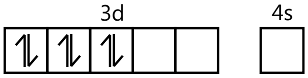
Due to presence of unpaired e⁻ $[Ni(H_2O)_6]^{2+}$ is coloured

Sol 10: Both the complexes have Fe^{2+} as the central metal ion, but H_2O is weak ligand, CN^- is strong ligand.

$[Fe(H_2O)_6]^{2+}$



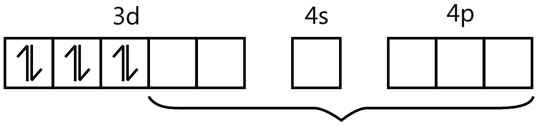
$[Fe(CN)_6]^{4-}$



Hence, no. of unpaired e$^\ominus$ are different in both cases which results in different colours in dilute solutions.

Sol 11: (i) $K_3[Co(C_2O_4)_3]$

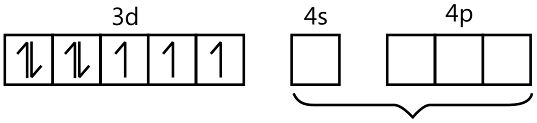
Co ⟶ +3



Co.no=6

(ii) $[CoF_4]^{2-}$

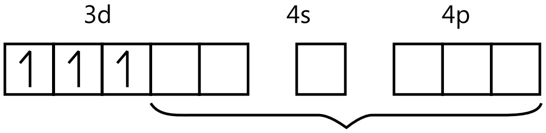
Co ⟶ +2



Co.no=4

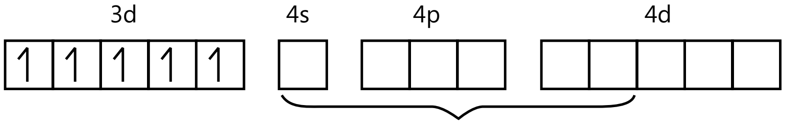
(iii) Cis $[Cr(en)_2Cl_2]Cl$

Cr ⟶ +3



Co.no=6

(iv) Mn ⟶ 2+

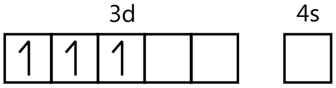


Co.no=6

Sol 12: (i)$K[Cr(H_2O)_2(C_2O_4)_2]\cdot 3H_2O$

Potassium diaquadioxalateochromate (III) Trihydrate

Cr ⟶ +3 Co. No. = 6



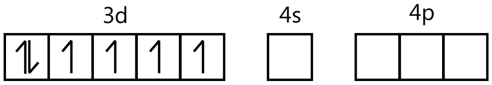
It shows geometric, optical isomerism

MM = $\sqrt{3(5)} = \sqrt{15}$ BM [$\because$ MM = $\sqrt{n(n+2)}$ BM] where n is no. of unpaired e$^-$

(ii) $[Co(NH_3)_4Cl]Cl_2$

Tetraammine chloro Cobalt (III) Chloride

Co $\longrightarrow$ +3 co. = 5



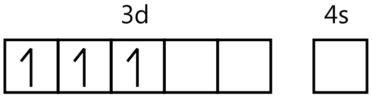
No stereo isomerism

MM = $\sqrt{4(6)} = \sqrt{24}$ BM

(iii) $CrCl_3(py)_3$

Trichloro Tripyridinium Chromium (III)

Cr $\longrightarrow$ +3 Co. No. = 6

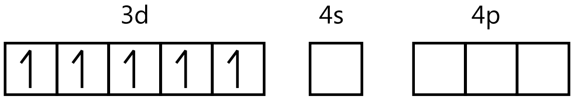


Shows geometric isomerism

MM = $\sqrt{3(5)} = \sqrt{15}$ BM

(iv) $Cs(FeCl_4)$ → Caesium Tetrachloro Ferrate (III)

Fe $\longrightarrow$ +3 Co. No. = 4

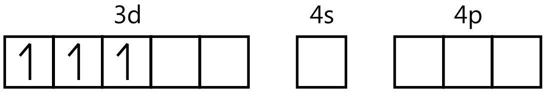


No. isomerism, MM = $\sqrt{5(7)} = \sqrt{35}$ BM

(v) $K_4[Mn(CN)_6]$

Potassium Hexacyano Maganate (II)

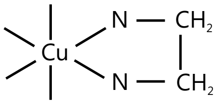
Mn $\longrightarrow$ +2, Co. No. = 6



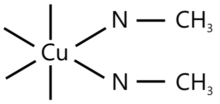
No Isomerism, MM = $\sqrt{(5)7}$ BM= $\sqrt{35}$BM

Sol 13: Chelation describes a particular way that ions and molecules bind metal ions. Chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate ligand and a metal atom.

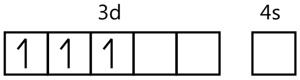
Chelate effect describes the enhanced affinity of chelating ligands for a metal ion compared to the affinity of collection of similar non-chelating ligands for same metal.



is stable than

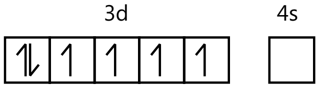


Sol 14: (i) $[Cr(H_2O)_6]^{3+}$, H_2O is weak ligand.



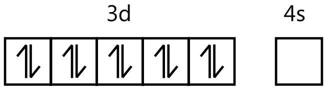
3 unpaired e$^-$ i.e. n = 3

(ii) $[Fe(H_2O)_6]^{2+}$, H_2O is weak ligand



3 unpaired e^- i.e. n = 4

(iii) $[Zn(H_2O)_6]^{2+}$, H_2O is weak ligand



No unpaired e^- i.e. n = 0

(ii) Has highest magnetic moment as it has highest no. of unpaired e^-

Sol 15: Strength of ligands $\longrightarrow$ $NO_2^- > NH_3 > H_2O$

$\therefore$ Wavelength of $[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$

Sol 16: NH_4^+ cannot form complexes due to lack of lone pair

Sol 17: $[Co(NH_3)_5Cl]^{2+}$

Exercise 2

Single Correct Choice Type

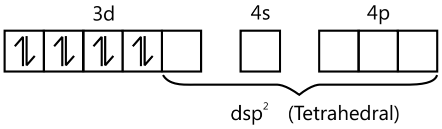
Sol 1: (D) $[CoF_6]^{3-}$ doesn't have synergic bonding due to lack of empty orbitals in F^-.

Sol 2: (D) CO, NH_3 are strong ligands. So all are low spin complexes

Sol 3: (D) $K[Fe(H_2O)_2(NCS)_3NO_3]$

Potassium di aqua-tri-isothiocynato-nitrato Ferrate (III)

Sol 4: (B) Fe $\longrightarrow$ 26



CO is a strong ligand. Pairing takes place.

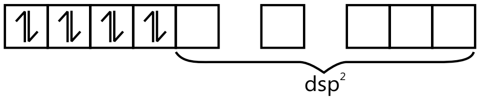
Sol 5: (D) NO $\longrightarrow$ NO^+, Co^{2+} $\longrightarrow$ Co^{3+} (Stable)

Mn^+ can form stable complex with strong ligand CO.

So, all are reducing agents

Sol 6: (D) Ni $\longrightarrow$ O (zero), dsp^2 hybridisation is not possible.

Pd^{2+} $\longrightarrow$ Square planar

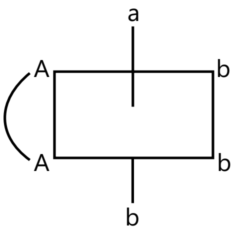


Sol 7: d^4, d^5, d^6, d^7

Sol 8: (D) Reasons are vacant d-orbitals and that their charge to size ratio is large but not that they are metals

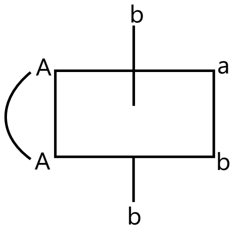
Sol 9: (B) In (A) charge is +4, so there is more donation in (A) from Co to O. So B.O. in A is low. So, bond length is A is higher.

Sol 10: (C)



Only 1 Isomer

Facial



Only 1 Isomer

Meridional

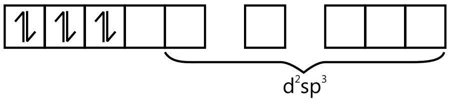
Sol 11: (B) It has 5 CN^- ligands (strong) Fe^{2+}, pairing takes place. So, d^2sp^3

Sol 12: (A) IUPAC of $[Cr(H_2O)_5ONO]Br_2$ Penta-aquo-nitrito-O chromium(III) Bromide

Sol 13: (B) By reduction or dimension, it can attain EAN of 36. So, oxidation doesn't lead to stability.

Sol 14: (D) V^{2+} because of presence of unpaired e^-. Rest all have no unpaired e^-.

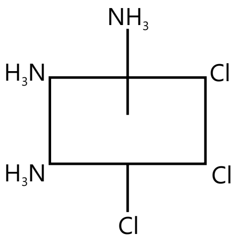
Sol 15: (B) Co^{3+} $\longrightarrow$ 24



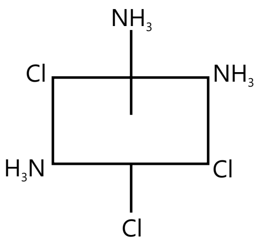
So, (b) is correct . In (a) Not exists as NO^+

In $[Fe(CO)_2(NO)_2]$, EAN = 36 (Since not exists as NO^+)

Sol 16: (B)



Facial



Meridional

Both have plane of symmetries

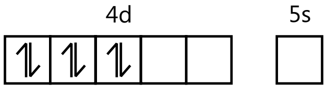
So, no optical isomer.

Stereo -2

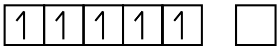
Sol 17: (B) Mohr's salt has very high mol wt but same reducing points. So, its less readily oxidizable than $FeSO_4$ and error in calculations decrease.

Sol 18: (B) $[RhF_6]^{3-} \longrightarrow Rh^{3+}$

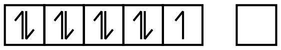
It's low spin inner orbital complex



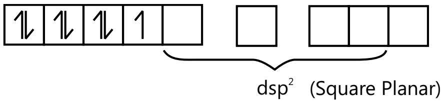
Sol19: (A) Fe^{3+}, weak Tetrahedral



$[Cu(CN)_4]^{3-} Cu^+$



$[AuCl_4]^- Au^{3+}$



Sol 20: (C) $[Co(NH_3)_6]Cl_2$

3 ions i.e. $[Co(NH_3)_6]^{2+}$, $2Cl^-$

Sol 21: (C) $K[Co(CO)_4]$

CO → Neutral

$K \rightarrow +1 \quad \Rightarrow Co \rightarrow -1$

Sol 22: (C) $[Fe(C_2O_4)_3]^{3-}$ is most stable because of chelate effect

Previous Years' Questions

Sol 1: (C) The number of atoms of the ligand that are directly bonded to the central metal atom or ion by coordinate bond is known as the coordination number of the metal atom or ion coordination number of metal = number of σ bonds formed by metal with ligand.

Sol 2: (A) CN^- ions acts both as reducing agent as well as good complexion agent.

Sol 4: (B) $+ 1 \times 4 + x - 1 \times 4 = 0$

$4 + x - 4 = 0 \Rightarrow x = 0$ for Ni.

Sol 5: (C) C.N. of E in complex is 6 and oxidation state is

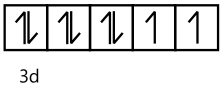
$x + 0 - 2 - 1 = 0 ; x = 3$

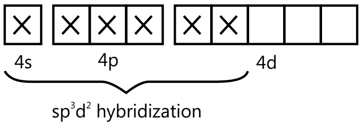
Sol 6: (B) $[Cr(en)_2Br_2]Br$

Dibromidobis (ethylenediamine) chromium (III) Bromide.

Sol 7: (A) Ni^{2+} in aqueous solution means $[Ni(H_2O)_6]^{2+}$. The electronic configuration of

Ni^{2+}(aq) :





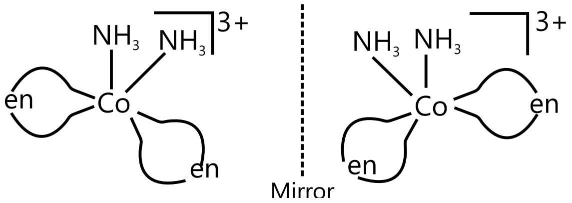
Total number of unpaired electron = 2

$\therefore$ Spin only magnetic moment of Ni^{2+} = $\sqrt{2(2+2)}$

= $2\sqrt{2}$ = 2.83 B.M.

Sol 8: (B) both have 4 unpaired electron.

Sol 9: (D) cis-form $[Co(en)_2(NH_3)_2]^{3+}$ has optical isomers.

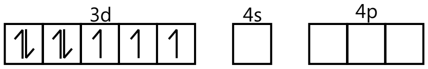


Sol 10: (B) SCN– ion can coordinate through the sulphur or nitrogen atom. Such possibilities give rise to linkage isomerism in coordination compounds.

M ← SCN Thiocyanato or thiocyanato-S

M ← NCS Isothiocyanato or thiocyanato-N

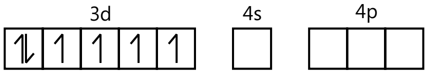
Sol 11: (D) ${}_{27}Co^{2+}$ – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^0$



As Cl^- is weak field ligand so no pairing up.

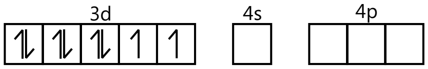
Hence it is sp^3 hybridized giving tetrahedral geometry.

Fe^{2+} – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^0$



Due to Cl^-, back pairing is not observed so it will be sp^3 hybridized giving tetrahedral geometry.

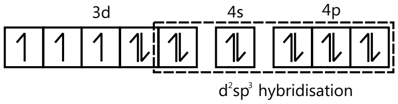
Ni^{2+} – $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^0$



Because of weak ligand, back pairing is not observed so it will be sp^3 i.e. tetrahedral geometry. All the complexes of Pt^{2+} are square planner including those with weak field ligand such as halide ions thus (d) is correct.

Sol 12: (C) In case of d^3 configuration, the number of unpaired electrons remains 3 whether the ligand is strong field or weak field. The hybridization scheme can be shown as follow

$[Cr(NH_3)_3]^{3+}$ =



Hence, the complex is inner orbital complex as it involves (n – 1)d orbitals for hybridization, 3.93 = $\sqrt{n(n+2)}$; so n = 3 (here n is number of unpaired electron(s)).

Sol 13: (A) $2Cl^-$ ions are ionizable

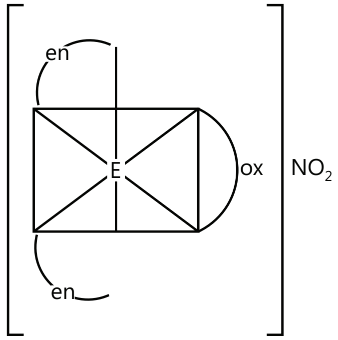
$$\therefore\ [Co(NH_3)_5Cl]Cl_2 \rightleftharpoons \underbrace{[Co(NH_3)_5Cl]^{2+}+2Cl^-}_{3\text{ ion}}$$

$2Cl^- + 2AgNO_3 \rightarrow 2AgCl + 2NO_3^-$.

Sol 14: (C) As EDTA is an Hexadentate Ligand, only one molecule of EDTA will be required to form an octahedral complex with a Ca^{2+} ion.

Sol 15: (B) There is dπ-pπ metal to ligand back bonding in Fe-C bond of the organometallic compound $Fe(CO)_5$. So it possesses both σ and π characters.

Sol 16: (D)



Coordination no = 6 and Oxidation no = 3

Sol 17: (A) CN^- is stronger ligand hence Δ_o is highest.

Sol 18: (D) It is octahedral complex of the type $[M(AA)_2x_2]$ Where AA is bidentate ligand.

Sol 19: (B) NSC^- is ambidentate ligand and it can be linked through N (or) S

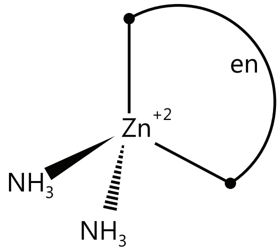
Sol 20: (A) $CoCl_3.6NH_3 \rightarrow xCl^- \xrightarrow{AgNO_3} x\ AgCl\downarrow$

$$n(AgCl) = x\ n(CoCl_3.6NH_3)$$

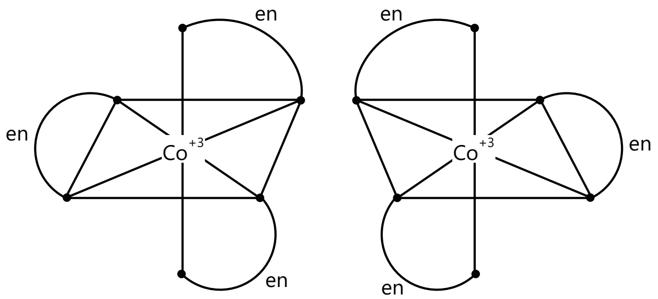
$$\frac{4.78}{143.5} = x\frac{2.675}{267.5} \qquad \therefore x = 3$$

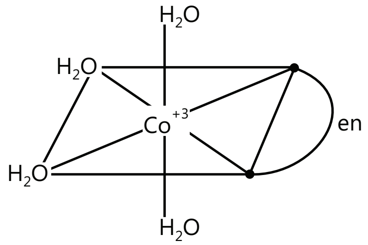
$\therefore$ The complex is $[Co(NH_3)_6]Cl_3$

Sol 21: (B) Only option (B) is having non-super imposable mirror image & hence one optical isomer.

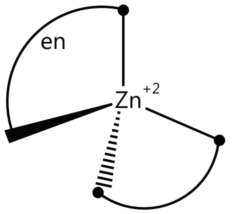


No optical isomer. It is
Tetrahedral with a plane of symmetry





Horizontal plane is plane symmetry



No optical isomer it is
tetrahedral with a plane of symmetry

Sol 22: (B) $\left[Cr\left(NH_3\right)_6\right]Cl_3$ involves $d^2\,sp^3$ hybridization and it is an inner orbital complex.

Sol 23: (B) In $\left[NiCl_4\right]^{2-}$, n = 2

$$\mu = \sqrt{n\left(n+2\right)}\text{ BM}$$

$$= \sqrt{2\left(2+2\right)} = 2.82\text{ BM}$$

Sol 24: (B) $\left[Cr\left(en\right)_2Br_2\right]Br$ - dibromido bis (ethylene diamine)chromium(III) bromide

Sol 25: (C) $\left[Co\left(NH_3\right)_3Cl_3\right]$ show facial as well as meridional isomerism. But both contain plane of symmetry. So, the answer is (C).

Sol 26: (B) The energy of red light is less than that of violet light.

So energy order is

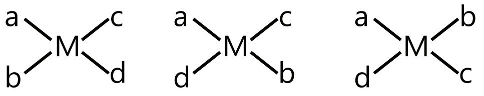
Red < Yellow < Green < Blue

The complex absorbs lower energy light lower will be its strength. So order of ligand strength is $L_1 < L_3 < L_2 < L_4$

Sol 27: (B) The complex is of the type [Mabcd]

M = metal

a, b, c, d = Monodentate ligands.



3 geometrical isomers

Sol 28: (A) $Zn_2\left[Fe\left(CN\right)_6\right]$ is white.

Sol 29: (A) Each $\left[Cr\left(H_2O\right)_6\right]^{2+}$ and $\left[Fe\left(H_2O\right)_6\right]^{2+}$

Contain 4 unpaired electron.

Sol 30: (A) With coordination number six, if two bidentate ligands in cis-position are present, then it is optically active.

JEE Advanced/Boards

Exercise 1

Sol 1: $[Co(NH)_3Cl_3] \longrightarrow$ Coordination entity

NH_3, Cl → ligand

Co. no = 6

Polyhedron ⟶ octahedral, different ligands so heteroleptic

$[Cr(C_2O_4)_3]^{3-}$

$CO_4^{2-} \rightarrow$ ligand

Co. no = 6

Octahedral and homoleptic

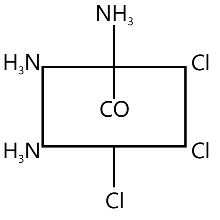
Sol 2: Unidentate → ligand with single e^- donor, ex. H_2O, NH_3

Bidentate → ligand with two e^- donor atoms, ex. $C_2O_4^{2-}$, en

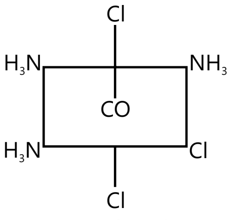
Ambidentate → ligand with more than $1e^-$ donor atom but both cannot donate pair at the same time.

Sol 3: (A) The main basis of the spectrochemical series is the energy difference in the orbitals of the control metal atom after coming close to the ligands. More is the Δ_0, stronger is ligand.

(B)

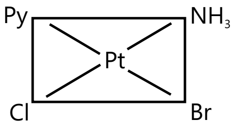


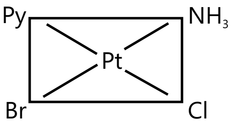
Facial

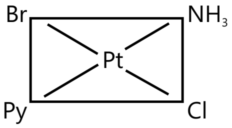


Meridional

Sol 4:







No one shows opitcal isomers as all of these are planare and have plane of symmetry.

Sol 5: Stability of a complex in solution refers to the degree of association between the species involved in the state of equilibrium.

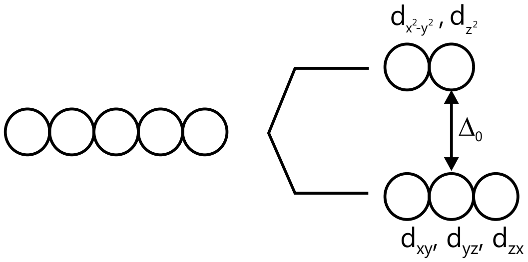
Ex. M + 4L $\Leftrightarrow$ ML4

$$\beta = \frac{[ML_4]}{[M]\,[L]^4}$$

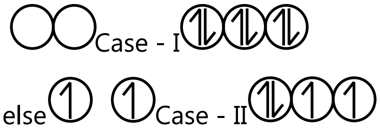
Their stability depends on

- Chelate effect
- Macrocyclic effect
- Geometric factors (like shape)
- Charge of metal ions
- Ionic radius

Sol 6:

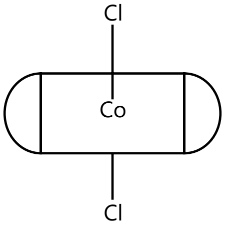


If energy released while pairing is higher than D. We get.



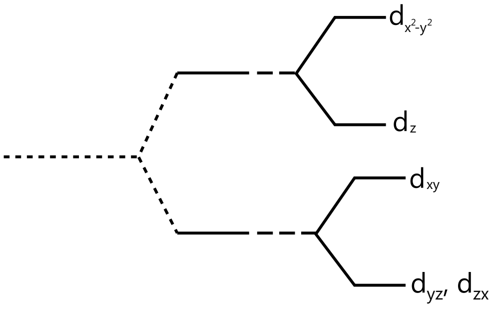
Sol 7: $[Co(en)_2Cl_2]Cl$

Dichloro Bisethylene Diamine Cobalt (III) Chloride



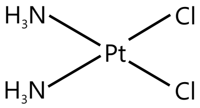
dl-pair

Sol 8:



Sol 9: (i) Enzymes

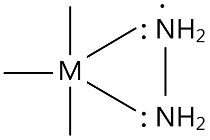
(ii) Ex. Cisplatin



(iii) For determining the presence of certain ions using complexing ligands

(iv) Au, Ag Complexes Ex. $[Au(CN)_2]^-$

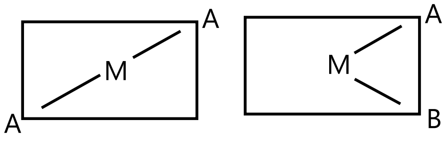
Sol 10: If it acts as a chelating agent



There is a formation of 3-membered ring. It's unstable because of high steric hindrance.

Sol 11: Square planar exhibit geometric isomerism because of possibility of 2 different locations from a single location.

E.g.



It's not possible in Tetrahedral. So, it can't show geometric isomerism

Sol 12: Let pt 0.5 be x

$x + (-6) = -2 \Rightarrow x = 4$

Pt → +4

Sol 13: In Hg_2Cl_2, $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$

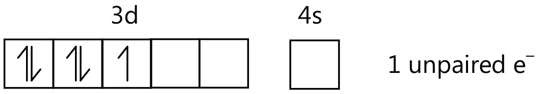
$$HgCl_2 + 2NH_3 \longrightarrow [Hg(NH_3)_2Cl_2]$$

$$\downarrow$$

$$[Hg(NH_2)Cl]\downarrow + NH_4Cl$$

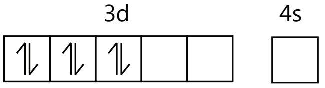
The liberated mercury renders this precipitate black

Sol 14: $[Fe(CN)_6]^{3-} \longrightarrow Fe^{3+}$



1 unpaired e$^-$

$[Fe(CN)_6]^{4-} \longrightarrow Fe^{2+}$

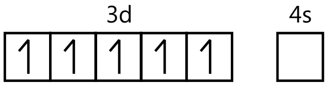


No unpaired e$^-$

Sol 15: $\sqrt{n(n+2)} = 5.92 \Rightarrow n = 5$

i.e. There are 5 unpaired e$^-$

$\therefore Mn^{2+} \longrightarrow$



Sol 16: Structural Isomerism

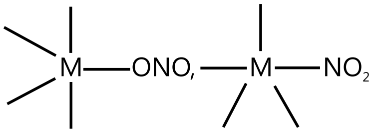
→ Ionisation Isomerism

$[Co(NH_3)_4Br_2]SO_4[Co(NH_3)SO_4]Br_2$

→ Hydrate Isomerism

$[Cr(H_2O)_6]Cl_3$ $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

→ Linkage Isomerism

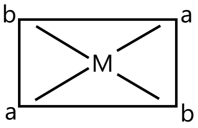


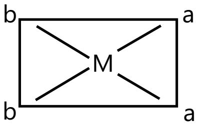
→ Coordination Isomerism

$[Co(NH_3)_6]$ $[Cr(CN)_6]$, $[CO(CN)_6]$ $[Cr(NH_3)_6]$

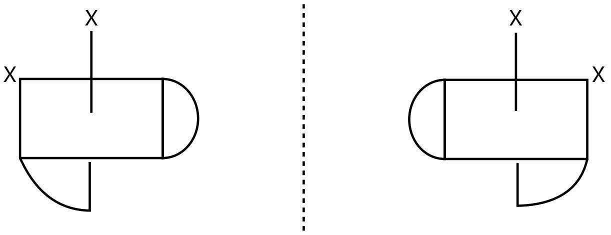
Stereo Isomerism

→ Geometrical Isomerism



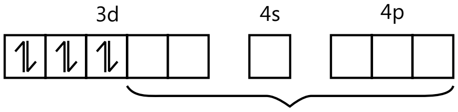


→ Optical Isomerism

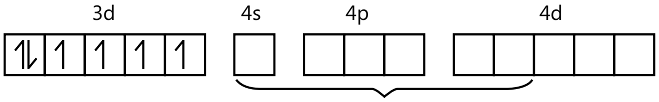


Sol 17: All the bonds between and ligand are coordinate covalent bonds.

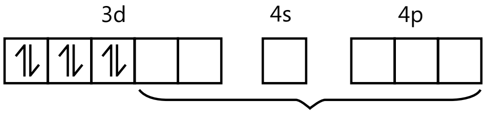
(i) $[Fe(CN)_6]^{4-} \longrightarrow Fe^{2+}$, strong ligand



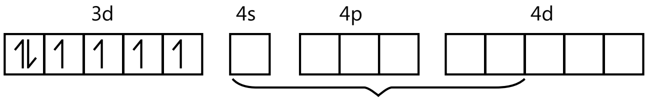
(ii) $[FeF_6]^{4-} \longrightarrow Fe^{2+}$, weak ligand



(iii) $[Co(C_2O_4)_3]^{3-} \longrightarrow Co^{3+}$, strong



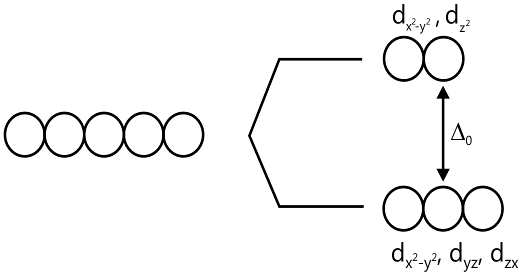
(iv) $[CoF_6]^{3-} \longrightarrow Co^{3+}$, weak



(i), (iii) → d^2sp^3

(ii), (iv) → sp^3d^2

Sol 18:



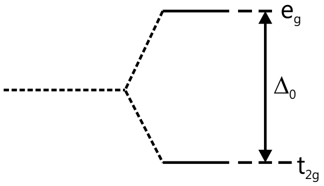
Sol 19: Spectrochemical series is a series depicting the strength of the ligands during complex formation.

Weak field ligand create small Δ_o (energy difference b/w newly formed orbitals) compared to strong field ligands.

So, pairing is not preferred against weak ligands

Sol 20: It's the energy difference between the new formed orbitals in the field of a ligand.

If Δ_o is high pairing is preferable

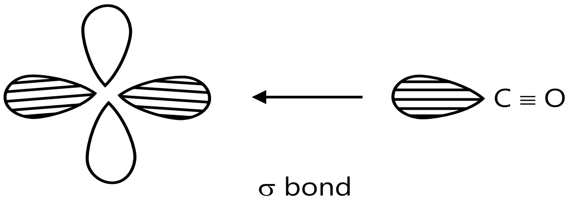


for ex. if we take d^6 configuration.

if Δ_o is high ⇅ ⇅ ⇅ is more stable

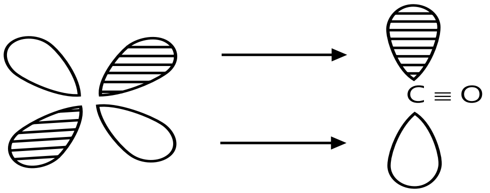
if Δ_o is low ⇅ ↓ ↓ is more stable

Sol 21: In metal carbonyls, CO acts as a ligand and forms



σ bond

After the formation of σ bonding. There is a possibility for back bonding from metals to CO.



The new e⁻ in CO enters into the anti bonding orbitals of CO and reduces its bond order. The bond order between M and C increase. The extent depends on no. of lone pairs present on metal for donation. It's called synergic effect

Sol 22: (i) $[Co(H_2O)CN(en)_2]^{2+}$

Co ⟶ +3, Octahedral

(ii) $[PtCl_4]^{2-}$

Pt ⟶ +2, Square Planar

(iii) $[Cr(NH_3)_3Cl_3]$

Cr ⟶ +3, Octahedral

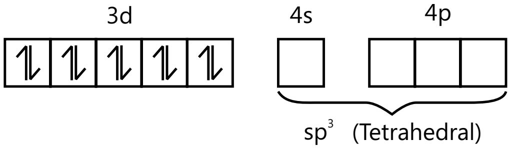
(iv) $[CoBr_2(en)_2]^+$

Co ⟶ +3, Octahedral

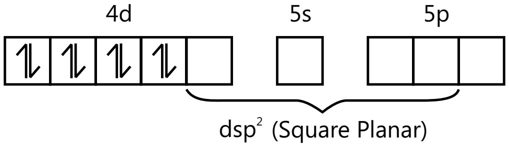
(v) $K_3[Fe(CN)_6]$

Fe ⟶ +3, Octahedral

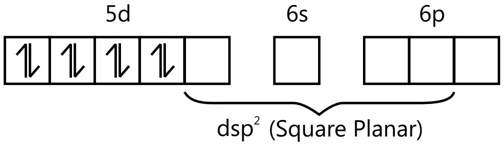
Sol 23: (i) $[Zn(H_2O)_4]^{2+}$ ⟶



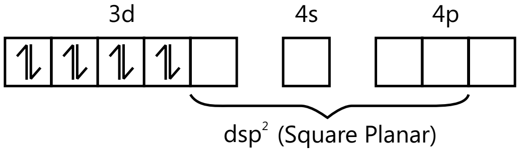
(ii) $K_2[PdCl_4]$ ⟶



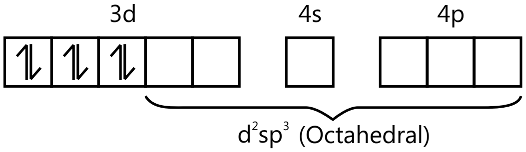
(iii) $[Pt(NH_3)_2Cl_2]$ ⟶



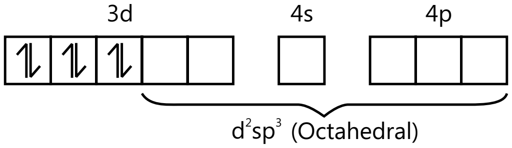
(iv) $K_2[Ni(CN)_4]$ ⟶



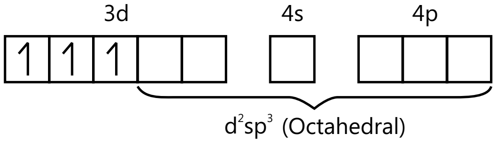
(v) $[Co(NH_3)_5ONO]^{2+}$ ⟶



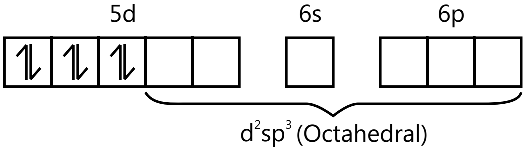
(vi) $[Co(NH_3)_6]_2(SO_4)_3 \longrightarrow$



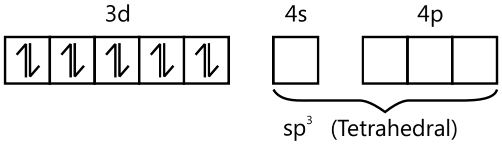
(vii) $K_3[Cr(C_2O_4)_3] \longrightarrow$



(viii) $[Pt(NH_3)_6]^{4+} \longrightarrow$



(ix) $[CoBr_4]^{2-} \longrightarrow$



Sol 24: VBT doesn't account for the difference in configuration with ligands of different strengths. It also doesn't account for the colour of complexes.

Where as CFT clearly explains the configurations of metals with different ligands using crystal field model so, that we can account for shape, colour and magnetic properties.

Sol 25: (i) $[Co(NH_3)_4H_2OCl]Cl_2$

(ii) $K_2[Zn(OH)_4]$

(iii) $K_3[Al(C_2O_4)_3]$

(iv) $[CoCl_2(NH_2 - CH_2 - CH_2 - NH_2)_2]^+$

(v) $[Ni(CO)_4]$

Exercise 2

Single Correct Choice Type

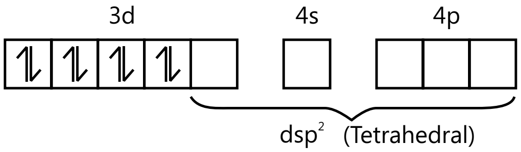
Sol 1: (D) Back bonding in PCl_3 > PMe_3

So complex having more PMe_3 will save higher back bonding to CO. So, it will have lower C–O bond order.

∴ BO of CO in.

$[M(CO)_3(PCl_3)_3]$ > $[M(CO)_3(PCl_3)_2PMe_3]$ > $[M(CO)_3PCl_3(PMe_2)_2]$

Sol 2: (B) Fe $\longrightarrow$ 26



Co is a strong ligand. Pairing takes place.

Sol 3: (D) NO $\longrightarrow$ NO^+, $Co^{2+} \longrightarrow Co^{3+}$ (Stable) Mn+ can form stable complex with strong ligand Co.

So, all are reducing agents

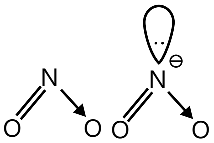
Sol 4: (A) By reduction or dimension, it can attain EAN of 36. So, oxidation doesn't lead to stability.

Sol 5: (B) Mohr's salt has very high mol wt but same reducing points. So, its less readily oxidizable than $FeSO_4$ and error in calculations decrease.

Multiple Correct Choice Type

Sol 6: (A, C) (A) is true because bridge CO will take e^- pair from 2 Fe atoms.

(B) is false.

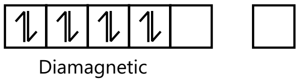


more repulsion by LP. So angle is less

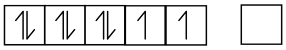
(C) is true.

No can also act as acceptor ligand

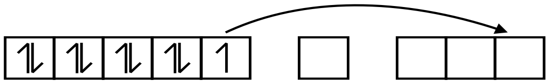
Sol 7: (C, D) (A) $Au^{3+} \longrightarrow$



(B) $Cu^{3+} \longrightarrow$

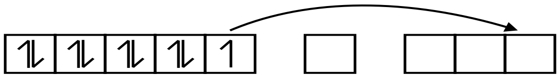


(C) $Cu^{2+} \longrightarrow$ Tetrahedral



Paramagnetic, Square Planar

(D) Co ⟶

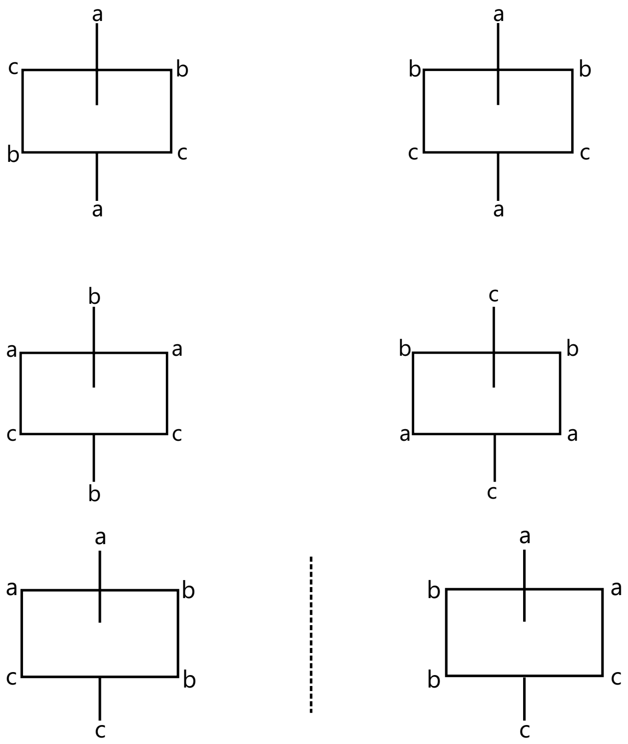


Paramagnetic, Square Planar

Sol 8: (C, D) Transition elements → last e⁻ enters in d-orbital and they are named as such because their properties lie between s and p block.

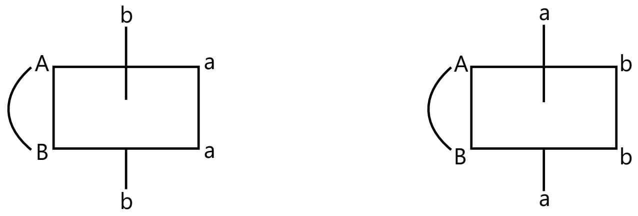
Lanthanum is a d-block transition metal

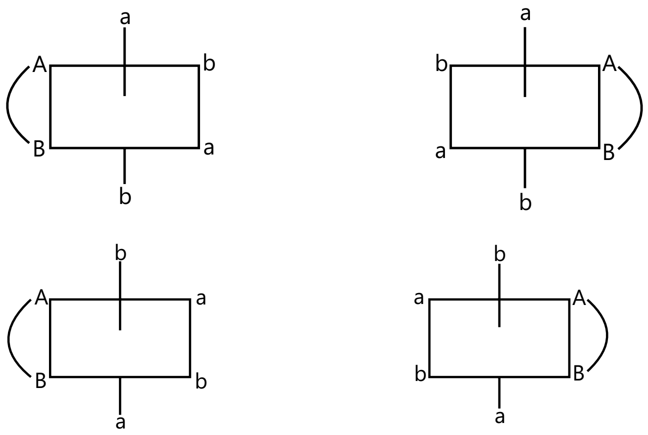
Sol 9: (A, D) (A)



(A) Has 6 stereoisomer

(D) $[M(AB)A_2B_2]$





6 Stereoisomers

(C) Will have less than (D) as (3), (5) and (4), (6) Coincide

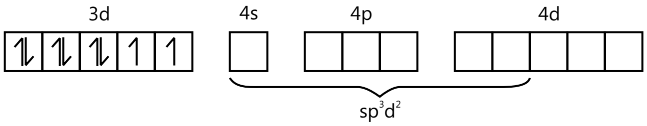
(B) Will have more than 6, as we can get 2 for each of (3), (4), (5), (6)

Sol 10: (A, B, C) $[Fe(CN)_6]^{4-}$ ⟶ low spin as CN^- is strong

$[PtCl_4]^{2-}$ ⟶ Pt^{2+} always forms low spin even with weak ligands

$[Co(C_2O_4)_3]^3$ ⟶ low spin as $C_2O_4^{2-}$ is strong ligand

$[Ni(NH_3)_6]^{2+}$ ⟶



High spin as 6 orbital are needed for hybridisation. Pairing need not occur.

Sol 11: (A, B, C) Cu^{2+} ⟶ 1 unpaired e⁻

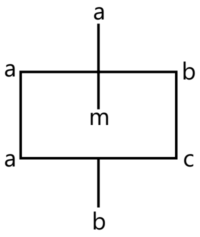
Ti^{3+} ⟶ 1

Fe^{3+}, strong ligand ⟶ 1

$[Cr(NH_3)_6]^{3+}$ ⟶ 3

Sol 12: (A, B, C, D) MA_4B_2 can't produce due to presence of plane of symmetry.

MA_3B_2C will also have plane of symmetry.



has a plane of symmetry

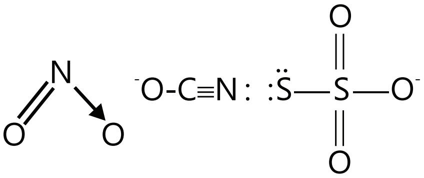
Sol 13: (A, C, D) (A) 22 + 4(2) = 30

(B) 26 + 2 + 4 (2) = 36 Not exists as NO+

(C) 46 + 2(2) = 50

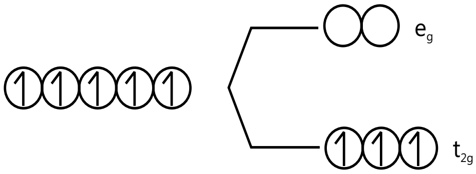
(D) 78 + 4(2) = 86

Sol 14: (B, C, D) NO_3^- can't show because of no LP on N.



Assertion Reasoning Type

Sol 15: (B) $Cr^{+3} \longrightarrow 21e^-$

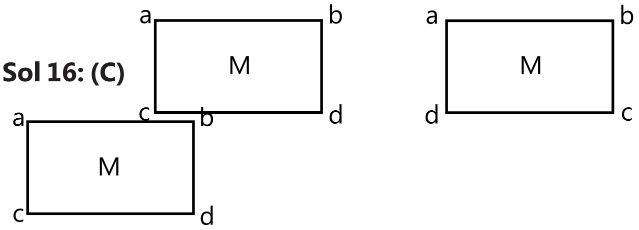


as all ligands are identical, it doesn't show geometrical isomerism.

But S-2 doesn't imply S-1

S-1 reason is that t_{2g} orbitals have less energy compared to eg orbitals.

Sol 16: (C)



S-2 is false, as rotation is possible around a single bond and $[MABCD]^{n\pm}$ can show geometrical isomerism

Comprehension Type

Paragraph 1:

Sol 17: (B) $NMe_3 \longrightarrow$ only N can donate e^- pair.

$SO_4^{2-} \longrightarrow$ only O can donate e^- pair.

$^{\ominus}OCN \longrightarrow$ O and N can donate e^- pair.

So, $OCN^{\ominus}$ can show linkage isomerism

Sol 18: (D) Due to synergic bonding M-L bond strength increases, so complex stability increases More negative charge of M, increases synergic bonding as more e^- pairs can be donated.

Sol 19: (C) C_2H_2 can act as π-acid ligand All $[MA_3B_2C]$ Isomers are optically inactive due to presence of plane of symmetry. Complex of type $[MABCDE_2]$ has 15 active isomers

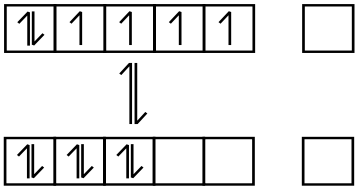
Paragraph 2:

Sol 20: (C) CN^-, because in CO_3^{2-}, OH^- the e^- donar.

N, Cl have same EN but CN^- is a strong ligand

Sol 21: (C) $Fe \longrightarrow 26$

$Fe^{2+} \longrightarrow 24$



as there are 2 d orbitals octahedral

Sol 22: (B) $[V(CO)_5]^-$ Metals are mostly unstable under negative charge

Match the Columns

Sol 23: A → p; B → q, r, t; C → p, q, s; D → q, r, t

(A) $Na[Co(CO)_4] \longrightarrow$ monodentate ligand Follows EAN rule

(B) $[Pt(triene)Cl_2] \longrightarrow$ no EAN (80) 5 membered ring chelating ligand (trien)

(C) $[Fe(H_2O)_5NO]SO_4 \longrightarrow$ No EAN (37) all monodentate NO^+ is +ve charged ligand

(D) $[Fe(EDTA)]^- \longrightarrow$ hexadentate ligand No EAN 5, membered ring (Chelating ligand)

Sol 24: A → q, s; B → r, s; C → p, q, s

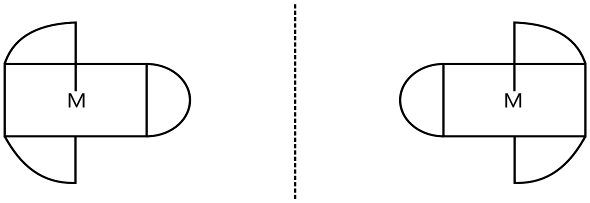
(A) $[Co(CO)_4]^- \longrightarrow$ EAN = 36 Synergic bonding is present Diamagnetic, no isomers

(B) $[Zn(sly)_2] \longrightarrow$ EAN = 36 dimagnetic, dl pair

(C) $[Ag(CN)_2]^- \longrightarrow$ EAN ≠36 (50) There is synergic bonding It's diamagnetic

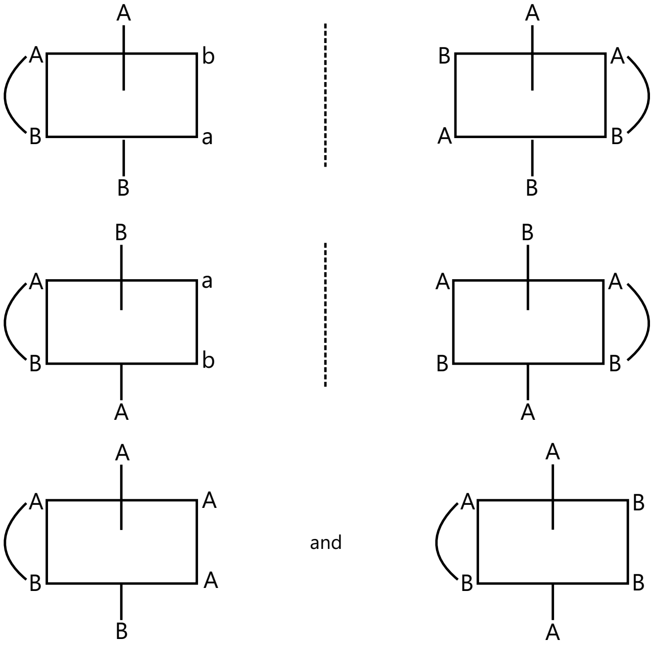
Sol 25: A → s; B → p, q, r; C → p; D → q, s

(A)

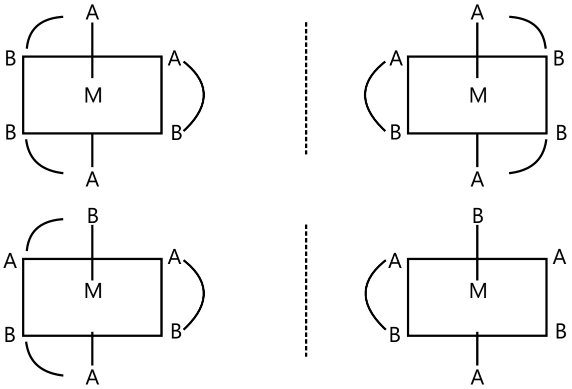


Two optically active isomers

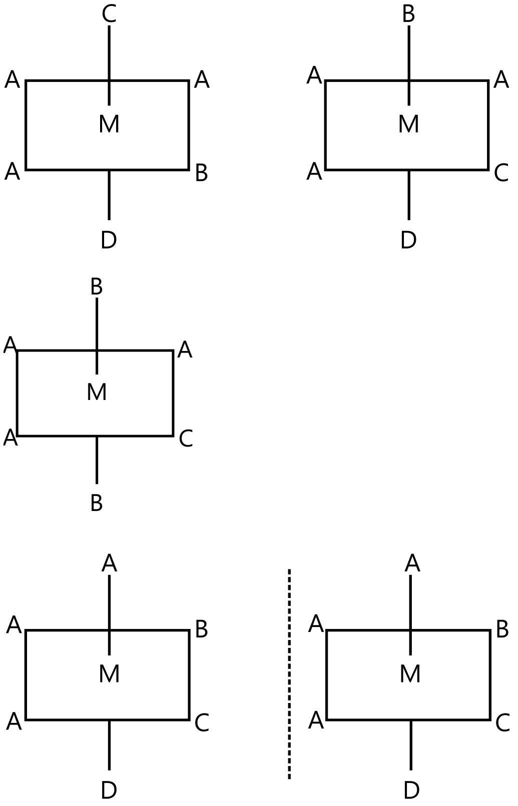
(B) $[M(AB)b_2c_2]$



(C) $[M(AB)_3]$



(D) $[Ma_3bcd]$



4 geometric, 2 optically active

Sol 26: A → q, s; B → r, s; C → p, q, r, t; D → q, r

(A) $Zn[Fe(CN)_5NO] \longrightarrow d^2sp^3$, $Fe \longrightarrow +2$, So diamagnetic, $NO \longrightarrow NO^+$

(B) $[Fe(H_2O)_5NO]SO_4 \longrightarrow sp^3d^2$ paramagnetic

[$\because$ H_2O is a weak ligand]$NO \longrightarrow NO^+$

(C) $Fe_4[Fe(CN)_6]_3$

$[Fe(CN)_6]^{4-}$ i.e. $F^{2+} \longrightarrow d^2sp^3$

There is charge transfer between Fe ions.

$Fe^{3+} \longrightarrow$ Paramagnetic

(D) $K_4[Fe(CN)_5O_2]$

$Fe^{3+} \longrightarrow d^2sp^3$ and paramagnetic

(CN^- is strong ligand)

Sol 27: A → r; B → p; C → q; D → s

(A) No. of ions $\longrightarrow 4$

(B) $\longrightarrow 3$

(C) $\longrightarrow 2$

(D) $\longrightarrow 5$

$\therefore$ C $\longrightarrow$ 97 (q)

B $\longrightarrow$ 229 (p)

A $\longrightarrow$ 404 (r)

D $\longrightarrow$ 523 (s)

Previous Years' Questions

Sol 1: (B) Salt with least no. of unpaired electrons in d-orbital of central metal will show lowest degree of paramagnetism.

Mn^{2+}($3d^5$, 5 unpaired electrons)

Cu^{2+}($3d^9$, 1 unpaired electron)

Fe^{2+}($3d^6$, 4 unpaired electrons)

Ni^{2+}($3d^8$, 2 unpaired electrons)

Hence, $CuSO_4 \cdot 5H_2O$ has lowest degree of paramagnetism.

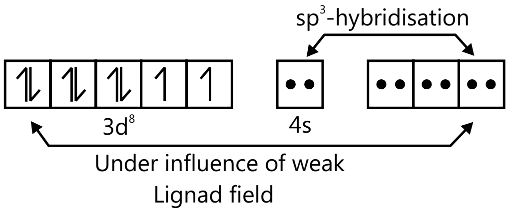
Sol 2: (D) $Cu^{2+} + CN^- \longrightarrow CuCN\downarrow$

$CuCN + 3CN^- \longrightarrow [Cu(CN)_4]^{3-}$

Sol 3: (A) In MnO^-_4, Mn^{+7} has $3d^0$ configuration.

Sol 4: (D) $[NiCl_4]^{2-}$: Ni^{2+} ($3d^8$)

(tetrahedral)



In all other complexes, hybridization at central metal is dsp^2 and complexes have square planar geometries.

Sol 5: (C) $[Ni(NH_3)_4]^{2+}$ = tetraamminenickel (II)

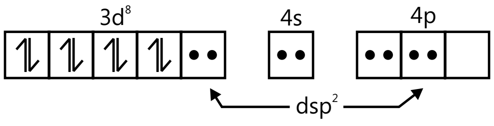
$[NiCl_4]^{2-}$ = tetrachloronickelate (II)

Cationic part is named first, hence :

tetraamminenickel (II)-tetrachloronickelate(II)

Sol 6: (B) $Ni^{2+} + 4CN^- \rightarrow [Ni(CN)_4]^{2-}$

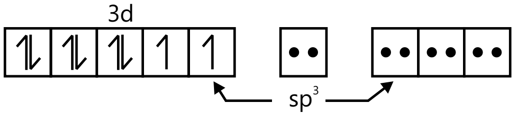
Here Ni^{2+} has d^8-configuration which CN^- as strong ligand



d^8-configuration in strong ligand field gives dsp^2 hybridisation, hence square planar geometry.

$N^{2+} + 4Cl^- \rightarrow [NiCl_4]^{2-}$

Here Ni^{2+} has d^8-configuration with Cl^- as weak ligand.



d^8- configuration in weak ligand field gives sp^3 hybridisation, hence tetrahedral geometry.

Ni^{2+} with H_2O forms $[Ni(H_2O)_6]^{2+}$ complex and H_2O is a weak ligand.

Sol 7: (B) (A) $Mn^+ = 3d^54s^1$ in presence of CO effective configuration = $3d^54s^0$ Three lone pair for back bonding with vacant orbital of C in CO.

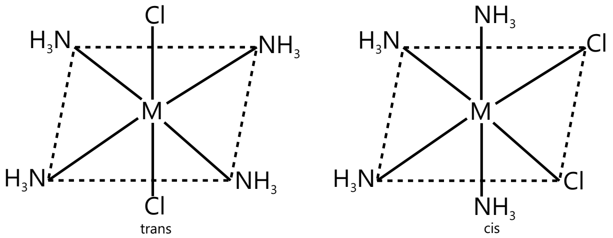
(B) $Fe^0 = 3d^64s^2$ in presence of CO effective configuration = $3d^8$ four lone pair for back bonding with CO.

(C) $Cr^0 = 3d^54s^1$ Effective configuration $3d^6$. Three lone pair for back bonding with CO.

(D) $V^- = 3d^44s^2$ effective configuration = $3d^6$ three lone pair for bonding with CO.

Maximum back bonding is present in $Fe(CO)_5$ there for CO bond order is lowest here.

Sol 8: (B) Both statements are true. However, axis of symmetry is not a criteria of optical isomerism. Optical inactivity of the two geometrical isomers of $[M(NH_3)_4Cl_2]$ is due to presence of lane of symmetry.

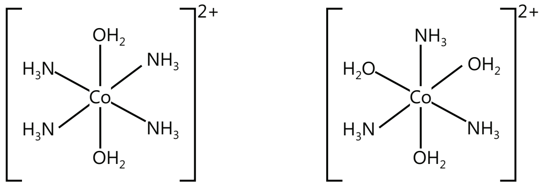


trans
(has several planes of symmetry)

cis
(has several planes of symmetry)

Sol 9:

(A)



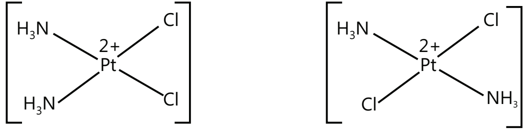
(trans)

(cis)

$Co^{2+} = 3d^7$ (Paramagnetic)

$[Pt(NH_3)_2Cl_2]$ is square planar.

(B)

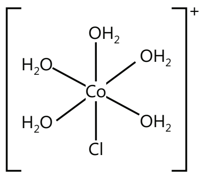


(cis)

(trans)

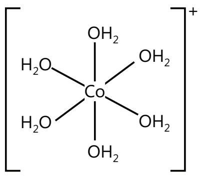
$Pt^{2+} = 5d^84s^0$ (Diamagnetic)

(C)



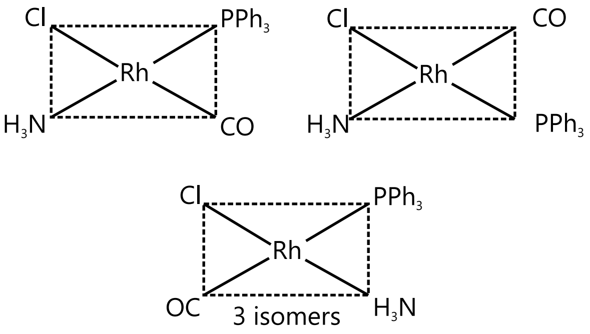
$Co^{2+}=3d^7$ (Paramagnetic)

(D)



$Ni^{2+}=3d^8$ (weak field ligand, paramagnetic)

Sol 10:



3 isomers

Sol 11: m mol of complex = 30 × 0.01 = 0.3

Also, 1 mole of complex $[Cr(H_2O)_5Cl]Cl_2$ gives only tow moles of chloride ion when dissolved in solution

$$[Cr(H_2O)_5Cl]Cl_2 \longrightarrow [Cr(H_2O)_5Cl]^{2+} + 2Cl^-$$

⇒ m mol of Cl^- ion produced from its 0.3 m mol = 0.6

Hence, 0.6 m mol of Ag^+ would be required for precipitation.

⇒ 0.60 m mol of Ag^+ = 0.1M × V(in mL) ⇒ V = 6 mL.

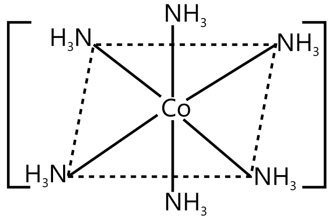
Sol 12: (i) $[Ti(NO_3)_4]$: Ti^{4+} ($3d^0$) No d-electron, no d-d transition possible, colourless.

(ii) $[Cu(NCCH_3)]BF_4$: Cu^+ ($3d^{10}$) All d-orbitals are completely filled, no d-d transition possible, colourless.

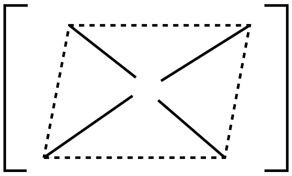
(iii) $[Cr(NH_3)_6]Cl_3$: Cr^{3+} ($3d^3$) Complex has allowed d-d transitions from t_{2g} to e_g level, hence, coloured.

(iv) $K_3[VF_6]$: V^{3+} ($3d^2$) Complex has allowed d-d transitions from t_{2g} to e_g level, hence, coloured.

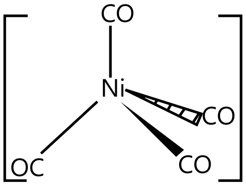
Sol 13:



d^2sp^3-octahedral



dsp^2-square planar

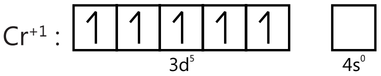


sp^3-tetrahedral

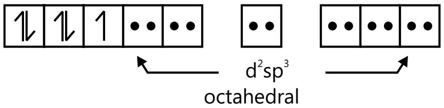
Sol 14: The spin-only magnetic moment (μ) of the complex is 1.73 BM. It indicates that nucleus of complex, chromium ion has one unpaired electron. So, the ligand NO is unit positively charged.

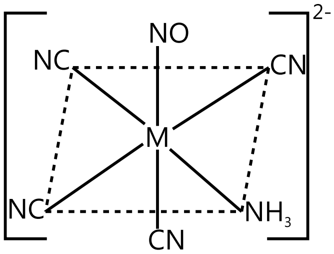
$K_2[Cr(NO)(CN)_4(NH_3)]$

Potassium ammine tetracyanonitrosonium-chromate (I)



Cr(I) “under influence of strong ligand field”.

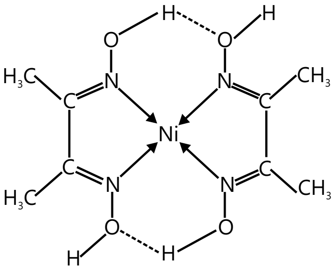




(octahedral geometry)

Sol 15: Oxidation state of Ni is +2 and hybridization is dsp^2. μ = 0

(nounpaired electron).



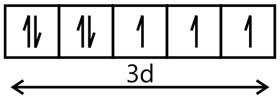
Ni-DMG complex

Sol 16: (A) $\left[Fe\left(H_2O\right)_5 NO\right]SO_4$

Here Fe has +1 oxidation state.

$Fe^+ = 3d^6 4s^1$ in presence of NO^+ $4s^1$ electron are paired in 3d sub shell.

So electronic configuration of Fe^+ is



Sol 17: (D) $\left[Co\left(H_2O\right)_4\left(NH_3\right)_2 Cl_3\right]$

Diamminetetraaquacobalt (III) chloride

Sol 18: (B) P = Fe^{+3} (no. of unpaired $\overline{e} = 5$)

Q = V^{+2} (no. of unpaired $\overline{e} = 3$)

R = Fe^{+2} (no. of unpaired $\overline{e} = 4$)

As all ligands are weak field, hence the no. of unpaired electrons remains same in the complex ion.

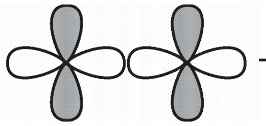
$\mu = \sqrt{n\left(n+2\right)}$B.M

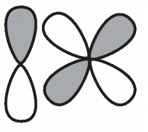
Hence (B) is correct.

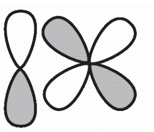
Sol19: (B,D) $\left[Co\left(NH_3\right)_4 Cl_2\right]^+$ and $\left[Pt\left(NH_3\right)_2\left(H_2O\right)Cl\right]^+$ (a square planar complex) will show geometrical isomerism.

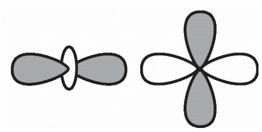
$\left[Pt\left(NH_3\right)_3\left(NO_3\right)\right]Cl$ and $\left[Pt\left(NH_3\right)_3 Cl\right]Br$ will show ionization isomerism.

Sol 20: (C)

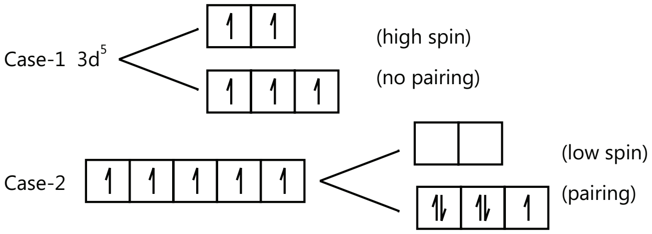
(p)  $\longrightarrow$ $d-d\sigma$ bonding

(q)  $\longrightarrow$ $p-d\pi$ bonding

(r)  $\longrightarrow$ $p-d\pi$ anticoding

(s)  $\longrightarrow$ $d-d\sigma$ anticoding

Sol 21: (D) $[Fe(SCN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$. In both the cases the electronic configuration of Fe^{3+} will be $1s^2$, $2s^2$, $2p^6$, $3p^6$, $3d^5$. Since $\overline{S}CN$ is a weak field ligand and $\overline{C}N$ is a strong field ligand, the pairing will occur in case of



Case-1 $\mu = \sqrt{n\left(n+2\right)} = \sqrt{5\left(5+2\right)} = \sqrt{35} = 5.91$ BM

Case-2 $\mu = \sqrt{n\left(n+2\right)} = \sqrt{1\left(1+2\right)} = \frac{3}{\ } = 1.73$ BM

Sol 22: (5) $[Co(en_2Cl_2)]^+ \rightarrow$ will show cis - trans isomerism

$[CrCl(C_2O_4)]^{3-} \rightarrow$ will show cis - trans isomerism

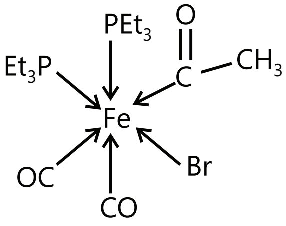
$[Fe(H_2O)_4(OH)_2]^+ \rightarrow$ will show cis trans isomerism

$[Fe(CN)_4(NH)_3]^- \rightarrow$ will show cis trans isomerism

$[Co(en)_2(NH_3)Cl]^{2+} \rightarrow$ will show cis trans isomerism

$[Co(NH_3)_4(H_3O)Cl]^{2+} \rightarrow$ Will not show cis – trans isomerism (Although it will show geometrical isomerism)

Sol 23: (D)



Sol 24: (B) $[Ni(CO)_4]$ – sp^3 – Diamagnetic

$[NiCl_4]^{2-}$ – sp^3 – Paramagnetic

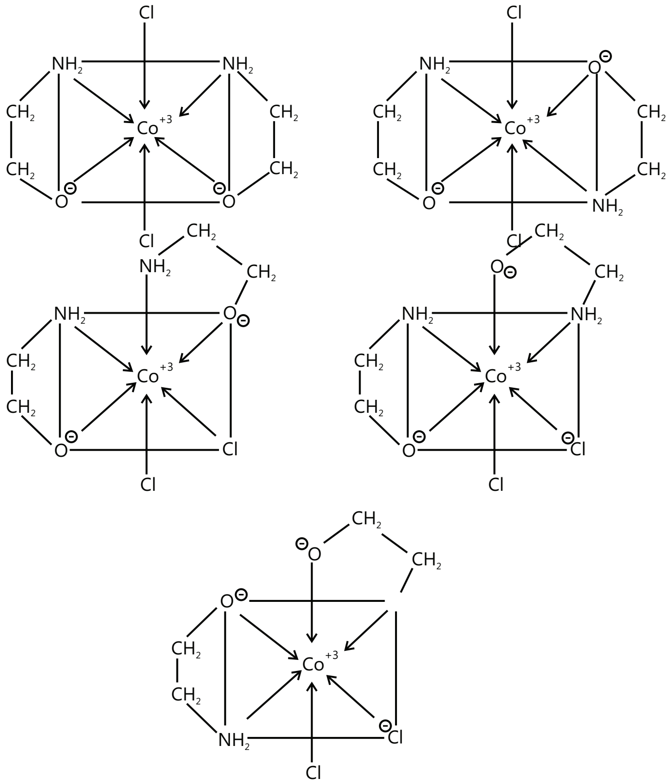
$[Co(NH_3)_4 Cl_2]Cl_2$ – d^2sp^3 – Diamagnetic

Na_3 $[CoF_6]$ – sp^3d^2 Paramagnetic

Na_2O_2 i.e. O_2^{2-} – Diamagnetic

CsO_2 i.e. O_2^- – Paramagnetic

Sol 25: (5)



Sol 26: (A) $[Ni(NH_3)_6]^{2+}$ = Octahedral

$[Pt(NH_3)_4]^{+2}$ = Square planar

$[Zn(NH_3)_4]^{+2}$ = Tetrahedral