## 19

## Co-ordination Compounds

## TOPIC 1

## Nomenclature, Isomerism and Werner's Theory

01 Ethylene diaminetetraacetate (EDTA) ion is
[NEET 2021]
(a) hexadentate ligand with four 0 and two $N$ donor atoms
(b) unidentate ligand
(c) bidentate ligand with two N donor atoms
(d) tridentate ligand with three N donor atoms
Ans. (a)
Ethylene diaminetetraacetate (EDTA) ion.


EDTA is a hexadentate ligand with four ' $O^{\prime}$ and two 'N' donor atoms.

02 The type of isomerism shown by the complex $\left[\mathrm{COCl}_{2}(\mathrm{en})_{2}\right]$ is
[NEET 2018]
(a) ionisation isomerism
(b) coordination isomerism
(c) geometrical isomerism
(d) linkage isomerism

Ans. (c)
Isomers in which the atoms or ligands occupy different positions around central metal/ion are called geometrical isomers. Complexes having coordination number of central atom/ion 6 with formula $M(A A)_{2} B_{2}$ exhibit geometrical isomerism [where, $A A$ is a bidentate ligand]. In $\left[\mathrm{CoCl}_{2}(\mathrm{en})_{2}\right]$, coordination
number of $C o$ is 6 with octahedral geometry.


Thus, $\left[\mathrm{CoCl}_{2}(e n)_{2}\right]$ show geometrical isomerism.

03 The geometry and magnetic behaviour of the complex $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$ are
[NEET 2018]
(a) square planar geometry and paramagnetic
(b) tetrahedral geometry and diamagnetic
(c) square planar geometry and diamagnetic
(d) tetrahedral geometry and paramagnetic
Ans. (b)
Key Concept The complexes having $s p^{3}$-hybridisation are tetrahedral while having $\mathrm{dsp}^{2}$-hybridisation are square planar. The magnetic behaviour of complexes can be paramagnetic and diamagnetic based on the presence and absence of unpaired electrons, respectively.
Electronic configuration of $\mathrm{Ni}(Z=28)$ is $[\mathrm{Ar}]_{18} 3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$. Due to presence of CO (neutral ligand), oxidation state of Ni in $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$ is 0.


Since, CO is a strong field ligand, it pair up the unpaired electrons of Ni .


There is no unpaired electron, hence, $\mathrm{Ni}(\mathrm{CO})_{4}$ is diamagnetic with tetrahedral geometry.


04 The correct order of the stoichiometrics of AgCl formed when $\mathrm{AgNO}_{3}$ in excess is treated with the complexes:
$\mathrm{CoCl}_{3} \cdot 6 \mathrm{NH}_{3}, \mathrm{CoCl}_{3} \cdot 5 \mathrm{NH}_{3}$, $\mathrm{CoCl}_{3} \cdot 4 \mathrm{NH}_{3}$ respectively is
(a) $1 \mathrm{AgCl}, 3 \mathrm{AgCl}, 2 \mathrm{AgCl}$
[NEET 2017]
(b) $3 \mathrm{AgCl}, 1 \mathrm{AgCl}, 2 \mathrm{AgCl}$
(c) $3 \mathrm{AgCl}, 2 \mathrm{AgCl}, 1 \mathrm{AgCl}$
(d) $2 \mathrm{AgCl}, 3 \mathrm{AgCl}, 1 \mathrm{AgCl}$

Ans. (c)
According to Werner's theory,

$$
\begin{aligned}
\mathrm{CoCl}_{3} \cdot 6 \mathrm{NH}_{3} & \longrightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+} 3 \mathrm{Cl}^{-} \\
\mathrm{CoCl}_{3} \cdot 5 \mathrm{NH}_{3} & \longrightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right]^{2+} 2 \mathrm{Cl}^{-} \\
\mathrm{CoCl}_{3} \cdot 4 \mathrm{NH}_{3} & \longrightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}\right]^{+} \mathrm{Cl}^{-}
\end{aligned}
$$

When $\mathrm{AgNO}_{3}$ in excess is treated with these complexes then following reactions takes place :

$$
\begin{gathered}
{\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+} 3 \mathrm{Cl}^{-}+\underset{(\text { Excess })}{\mathrm{AgNO}_{3}} \longrightarrow 3 \mathrm{AgCl}} \\
+\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+} \\
{\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right]^{2+} 2 \mathrm{Cl}^{-}+\underset{(\text { Excess })}{\mathrm{AgNO}} \longrightarrow}
\end{gathered}
$$

05 The correct increasing order of trans-effect of the following species is
[NEET 2016, Phase II]
(a) $\mathrm{NH}_{3}>\mathrm{CN}^{-}>\mathrm{Br}^{-}>\mathrm{C}_{6} \mathrm{H}_{5}^{-}$
(b) $\mathrm{CN}^{-}>\mathrm{C}_{6} \mathrm{H}_{5}^{-}>\mathrm{Br}^{-}>\mathrm{NH}_{3}$
(c) $\mathrm{Br}^{-}>\mathrm{CN}^{-}>\mathrm{NH}_{3}>\mathrm{C}_{6} \mathrm{H}_{5}^{-}$
(d) $\mathrm{CN}^{-}>\mathrm{Br}^{-}>\mathrm{C}_{6} \mathrm{H}_{5}^{-}>\mathrm{NH}_{3}$

Ans. (b)
Trans effect is the effect of a coordinated group upon the rate of substitution at the position trans to itself in a square or octahedral complex. As the rate of substitution of the trans ligand increases, the intensity of trans effect also increases. Thus, correct order is,

$$
\mathrm{CN}^{-}>\mathrm{C}_{6} \mathrm{H}_{5}^{-}>\mathrm{Br}^{-}>\mathrm{NH}_{3}
$$

06 Jahn-Teller effect is not observed in high spin complexes of
[NEET 2016, Phase II]
(a) $d^{7}$
(b) $d^{8}$
(c) $d^{4}$
(d) $d^{9}$

Ans. (b)
Key Idea Jahn-Teller distortion is observed in those octahedral complexes in which d-electrons are filled unsymmetrically.


Except $d^{8}$, all are unsymmetrically filled, thus $d^{8}$ complex will not show Jahn-Teller distortion.

07 Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at $25^{\circ} \mathrm{C}$ ?
[CBSE AIPMT 2015]
(a) $\mathrm{CoCl}_{3} \cdot 3 \mathrm{NH}_{3}$
(b) $\mathrm{CoCl}_{3} \cdot 4 \mathrm{NH}_{3}$
(c) $\mathrm{CoCl}_{3} \cdot 5 \mathrm{NH}_{3}$
(d) $\mathrm{CoCl}_{3} \cdot 6 \mathrm{NH}_{3}$

Ans. (a)

$$
\begin{gathered}
{\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3} \longrightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}+3 \mathrm{Cl}} \\
{\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right] \longrightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]} \\
\left.\left.\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}\right)_{2}\right] \mathrm{Cl} \longrightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}\right]_{2}\right]^{+} \\
+\mathrm{Cl} \\
{\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2} \longrightarrow}
\end{gathered}\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right]^{2+}+2 \mathrm{Cl}^{-} .
$$

08 Number of possible isomers for the complex[Co(en) $\mathrm{Cl}_{2}$ ]Cl will be (en = ethylenediamine)
[CBSE AIPMT 2015]
(a) 2
(b) 1
(c) 3
(d) 4

Ans. (c)
[Co(en) $2_{2} \mathrm{Cl}_{2}$ ]Cl
Possible isomers are


Hence, total number of stereoisomers $=2+1=3$.

09 The sum of coordination number and oxidation number of the metal $M$ in the complex $\left[\mathrm{M}(\mathrm{en})_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)\right] \mathrm{Cl}$ (where, en is ethylenediamine) is
[CBSE AIPMT 2015]
(a) 9
(b) 6
(c) 7
(d) 8

Ans. (b)
Given complex compound is
$\left[\mathrm{M}(\mathrm{en})_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)\right] \mathrm{Cl}$
Let oxidation number of $M$ is $x$.

$$
\begin{array}{rlrl}
\therefore & x-2-2 & =-1 \\
\text { or } & & x & =+3
\end{array}
$$

Now, as coordination number is defined as the total number of binding sites attached to the metal. Hence, in the given complex coordination number is 6 .

10 The name of complex ion, $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$ is
[CBSE AIPMT 2015]
(a) hexacyanoiron (III) ion
(b) hexacyanitoferrate (III) ion
(c) tricyanoferrate (III) ion
(d) hexacyanidoferrate (III)ion

Ans. (d)
Key Concept When complex ion is an anion, the name of the metal ends with suffix -ate along with its oxidation number in the complex ion.
$\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}=$ Hexacyanoferrate (III) ion
11 The complex $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Cr}(\mathrm{CN})_{6}\right]$ and $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ are the examples of which type of isomerism? [CBSE AIPMT 2011]
(a) Ionisation isomerism
(b) Coordination isomerism
(c) Geometrical isomerism
(d) Linkage isomerism

Ans. (b)
The complexes $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Cr}(\mathrm{CN})_{6}\right]$ and $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$ are the examples of coordination isomerisms. This isomerism occurs only in those complexes in which both cation and anion are complex. It occurs due to exchange of ligands between cation and anion.

12 The complex, [ $\left.\mathrm{Pt}(\mathrm{Py})\left(\mathrm{NH}_{3}\right) \mathrm{BrCl}\right]$ will have how many geometrical isomers?
[CBSE AIPMT 2011]
(a) 4
(b) 0
(c) 2
(d) 3

Ans. (d)
The complex is square planar and is of the type [M(abcd)]. It has three geometrical isomers.


13 The existence of two different coloured complexes with the composition of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}\right]^{+}$is due to
[CBSE AIPMT 2010]
(a) linkage isomerism
(b) geometrical isomerism
(c) coordination isomerism
(d) ionisation isomerism

Ans. (b)
Key Idea Complexes of $\left[\mathrm{MA}_{4} \mathrm{~B}_{2}\right]$ type exhibit geometrical isomerism.
The complex $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}\right]^{+}$is a $\left[\mathrm{MA}_{4} \mathrm{~B}_{2}\right]$ type complex and thus, fulfills the conditions that are necessary to exhibit geometrical isomerism. Hence, it has two geometrical isomers of different colours as :
The structure of the geometrical isomers is as



For linkage isomerism, presence of ambidentate ligand is necessary.
For coordination isomerism, both the cation and anion of the complex must be complexions.
For ionisation isomerism, an anion different to the ligands must be present outside the coordination sphere. All these conditions are not satisfied by this complex. Hence, it does not exhibit other given isomerisms.

14 Which of the following does not show optical isomerism? (en = ethylenediamine)
[CBSE AIPMT 2009]
(a) $\left[\mathrm{Co}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right]^{+}$
(b) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]^{0}$
(c) $\left[\mathrm{Co}(\mathrm{en}) \mathrm{Cl}_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$
(d) $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$

Ans. (b)
Optical isomerism is exhibited only by those complexes in which plane of symmetry are absent. Octahedral complexes of the types $\left[M(a a)_{3}\right]_{1}$, $\left[M(a a) x_{2}, y_{2}\right]$ and $\left[M(a a)_{2} x_{2}\right]$ have absence of plane of symmetry, thus exhibit optical isomerism. Here, aa represents bidentate ligand, $x$ or $y$ represents monodentate ligand and $M$ represents central metal ion.
Hence, $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]^{0}$ due to presence of symmetry elements does not exhibit optical isomerism.
or
Octahedral complexes of $\left[M(A A)_{2} B_{2}\right]$
type, e.g. $\left[\mathrm{Co}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right]^{+},\left[\mathrm{M}(\mathrm{AA}) \mathrm{B}_{2} \mathrm{C}_{2}\right]$ type, e.g. [Co(en)Cl 2 $\left.\left(\mathrm{NH}_{3}\right)_{2}\right]$ and $\left[\mathrm{M}(\mathrm{AA})_{3}\right]$ type, e.g. $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$ show optical isomensim, whereas complexes of $\left[M A_{3} B_{3}\right]$ type, e.g. $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right) \mathrm{Cl}_{2}\right]^{0}$ do not show optical isomerism.

15 Which of the following will give a pair of enantiomers?
(en $=\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ )
[CBSE AIPMT 2007]
(a) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$
(b) $\left[\mathrm{Co}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right] \mathrm{Cl}$
(c) $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4}\right]\left[\mathrm{PtCl}_{6}\right]$
(d) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}\right] \mathrm{NO}_{2}$

Ans. (b)
Enantiomorphs or Enantiomers A pair of molecules related to each other as an object and its mirror images are known as enantiomorphs or enantiomers.
These are not superimposable on its mirror image.
The example is [Co(en) $\left.2_{2} \mathrm{Cl}_{2}\right]^{+}$
Dichlorobis (ethylene diamine) cobalt (III)

$\overline{16}\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{NO}_{2}\right)_{2}\right] \mathrm{Cl}$ exhibits
[CBSE AIPMT 2006]
(a) linkage isomerism, geometrical isomerism and optical isomerism
(b) linkage isomerism, ionisation isomerism and optical isomerism
(c) linkage isomerism, ionisation isomerism and geometrical isomerism
(d) ionisation isomerism, geometrical isomerism and optical isomerism
Ans. (c)
The compound $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{NO}_{2}\right)_{2}\right] \mathrm{Cl}$ exhibits linkage, ionisation and geometrical isomerism. Hence,
(i) its linkage isomers are
$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{NO}_{2}\right)_{2}\right] \mathrm{Cl}$ and
$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}(\mathrm{ONO})_{2}\right] \mathrm{Cl}$
(ii) its ionisation isomers are $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{NO}_{2}\right) \mathrm{Cl}\right] \mathrm{NO}_{2}$ and $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{NO}_{2}\right)_{2}\right] \mathrm{Cl}$
(iii) its geometrical isomers are


Cis-isomer

$\overline{\mathbf{1 7}}$ Which one of the following is expected to exhibit optical isomerism? (en = ethylenediamine)
[CBSE AIPMT 2005]
(a) $\mathrm{Cis}-\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$
(b) Trans-[Co(en) $\left.2_{2} \mathrm{Cl}_{2}\right]^{+}$
(c) Trans-[Pt( $\left.\left.\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$
(d) Cis-[Co(en) $\left.\mathrm{Cl}_{2}\right]^{+}$

Ans. (d)
Cis- $\left[\mathrm{Co}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right]^{+}$is able to show the phenomenon of optical isomerism because it can form a superimposable mirror image.


It gives super imposable structure. but trans-form is optically inactive


18 Which of the following coordination compounds would exhibit optical isomerism?
[CBSE AIPMT 2004]
(a) Pentaamminenitrocobalt (III) iodide
(b) Diamminedichloroplatinum (II)
(c) Trans-dicyanobis (ethylenediamine) chromium (III) chloride
(d) Tris-(ethylenediamine) cobalt (III) bromide

## Ans. (d)

Tris-(ethylenediamine) cobalt (III) bromide $\left[\mathrm{Co}(\mathrm{en})_{3}\right] \mathrm{Br}_{3}$ exhibits optical isomerism:


19 According to IUPAC nomenclature sodium nitroprusside is named as
[CBSE AIPMT 2003]
(a) sodium pentacyanonitrosyl ferrate (II)
(b) sodium pentacyanonitrosyl ferrate (III)
(c) sodium nitroferricyanide
(d) sodium nitroferrocyanide

Ans. (b)
IUPAC name of sodium nitroprusside $\mathrm{Na}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{5} \mathrm{NO}\right]$ is sodium pentacyanoni trosyl ferrate (III) because in it NO is neutral ligand and the oxidation number of Fe is +3 . Which is calculated as

$$
\mathrm{Na}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{5} \mathrm{NO}\right]
$$

$2 \times(+1)+x+5 \times(-1)+1 \times 0=0$
[where $x=0 x i d a t i o n ~ s t a t e ~ o f ~ F e] ~$

$$
\begin{aligned}
& 2+x-5=0 \\
& x-3=0 \Rightarrow x=+3
\end{aligned}
$$

20 Which one of the following octahedral complexes will not show geometrical isomerism? ( $A$ and $B$ are monodentate ligands)
[CBSE AIPMT 2003]
(a) $\left[\mathrm{MA}_{4} \mathrm{~B}_{2}\right]$
(b) $\left[M A_{5} B\right]$
(c) $\left[\mathrm{MA}_{2} \mathrm{~B}_{4}\right]$
(d) $\left[M A_{3} B_{3}\right]$

Ans. (b)
[ $\mathrm{MA}_{5} \mathrm{~B}$ ] due to absence of symmetry of $B$ cannot exist in the form of cis-trans-isomer.

21 The hypothetical complex chloro diaquatriammine cobalt (III) chloride can be represented as
[CBSE AIPMT 2002]
(a) $\left[\mathrm{CoCl}\left(\mathrm{NH}_{3}\right)_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{Cl}_{2}$
(b) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3}\left(\mathrm{H}_{2} \mathrm{O}\right) \mathrm{Cl}_{3}\right]$
(c) $\left[\mathrm{Co}\left(\mathrm{NH}_{2}\right)_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2} \mathrm{Cl}\right]$
(d) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}\right] \mathrm{Cl}_{3}$

Ans. (a)
Chlorodiaquatriammine cobalt (III) chloride is $\left[\mathrm{CoCl}\left(\mathrm{NH}_{3}\right)_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{Cl}_{2}$.

22 Which of the following will give maximum number of isomers?
[CBSE AIPMT 2001]
(a) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}\right]$
(b) $\left[\mathrm{Ni}(\mathrm{en})\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$
(c) $\left[\mathrm{Ni}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)(e n)_{2}\right]^{2-}$
(d) $\left[\mathrm{Cr}(\mathrm{SCN})_{2}\left(\mathrm{NH}_{3}\right)_{4}\right]^{+}$

Ans. (d)
$\left.[\mathrm{Cr(SCN})_{2}\left(\mathrm{NH}_{3}\right)_{4}\right]^{+}$Oxidation number of Cr is 6 shows linkage, geometrical and optical isomerism.

23 Which one of the following complexes will have four isomers?
[CBSE AIPMT 2000]
(a) $\left[\mathrm{Co}(\mathrm{en})_{3}\right] \mathrm{Cl}_{3}$
(b) $\left[\mathrm{Co}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right] \mathrm{Cl}$
(c) $\left[\mathrm{Co}\left(\mathrm{PPh}_{3}\right)_{2}\left(\mathrm{NH}_{3}\right) \mathrm{Cl} I_{2}\right] \mathrm{Cl}$
(d) $\left[\mathrm{Co}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}\right] \mathrm{Cl}_{2}$

Ans. (b)
Complex $\left[\mathrm{Co}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right] \mathrm{Cl}$ will have four different isomers.
(i) Geometrical isomers

(ii) Optical isomers


Optically active cis-[Co(en) $\left.)_{2} \mathrm{Cl}_{2}\right] \mathrm{Cl}$
24 A coordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of $\mathrm{AgNO}_{3} \mathrm{~s}$ olution, we get two moles of AgCl precipitate. The ionic formula for this complex would be
[CBSE AIPMT 1998]
(a) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{NO}_{2}\right)\right] \mathrm{Cl} \mathrm{I}_{2}$
(b) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right]\left[\mathrm{Cl}\left(\mathrm{NO}_{2}\right)\right]$
(c) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4}\left(\mathrm{NO}_{2}\right) \mathrm{Cl}\right]\left[\left(\mathrm{NH}_{3}\right) \mathrm{Cl}\right]$
(d) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\right]\left[\left(\mathrm{NO}_{2}\right)_{2} \mathrm{Cl}_{2}\right]$

Ans.
(a)

The complex gives three ions in aqueous solution.
$\therefore$ The complex should be
$\left[\mathrm{CO}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NO}_{2}\right] \mathrm{Cl}_{2}$.
It will give three ions on dissociation as follows:

$$
\begin{aligned}
& {\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NO}_{2}\right]_{\mathrm{Cl}}^{2} \longrightarrow } {\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{NO}_{2}\right]^{2+} } \\
& 1 \text { mol } \\
&+ 2 \mathrm{Cl}^{-}(\text {Counter ion }) \\
& 2 \mathrm{~mol} \\
& 2 \mathrm{Cl}^{-}+2 \mathrm{AgNO}_{3} \longrightarrow 2 \mathrm{AgCl}+2 \mathrm{NO}_{3}^{-}
\end{aligned}
$$

25 The total number of possible isomers for the complex compound $\left[\mathrm{Cu}^{\prime \prime}\left(\mathrm{NH}_{3}\right)_{4}\right]\left[\mathrm{Pt}^{\prime \prime} \mathrm{Cl}_{4}\right]$ are
[CBSE AIPMT 1998]
(a) 5
(b) 6
(c) 3
(d) 4

Ans. (d)
Given complex gives four isomers that are as follow.
(i) $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]\left[\mathrm{PtCl}_{4}\right]$
(ii) $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}\right]\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right) \mathrm{Cl}_{3}\right]$
(iii) $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}\right]\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right) \mathrm{Cl}_{3}\right]$
(iv) $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4}\right]\left[\mathrm{CuCl}_{4}\right]$

26 IUPAC name of
$\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{3}(\mathrm{Br})\left(\mathrm{NO}_{2}\right) \mathrm{Cl}\right] \mathrm{Cl}$ is
[CBSE AIPMT 1998]
(a) triamminebromochloronitroplatinum (IV) chloride
(b) triamminebromonitrochloroplatinum (IV) chloride
(c) triamminechlorobromonitroplatinum (IV) chloride
(d) triamminenitrochlorobromoplatinum (IV) chloride

Ans. (a)
The IUPAC name of
$\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{3}(\mathrm{Br})\left(\mathrm{NO}_{2}\right) \mathrm{Cl}\right] \mathrm{Cl}$ is
triamminebromochloronitroplatinum (IV) chloride.
(Oxidation number of $\mathrm{Pt}=+4$, and ligands are arranged in alphabetical order)

27 The number of geometrical isomers of the complex
$\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)_{3}\left(\mathrm{NH}_{3}\right)_{3}\right]$ is
[CBSE AIPMT 1997]
(a) 4
(b) 0
(c) 2
(d) 3

Ans. (c)
Geometrical isomers of the complex $\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)_{3}\left(\mathrm{NH}_{3}\right)_{3}\right.$ ] are two. These are


Maridonal isomers
Facial isomers

28 The formula of dichlorobis (urea) copper (II) is [CBSE AIPMT 1997]
(a) $\left[\mathrm{Cu}\left\{\mathrm{O}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2} \mathrm{Cl}\right\}\right] \mathrm{Cl}$
(b) $\left[\mathrm{CuCl}_{2}\left\{\mathrm{O}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}\right\}_{2}\right]$
(c) $\left[\mathrm{Cu}\left\{\mathrm{O}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}\right\}\right] \mathrm{Cl}_{2}$
(d) $\left[\mathrm{CuCl}_{2}\left\{\mathrm{O}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2} \mathrm{H}_{2}\right\}\right]$

Ans. (b)
The formula of dichlorobis (urea) copper (II) is $\left[\mathrm{CuCl}_{2}\left\{\mathrm{O}=\mathrm{C}\left(\mathrm{NH}_{2}\right)_{2}\right\}_{2}\right]$.

29 The number of geometrical isomers for $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2}\right] \mathrm{Cl}_{2}$ is
[CBSE AIPMT 1995]
(a) 3
(b) 4
(c) 1
(d) 2

Ans. (d)
Geometrical isomers for $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$ is

pale yellow


30 An example of a double salt is
[CBSE AIPMT 1989]
(a) bleaching powder
(b) $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
(c) hypo
(d) potash alum

Ans. (d)
Double salts are additon or molecular compounds which are formed by two apparently saturated compounds but they lose their identity when dissolved in water. The most common example of double salt is potash alum $\mathrm{K}_{2} \mathrm{SO}_{4} \cdot \mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot 24 \mathrm{H}_{2} \mathrm{O}$.

## TOPIC 2

## Bonding in Coordination Compounds

31 Match List-I with List-II. [NEET 2021]

| List-I |  | List-II |  |
| :--- | :--- | :--- | :---: |
| A. $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$ | 1. | 5.92 BM |  |
| B. $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ | 2. 0 BM |  |  |
| C. $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$ | 3. | 4.90 BM |  |
| D. $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ | 4. 1.73 BM |  |  |

Choose the correct answer from the options given below

|  | $A$ | $B$ | $C$ | $D$ | $A$ | $B$ | $C$ | $D$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| (a) | 4 | 2 | 1 | 3 | (b) 2 | 4 | 3 | 1 |
| (c) 1 | 3 | 4 | 2 | (d) 4 | 1 | 2 | 3 |  |

Ans. (d)
A. $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$ Oxidation number of $\mathrm{Fe}=x+6(-1)=-3$
$x-6=-3 \Rightarrow x=+3$
Electronic configuration of
$\mathrm{Fe} \rightarrow[\mathrm{Ar}] 3 d^{6} 4 s^{2}$
Electronic configuration of $\mathrm{Fe}^{3+} \rightarrow[\mathrm{Ar}] 3 d^{5} 4 \mathrm{~s}^{0}$

$\mathrm{CN}^{-}$is a strong field ligand so, pairing of electrons occurs.

Number of unpaired electrons $=1$
$\mu_{s}=\sqrt{n(n+1)}=\sqrt{1(1+2)}=\sqrt{3}$

$$
=1.73 \mathrm{BM}
$$

B. $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}_{6}\right]^{3+}\right.$ Oxidation state of Fe is +3 .
Water is weak field ligand, so pairing of electron do not take place.


Number of unpaired electrons $=5$.

$$
\begin{aligned}
\mu_{s} & =\sqrt{n(n+2)}=\sqrt{5 \times(5+2)} \\
& =\sqrt{5 \times 7}=\sqrt{35}=5.92 \mathrm{BM}
\end{aligned}
$$

C. $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$ Oxidation state of Fe is +2 .
Electronic configuration of
$\mathrm{Fe}^{2+}=[\mathrm{Ar}] 3 d^{6} 4 \mathrm{~s}^{0}$
$\mathrm{CN}^{-}$is a strong field ligand, so pairing of electrons take place.


Number of unpaired electrons $=0$

$$
\mu_{s}=\sqrt{0(0+1)}=0 \mathrm{BM}
$$

D. $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{4-}$ Oxidation state of Fe is $+2\left(3 d^{6}\right)$.
Water is weak field ligand, so pairing of electron do not take place.


Number of unpaired electrons $=4$

$$
\begin{aligned}
\mu_{s} & =\sqrt{4(4+2)}=\sqrt{4 \times 6} \\
& =\sqrt{24}=4.90 \mathrm{BM}
\end{aligned}
$$

Hence, correct match is

$$
\mathrm{A} \rightarrow 4, \rightarrow \mathrm{~B} \rightarrow 1, \mathrm{C} \rightarrow 2, \mathrm{D} \rightarrow 3 .
$$

32 Urea reacts with water to form A which will decompose to form B. B when passed through $\mathrm{Cu}^{2+}(a q)$, deep blue colour solution $C$ is formed. What is the formula of $C$ from the following?
[NEET (Sep.) 2020]
(a) $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$
(b) $\mathrm{Cu}(\mathrm{OH})_{2}$
(c) $\mathrm{CuCO}_{3} \cdot \mathrm{Cu}(\mathrm{OH})_{2}$
(d) $\mathrm{CuSO}_{4}$

Ans. (a)
Complete reaction is



33 Which of the following is the correct order of increasing field strength of ligands to form coordination compounds?
[NEET (Sep.) 2020]
(a) $\mathrm{SCN}^{-}<\mathrm{F}^{-}<\mathrm{CN}^{-}<\mathrm{C}_{2} \mathrm{O}_{4}^{2-}$
(b) $\mathrm{F}^{-}<\mathrm{SCN}^{-}<\mathrm{C}_{2} \mathrm{O}_{4}^{2-}<\mathrm{CN}^{-}$
(c) $\mathrm{CN}^{-}<\mathrm{C}_{2} \mathrm{O}_{4}^{2-}<\mathrm{SCN}^{-}<\mathrm{F}^{-}$
(d) $\mathrm{SCN}^{-}<\mathrm{F}^{-}<\mathrm{C}_{2} \mathrm{O}_{4}^{2-}<\mathrm{CN}^{-}$

Ans. (d)
Increasing field strength of ligands to form coordination compounds, we have to follow the spectrochemical series.
$I^{-}<\mathrm{Br}^{-}<\mathrm{SCN}^{-}<\mathrm{Cl}^{-}<\mathrm{S}^{2-}<\mathrm{F}^{-}<\mathrm{OH}^{-}<$
$\mathrm{C}_{2} \mathrm{O}_{4}^{2-}<\mathrm{H}_{2} \mathrm{O}<\mathrm{NCS}^{-}<\mathrm{EDTA}^{4-}<\mathrm{NH}_{3}<\mathrm{en}<$ $\mathrm{CN}^{-}<\mathrm{CO}$
So, the order given in option (d):
$\mathrm{SCN}^{-}<\mathrm{F}^{-}<\mathrm{C}_{2} \mathrm{O}_{4}^{2-}<\mathrm{CN}^{-}$is correct.
34 The Crystal Field Stabilisation Energy (CFSE) for $\left[\mathrm{CoCl}_{6}\right]^{4-}$ is $18000 \mathrm{~cm}^{-1}$. The CFSE for $\left[\mathrm{CoCl}_{4}\right]^{2-}$ will be
[NEET (Odisha) 2019]
(a) $6000 \mathrm{~cm}^{-1}$
(b) $16000 \mathrm{~cm}^{-1}$
(c) $18000 \mathrm{~cm}^{-1}$
(d) $8000 \mathrm{~cm}^{-1}$

Ans. (d)
$\left[\mathrm{CoCl}_{6}\right]^{4-}$ is an octahedral while
$\left[\mathrm{CoCl}_{4}\right]^{2-}$ is a tetrahedral complex.

$$
\Delta_{\text {octahedral }}=18000 \mathrm{~cm}^{-1}
$$

We know that,

$$
\begin{aligned}
\Delta_{\text {tetrahedral }} & =\frac{4}{9} \Delta_{\text {octahedral }} \\
& =\frac{4}{9} \times 18000 \mathrm{~cm}^{-1}=8000 \mathrm{~cm}^{-1}
\end{aligned}
$$

35 Aluminium chloride in acidified aqueous solution forms a complex' $A^{\prime}$, in which hybridisation state of Al is ' $B$. What are ' $A$ ' and ' $B$ ', respectively? [NEET (Odisha) 2019]
(a) $\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}, s p^{3} d^{2}$
(b) $\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{3+}, s p^{3}$
(c) $\left[\mathrm{Al(H}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{3+}, d s p^{2}$
(d) $\left[\mathrm{All}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}, d^{2} s p^{3}$

Ans. (a)
Aluminium chloride in acidified aqueous solution forms an octahedral complex. Aqueous solution is mostly water and when the compound is dissolved in acidified aqueous solution, the water fills its vacancies and an octahedral complex, 'A' which is $\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ is formed.

$$
\begin{aligned}
\text { Al( } 13) & =s^{2} 22 s^{2}, 2 p^{6}, 3 s^{2}, 3 p^{1} \\
A^{3+} & =1 s^{2}, 2 s^{2}, 2 p^{6} .
\end{aligned}
$$



Thus, the hybridisation state of Al in $\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ is $s p^{3} d^{2}(\mathrm{~B})$.

36 Which of the following species is not stable? [NEET (Nationa) 2019]
(a) $\left[\mathrm{GeCl}_{6}\right]^{2-}$
(b) $\left[\mathrm{Sn}(\mathrm{OH})_{6}\right]^{2-}$
(c) $\left[\mathrm{SiCl}_{6}\right]^{2-}$
(d) $\left[\mathrm{SiF}_{6}\right]^{2-}$

Ans. (c)
$\left[\mathrm{SiCl}_{6}\right]^{2-}$ is not stable and does not exist because
(i) six large chloride ions cannot be accomdated around $\mathrm{Si}^{4+}$ due to limitation of its size.
(ii) interaction between lone pair of chloride ion and $\mathrm{Si}^{4+}$ is not very strong.
On the other hand, due to presence of $d$-orbital in $\mathrm{Si}, \mathrm{Ge}$ and Sn they form species like $\left[\mathrm{SiF}_{6}\right]^{2-},\left[\mathrm{GeCl}_{6}\right]^{2-}$ and $\left[\mathrm{Sn}(\mathrm{OH})_{6}\right]^{2-}$. Hence, option (c) is correct.

37 What is the correct electronic configuration of the central atom in $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ based on crystal field theory? [NEET (National) 2019]
(a) $t_{2 q}^{6} e_{g}^{0}$
(b) $e^{3} t_{2}^{3}$
(c) $e^{4} t_{2}^{2}$
(d) $t_{2 q}^{4} e_{g}^{2}$

Ans.
(a)
$\mathrm{InK}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$,
$\mathrm{Fe}^{2+}=[\mathrm{Ar}] 3 d^{6} 4 \mathrm{~s}^{0}$.
$\mathrm{CN}^{-}$is a strong field ligand and as it approaches the metal ion, the electrons must pair up.
The splitting of the $d$-orbitals in two sets orbitals in an octahedral complex, $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ may be represented as :


Hence, the electronic configuration of the central atom in $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ is $t_{2 g}^{6} e_{g}^{0}$.

38 Iron carbonyl, $\mathrm{Fe}(\mathrm{CO})_{5}$ is
[NEET 2018]
(a) trinuclear
(b) mononuclear
(c) tetranuclear
(d) dinuclear

Ans. (b)
Key Concept Compounds of transition metal with carbonyls (carbon monoxide) are known as metal carbonyls. These are classified into mononuclear, dinuclear, trinuclear and so on based on the number of central metal atoms/ions present in a complex.
Complexes following EAN rule have EAN of central metal/ion equal to nearest inert gas configuration and hence, are stable.
Effective atomic number (EAN) of the metal in a complex is given by
EAN =Atomic number (Z)

$$
\begin{aligned}
&- \text { Oxidation number (O.N) } \\
&+2(\text { Coordination number) } \\
&=26-0+2(5)=36
\end{aligned}
$$

Thus, $\mathrm{Fe}(\mathrm{CO})_{5}$ is a stable complex/ion. Since, there is only one central metal atom present in iron carbonyl, $\mathrm{Fe}(\mathrm{CO})_{5}$, thus it is mononuclear. The structure of $\mathrm{Fe}(\mathrm{CO})_{5}$ is shown below:


The examples of dinuclear, trinuclear complexes are $\mathrm{Co}_{2}(\mathrm{CO})_{18}, \mathrm{Fe}_{3}(\mathrm{CO})_{12}$ respectively.

39 An example of a sigma bonded organometallic compound is
[NEET 2017]
(a) ruthenocene
(b) Grignard's reagent
(c) ferrocene
(d) cobaltocene

Ans. (b)
The organometallic compounds having sigma bond between carbon and metal are sigma bonded organometallic. An example of a sigma bonded organometallic compound is Grignard's reagent.

$$
\underbrace{R-M g}_{\sigma-\text { bond }}-X
$$

Whereas, ruthenocene, ferrocene and cobaltocene are not sigma bonded organometallic compound.


40 Correct increasing order for the wavelengths of absorption in the visible region for the complexes of $\mathrm{CO}^{3+}$ is
[NEET 2017]
(a) $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+},\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$, $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
(b) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+},\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$, $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(c) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+},\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$, $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$
(d) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+},\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$, $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
Ans. (a)
Key concept Wavelength ( $\lambda$ ) of absorption is inversely proportional to $\operatorname{CFSE}\left(\Delta_{0}\right.$ value) of ligands attached with the central metal ion

$$
\text { i.e. } \quad \lambda \propto \frac{1}{\Delta_{0}}
$$

According to spectrochemical series.
$\mathrm{I}^{-}<\mathrm{Br}^{-}<\mathrm{S}^{2-}<\mathrm{SCN}^{-}<\mathrm{Cl}^{-}<\mathrm{F}^{-}<\mathrm{OH}^{-}$
$<\mathrm{C}_{2} \mathrm{O}_{4}^{2-}<\mathrm{O}^{2-}<\mathrm{H}_{2} \mathrm{O}<\mathrm{NSS}^{-}<\mathrm{NH}_{3}<$ en $<$ $\mathrm{NO}_{2}^{-}<\mathrm{CN}^{-}$


The CFSE of ligands attached with $\mathrm{Co}^{3+}$ ion is in the order
en $>\mathrm{NH}_{3}>\mathrm{H}_{2} \mathrm{O}$ (From spectrochemical series)
$\because$ Wavelength of absorbed light $(\lambda) \propto \frac{1}{\Delta_{0}}$
$\therefore$ For ligand the order of wavelength of absorption in the visible region will be : en $<\mathrm{NH}_{3}<\mathrm{H}_{2} \mathrm{O}$
or, $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}<\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}<$ $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$

41 Pick out the correct statement with respect to $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$
[NEET 2017]
(a) It is $s p^{3} d^{2}$ hybridised and octahedral
(b) It is $s p^{3} d^{2}$ hybridised and tetrahedral
(c) It is $d^{2} s p^{3}$ hybridised and octahedral
(d) It is $d s p^{2}$ hybridised and square planar
Ans. (c)
$\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ is $d^{2} s p^{3}$-hybridised and octahedral complex. In $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}, \mathrm{Mn}$ is in +3 oxidation state


42 Which of the following has longest $\mathrm{C}-0$ bond length? (Free $\mathrm{C}-0$ bond length in CO is $1.128 \AA$.)
[NEET 2016, Phase I]
(a) $\left[\mathrm{Co}(\mathrm{CO})_{4}\right]^{-}$
(b) $\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]^{2-}$
(c) $\left[\mathrm{Mn}(\mathrm{CO})_{6}\right]^{+}$
(d) $\mathrm{Ni}(\mathrm{CO})_{4}$

Ans. (b)
As negative charge on metal carbonyl complex increases, back $\pi$-bonding increases and hence bond length of $\mathrm{C}-\mathrm{O}$ bond increases while bond length of metal-carbon bond decreases.
Hence, $\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]^{2-}$ has longest $\mathrm{C}-0$ bond length among the given complexes. The correct order of bond length of the given complexes is
$\left[\mathrm{Mn}(\mathrm{CO})_{6}\right]^{+}<\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]<\left[\mathrm{Co}(\mathrm{CO})_{4}\right]^{-}$ $<\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]^{2-}$

43 Which of these statements about $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ is true?
[CBSE AIPMT 2015]
(a) $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ has no unpaired electrons and will be in a low-spin configuration.
(b) $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ has four unpaired electrons and will be in a low-spin configuration.
(c) $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ has four unpaired electrons and will be in a high-spin configuration.
(d) $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ has no unpaired electrons and will be in a high-spin configuration.
Ans. (a)
$\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$
$\mathrm{Co}^{3+}=1 s^{2} 2 s^{2} 2 p^{6} 3 s^{2} 3 p^{6} 3 d^{6}$
$\mathrm{CN}^{-}$is a strong field ligand and as it approaches the metal ion, the electrons must pair up.
The splitting of the $d$-orbitals into two sets of orbitals in an octahedral $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ may be represented as


Here, for $d^{6}$ ions, three electrons first enter orbitals with parallel spin put the remaining may pair up in $t_{2 g}$ orbital giving rise to low spin complex (strong ligand) field.
$\therefore\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ has no unpaired electron and will be in a low spin configuration.

44 The hybridisation involved in complex $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ is (Atomic number of $\mathrm{Ni}=28$ )
[CBSE AIPMT 2015]
(a) $d s p^{2}$
(b) $s p^{3}$
(c) $d^{2} s p^{2}$
(d) $d^{2} s p^{3}$

Ans. (a)
$\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$
Let oxidation state of Ni in $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ is
X.
$\therefore \quad x-4=-2$
or $\quad x=2$
Now, $\mathrm{Ni}^{2+}=[\mathrm{Ar}] 3 d^{8} 4 \mathrm{~s}^{0}$

$\because \mathrm{CN}^{-}$is a strong field ligand. Hence, all unpaired electrons are paired up.

$\therefore$ Hybridisation of $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ is $d s p^{2}$

45 Among the following complexes, the one which shows zero crystal field stabilisation energy (CFSE) is
[CBSE AIPMT 2014]
(a) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
(b) $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
(c) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
(d) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$

Ans. (b)
The CFSE for octahedral complex is given by

$$
\begin{aligned}
& \text { CFSE }=\left[-0.4 t_{2 g} e^{-}+0.6 e_{g} e^{-}\right] \\
& \text {ForMn }{ }^{3+},\left[3 d^{4}\right] \rightarrow t_{2 g}^{3} e_{g}^{1} \\
& \therefore \text { CFSE }=[(-0.4 \times 3)+(0.6 \times 1)]=-0.6 \\
& \text { ForFe }{ }^{3+},\left[3 d^{5}\right] \rightarrow t_{2 g}^{3} e_{g}^{2} \\
& \text { CFSE }=[-(0.4 \times 3)+(0.6 \times 2)]=0 \\
& \text { For } \mathrm{Co}^{2+},\left[3 d^{7}\right] \rightarrow t_{2 g}^{5} e_{g}^{2} \\
& \text { CFSE }=[(-0.4 \times 5)+(2 \times 0.6)]=-0.8 \\
& \text { For } \mathrm{Co}^{3+},\left[3 d^{6}\right] \rightarrow t_{2 g}^{4} e_{g}^{2} \\
& \text { CFSE }=[(-0.4 \times 4)+(2 \times 0.6)]=-0.4
\end{aligned}
$$

46 A magnetic moment of 1.73 BM will be shown by one among the following
[CBSE AIPMT 2013]
(a) $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$
(b) $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$
(c) $\mathrm{TiCl}_{4}$
(d) $\left[\mathrm{CoCl}_{6}\right]^{4-}$

Ans. (a)
Magnetic moment $\mu$ is related with number of unpaired electrons as

$$
\begin{aligned}
\mu & =\sqrt{n(n+2)} B M \\
(1.73)^{2} & =n(n+2) \\
\text { On solving } \quad n & =1
\end{aligned}
$$

Thus, the complex/compound having one unpaired electron exhibit a magnetic moment of 1.73 BM .
(a) $\ln \left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$

$$
\mathrm{Cu}^{2+}=[\mathrm{Ar}] 3 \mathrm{~d}^{9}
$$


(Although in the presence of strong field ligand $\mathrm{NH}_{3}$, the unpaired electron gets excited to higher energy level but it still remains unpaired).
(b) $\operatorname{In}\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$

$$
\mathrm{Ni}^{2+}=[\mathrm{Ar}] 3 d^{8}
$$



But $\mathrm{CN}^{-}$being strong field ligand pair up the unpaired electrons and hence in this complex, number of unpaired electrons $=0$.
(c) $\ln \left[\mathrm{TiCl}_{4}\right]$
$\mathrm{Ti}^{4+}=[\mathrm{Ar}]$
no unpaired electron.
(d) $\ln \left[\mathrm{CoCl}_{6}\right]^{4-}$
$\mathrm{Co}^{2+}=[\mathrm{Ar}] 3 \mathrm{Cl}^{7}$

| 1 | 1 | 1 | 1 | 1 |
| :--- | :--- | :--- | :--- | :--- |

It contains three unpaired electrons. Thus, $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ is the complex that exhibits a magnetic moment 1.73 BM .

47 Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?
[CBSE AIPMT 2012]
(a) $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
(b) $\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
(c) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(d) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$

Ans. (a)
Outer orbital complex utilises $(n-1) d$-orbitals for bonding and exhibit paramagnetic behaviour, only if there present unpaired electrons.
(a) $\operatorname{In}\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$ :

$\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}=$


So, this is an outer orbital complex as it involve 4d- orbitals for bonding, but having paramagnetic character.
(b) $\ln \left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$ :

$$
\mathrm{Zn}^{2+}=[\mathrm{Ar}] 3 d^{10}
$$



Thus, it is also an outer orbital complex as it involve $4 d$ - orbitals for bonding but it is diamagnetic as all the electrons are paired.
(c) $\operatorname{In}\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$,

$$
C r^{3+}=[\mathrm{Ar}] 3 d^{3}
$$

$\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}=$


Because of the involvement of $(n-1) d$, i.e.3d-orbital in hybridisation, it is an inner orbital complex. Its nature is paramagnetic because of the presence of three unpaired electrons.
(d) $\ln \left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
$\mathrm{Co}^{3+}=[\mathrm{Ar}] 3 d^{6}$

$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}=$


Because of the involvement of $(n-1) d$ orbital in hybridisation, it is an inner orbital complex. As all the electrons are paired, it is a diamagnetic complex.

48 Of the following complex ions which is diamagnetic in nature?
[CBSE AIPMT 2011]
(a) $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$
(b) $\left[\mathrm{CuCl}_{4}\right]^{2-}$
(c) $\left[\mathrm{CoF}_{6}\right]^{3-}$
(d) $\left[\mathrm{NiCl}_{4}\right]^{2-}$

Ans. (a)
Electronic configuration of $\mathrm{Ni}^{2+}$ in $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ is
$\mathrm{Ni}^{2+}=3 d^{8} 4 s^{0}$

$\mathrm{Ni}^{2+}$ has $d s p^{2}$ hybridisation, as $\mathrm{CN}^{-}$is a strong field ligand.

$\therefore\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ is diamagnetic (because of the absence of unpaired electrons).

49 Which of the following complex ions is not expected to absorb visible light?
[CBSE AIPMT 2010]
(a) $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$
(b) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(c) $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
(d) $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$

Ans. (a)
Key Idea For the absorption of visible light, presence of unpaired d-electrons is the necessity.
(a) $\ln \left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$, Ni is present as $\mathrm{Ni}^{2+}$.

(Pairing occurs because $\mathrm{CN}^{-}$is a strong field ligand).
Since, in $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$, no unpaired electron is present in $d$-orbitals so it does not absorb visible light.
(b) $\operatorname{In}\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}, \mathrm{Cr}$ is present as $\mathrm{Cr}^{3+}$. $\mathrm{Cr}^{3+}=[\mathrm{Ar}] 3 d^{3} 4 s^{0}$ (Three unpaired electrons)
(c) $\ln \left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$, Fe is present as $\mathrm{Fe}^{2+}$.
[Ar]3d $d^{6} 4 s^{0}$ (Four unpaired electrons)
(d) $\ln \left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$, Ni is present as $\mathrm{Ni}^{2+}$. $\mathrm{Ni}^{2+}=[\mathrm{Ar}] 3 d^{8} 4 \mathrm{~s}^{0}$ (Two paired electrons)
The complex given in option (b), (c), (d) have unpaired electrons, thus absorb visible light.
NOTE In presence of $\mathrm{NH}_{3}$ and $\mathrm{H}_{2} \mathrm{O}$ pairing does not occur as they are strong field ligand.

50 Crystal field stabilisation energy for high spin $d^{4}$ octahedral complex is
[CBSE AIPMT 2010]
(a) $-1.8 \Delta_{0}$
(b) $-1.6 \Delta_{0}+P$
(c) $-1.2 \Delta_{0}$
(d) $-0.6 \Delta_{0}$

Ans. (d)
Key Idea In case of high spin complex, $\Delta_{0}$ is small. than the pairing energy. That means, the energy required to pair up the fourth electron with the electrons of lower energy d-orbitals would be higher than that required to place the electrons in the higherd-orbital. Thus, pairing does not occur.
For high spind ${ }^{4}$ octahedral complex,

$\therefore$ Crystal field stabilisation energy

$$
\begin{aligned}
& =(-3 \times 0.4+1 \times 0.6) \Delta_{0} \\
& =(-1.2+0.6) \Delta_{0} \\
& =-0.6 \Delta_{0}
\end{aligned}
$$

51 Out of $\mathrm{TiF}_{6}^{2-}, \mathrm{CoF}_{6}^{3-}, \mathrm{Cu}_{2} \mathrm{Cl}_{2}$ and $\mathrm{NiCl}_{4}^{2-}$ (At. no. Z of $\mathrm{Ti}=22, \mathrm{Co}=27$, $\mathrm{Cu}=29, \mathrm{Ni}=28$ ), the colourless species are [CBSE AIPMT 2009]
(a) $\mathrm{TiF}_{6}^{2-}$ and $\mathrm{CoF}_{6}^{3-}$
(b) $\mathrm{Cu}_{2} \mathrm{Cl}_{2}$ and $\mathrm{NiCl}_{4}^{2-}$
(c) $\mathrm{TiF}_{6}^{2-}$ and $\mathrm{Cu}_{2} \mathrm{Cl}_{2}$
(d) $\mathrm{CoF}_{6}^{3-}$ and $\mathrm{NiCl}_{4}^{2-}$

Ans. (c)
$\ln \mathrm{TiF}_{6}^{2-}$, Ti is present as $\mathrm{Ti}^{4+}$.
$\mathrm{Ti}^{4+}=[\mathrm{Ar}] 3 d^{0} 4 \mathrm{~s}^{0}$
Hence, $\mathrm{TiF}_{6}^{2-}$ is colourless due to the absence of unpaired electrons.
In $\mathrm{Cu}_{2} \mathrm{Cl}_{2}, \mathrm{Cu}$ is present as $\mathrm{Cu}^{+}$.
$\mathrm{Cu}^{+}=[\mathrm{Ar}]$


Due to absence of unpaired electrons, $\mathrm{Cu}_{2} \mathrm{Cl}_{2}$ is colourless.

52 Which of the following complex ions is expected to absorb visible light? (At. no. of $\mathrm{Zn}=30, \mathrm{Sc}=21, \mathrm{Ti}=22, \mathrm{Cr}=24$ )
[CBSE AIPMT 2009]
(a) $\left[\mathrm{Sc}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}\left(\mathrm{NH}_{3}\right)_{3}\right]^{3+}$
(b) $\left[\mathrm{Ti}(\mathrm{en})_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]^{4+}$
(c) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(d) $\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$

Ans. (c)
$\ln \left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}, \mathrm{Cr}$ is present as $\mathrm{Cr}^{3+}$.

$$
\mathrm{Cr}^{3+}=[\mathrm{Ar}] 3 d^{3}, 4 s^{0}
$$

$$
\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}=[\mathrm{Ar}] 3 d^{3}
$$



Electron donated by $\mathrm{NH}_{3}$ ligand hybridisation $d^{2} s p^{3}$

Since, this complex has three unpaired electrons, excitation of electrons is possible and thus, it is expected that this complex will absorb visible light.

53 In which of the following coordination entities the magnitude of $\Delta_{\mathbf{o}}$ (CFSE in octahedral field) will be maximum?
(At. no. of $\mathrm{Co}=27$ )
[CBSE AIPMT 2008]
(a) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
(b) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(c) $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$
(d) $\left[\mathrm{Co}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$

Ans. (c)
As in all the given complex the central metal atom is same and contains same number of $d$ electrons, thus CFSE is decided by ligands. In case of strong field ligand, CFSE is maximum. $\mathrm{CN}^{-}$is a strong field ligand, Hence, in $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ magnitude of CFSE i.e. $\Delta_{0}$ is maximum.

54 Which of the following complexes exhibits the highest paramagnetic behaviour?
where, gly = glycine, en = ethylenediamine and bpy = bipyridyl moities)
(At. no. of $\mathrm{Ti}=22, \mathrm{C}=23, \mathrm{Fe}=26$,
$\mathrm{Co}=27$ )
[CBSE AIPMT 2008]
(a) $\left[\mathrm{V}(\mathrm{gly})_{2}(\mathrm{OH})_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$
(b) $\left[\mathrm{Fe}(\mathrm{en})(\mathrm{py})\left(\mathrm{NH}_{3}\right)_{2}\right]^{2+}$
(c) $\left[\mathrm{Co}(\mathrm{OX})_{2}(\mathrm{OH})_{2}\right]^{-}$
(d) $\left[\mathrm{Ti}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$

Ans. (c)
The electronic configuration of

$$
V(23)=[A r] 4 s^{2}, 3 d^{3}
$$

Let in $\left[\mathrm{V}(\mathrm{gly})_{2}(\mathrm{OH})_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$oxidation state of V is $x$.

$$
\begin{gathered}
x+(-1) \times 2+(-1) 2+(0 \times 2)=+1 \\
x=+5 \\
\mathrm{~V}^{5+}=[\mathrm{Ar}] 4 \mathrm{~s}^{0}, 3 d^{0}
\end{gathered}
$$

(no unpaired electrons)
The electronic configuration of

$$
\mathrm{Fe}(26)=[\mathrm{Ar}] 4 \mathrm{~s}^{2}, 3 d^{6}
$$

Let the oxidation state of Fe in
$\left.\left[\mathrm{Fe}(\mathrm{en})(\mathrm{ppy})(\mathrm{NH})_{3}\right)_{2}\right]^{2+}$ is $x$.

$$
\begin{gathered}
{[x+(0)+(0)+(0) \times 2]=+2} \\
x=+2 \\
\mathrm{Fe}^{2+}=[\mathrm{Ar}], 3 d^{6}
\end{gathered}
$$

( $\because 4$ unpaired electron)
but, bpy, en and $\mathrm{NH}_{3}$ all are strong field ligands, so pairing occurs and thus, $\mathrm{Fe}^{2+}$ contains no unpaired electron.
The electronic configuration of

$$
\mathrm{Co}(27)=[\mathrm{Ar}] 4 s^{2}, 3 d^{7}
$$

Let the oxidation state of Co in $\left[\mathrm{Co}(\mathrm{ox})_{2}(\mathrm{OH})_{2}\right]^{-}$is $x$

$$
\begin{array}{r}
x+(-2) \times 2+(-1) \times 2=-1 \\
x=+5
\end{array}
$$

$\mathrm{Co}^{5+}=[\mathrm{Ar}], 3 d^{4} \quad$ [ 4 unpaired electrons]
ox and OH are weak field ligands, thus pairing of electron units does not occur. The electronic configuration of

$$
\mathrm{Ti}(22)=[\mathrm{Ar}] 4 \mathrm{~s}^{2}, 3 d^{2}
$$

Oxidation state of Ti in $\left[\mathrm{Ti}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ is 3 .

$$
\begin{aligned}
\mathrm{Ti}^{3+}= & {[\mathrm{Ar}] 3 d^{1} } \\
& \text { (one unpaired electron) }
\end{aligned}
$$

Hence, complex $\left[\mathrm{Co}(\mathrm{Ox})_{2}(\mathrm{OH})_{2}\right]^{-}$has maximum number of unpaired electrons, thus show maximum paramagnetism.
$\overline{55}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{Cl}_{3}$ (at. no. of $\mathrm{Cr}=24$ ) has a magnetic moment of 3.83 BM, the correct distribution of $3 d$ electrons in the chromium of the complex is [CBSE AIPMT 2006]
(a) $3 d_{x y}^{1}, 3 d_{y z}^{1} 3 d_{z^{2}}^{1}$
(b) $3 d_{\left(x^{2}-y^{2}\right)^{\prime}} 3 d_{z^{2}}^{4}, 3 d_{x z}^{1}$
(c) $3 d_{x y}, 3 d_{\left(x^{2}-y^{2}\right)^{\prime}} 3 d_{y z}^{1}$
(d) $3 d_{x y}^{1}, 3 d_{y z}^{1}, 3 d_{z x}^{1}$

Ans. (d)
Magnetic moment $(\mu)=\sqrt{n(n+2)} B M$

$$
\text { or } \quad 3.83=\sqrt{n(n+2)}
$$

or $\quad 3.83 \times 3.83=n^{2}+2 n$
$14.6689=n^{2}+2 n$
$\mathrm{n} \simeq 3$
Hence, number of unpaired electrons in $d$-subshell of chromium $(\mathrm{Cr}=24)=3$.
So, the configuration of chromium ion is $C r^{3+}=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{3}$
$\ln \left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{Cl}_{2}$, oxidation state of Cr is +3 . Hence, in $3 d^{3}$ the distribution of electrons

$$
3 d_{x y}^{1}, 3 d_{y z^{2}}^{1}, 3 d_{z x}^{1}, 3 d_{x^{2}-y^{2}}^{0}, 3 d_{z^{2}}^{0}
$$

56 Which one of the following is an inner orbital complex as well as diamagnetic in behaviour?
(At. no. of $\mathrm{Zn}=30, \mathrm{Cr}=24, \mathrm{Co}=$ 27, $\mathrm{Ni}=28$ )
[CBSE AIPMT 2005]
(a) $\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
(b) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(c) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(d) $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$

Ans.
(c) In $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$, oxidation state of $\mathrm{Co}=+3$ and its coordination number is six.
${ }_{27} \mathrm{Co}=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{7}, 4 s^{2}$
$\mathrm{Co}^{3+}=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{6}$

$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ is an inner orbital complex as well as diamagnetic in behaviour (due to absence of unpaired electrons).

$$
\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+} \rightarrow s p^{3} d^{2}
$$

hybridisation (outer orbital complex and diamagnetic in nature).
$\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+} \rightarrow d^{2} s p^{3}$
hybridisation (inner orbital complex and paramagnetic in nature).

57 Among $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right],\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$, $\left[\mathrm{NiCl}_{4}\right]^{2-}$ species, the hybridisation states of the Ni atom are, respectively ( At . no. of $\mathrm{Ni}=28$ )
[CBSE AIPMT 2004]
(a) $s p^{3}, d s p^{2} d s p^{2}$
(b) $s p^{3}, d s p^{2}, s p^{3}$
(c) $s p^{3}, s p^{3}, d s p^{2}$
(d) $d s p^{2}, s p^{3}, s p^{3}$

Ans. (b)
In Ni(CO) ${ }_{4}$, nickel is sp $^{3}$ hybridised because in it oxidation state of Ni is zero. So, configuration of
${ }_{28} \mathrm{Ni}=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{8}, 4 s^{2}$

(CO is a strong field ligand, hence pairing of electrons will occur)
$\ln \left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$, nickel is present as $\mathrm{Ni}^{2+}$, so its configuration
$=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{8}$

$\mathrm{CN}^{-}$is strong field ligand, hence it makes $\mathrm{Ni}^{2+}$ electrons to be paired up.
$\ln \left[\mathrm{NiCl}_{4}\right]^{2-}$, nickel is present as $\mathrm{Ni}^{2+}$, so its configuration
$=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6}, 3 d^{8}$

$\mathrm{Cl}^{-}$is a weak field ligand, hence in $\mathrm{Ni}^{2+}$ electrons are not paired.

58 Considering $\mathrm{H}_{2} \mathrm{O}$ as a weak field ligand, the number of unpaired electrons in $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ will be (At. no. of $\mathrm{Mn}=25$ )
[CBSE AIPMT 2004]
(a) 3
(b) 5
(c) 2
(d) 4

Ans. (b)
$\ln \left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}, \mathrm{Mn}$ is present as $\mathrm{Mn}^{2+}$ or $\mathrm{Mn}(I I)$, so its electronic configuration $=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6}, 3 d^{5}$

$\ln \left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ the coordination number of Mn is six, and in presence
of weak field, ligand there will be no pairing of electrons in $3 d$. So, it will form high spin complex due to presence of five unpaired electrons.
$59 \mathrm{CN}^{-}$is strong field ligand. This is due to the fact that
[CBSE AIPMT 2004]
(a) it carries negative charge
(b) it is a pseudohalide
(c) it can accept electrons from metal species
(d) it forms high spin complexes with metal species
Ans. (b)
$\mathrm{CN}^{-}$is a strong field ligand because it is an example of pseudohalide. Pseudohalide ions are stronger coordinating ligands and they have the ability to form $\sigma$ and $\pi$-bonds.

60 Among the following which is not the $\pi$-bonded organometallic compound?
[CBSE AIPMT 2003]
(a) $\mathrm{K}\left[\mathrm{PtCl}_{3}\left(\eta^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)\right]$
(b) $\mathrm{Fe}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$
(c) $\mathrm{Cr}\left(\eta^{6}-\mathrm{C}_{6} \mathrm{H}_{6}\right)_{2}$
(d) $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{Sn}$

Ans. (d)
In $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{Sn}$ (organometallic compounds of tin) single bonds are present in form of sigma bond. pi-bonded organometallic compound includes alkenes, alkynes and some other carbon containing compounds having pi-electrons in their molecular orbitals.


61 The number of unpaired electrons in the complex ion $\left[\mathrm{CoF}_{6}\right]^{3-}$ is
[CBSE AIPMT 2003]
(At. no. of $\mathrm{Co}=27$ )
(a) 3
(b) 2
(c) 4
(d) 0

Ans. (c)
In complex ion $\left[\mathrm{CoF}_{6}\right]^{3-}$, Co is present in +3 oxidation state

$$
\begin{aligned}
& 27 \mathrm{Co}=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{7}, 4 s^{2} \\
& \mathrm{Co}^{3+}=1 s^{2}, 2 s^{2} 2 s^{6}, 3 s^{2} 3 p^{6} 3 d^{6}
\end{aligned}
$$

Therefore, the number of unpaired electrons in $3 d$ subshell of $\left[\mathrm{CoF}_{6}\right]^{3-}$ is 4 .

62 Atomic number of Cr and Fe are respectively 24 and 26 , which of the following is paramagnetic with the spin of electron?
[CBSE AIPMT 2002]
(a) $\left[\mathrm{Cr}(\mathrm{CO})_{6}\right]$
(b) $\left[\mathrm{Fe}(\mathrm{CO})_{5}\right]$
(c) $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$
(d) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$

Ans. (d)
Atoms, ions or molecules having unpaired electrons are paramagnetic. In $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$, Cr is present as $\mathrm{Cr}(\mathrm{III})$.

$$
\mathrm{Cr}^{3+}=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{3}
$$

In excited state


Number of unpaired electrons $=3$, so it is paramagnetic while rest of the species are diamagnetic.

63 Which of the following organometallic compounds is $\sigma$ and $\pi$-bonded? [CBSE AIPMT 2001]
(a) $\left[\mathrm{Fe}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}\right]$
(b) $\mathrm{K}\left[\mathrm{PtCl}_{3}\left(\eta^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)\right]$
(c) $\left[\mathrm{Co}(\mathrm{CO})_{5} \mathrm{NH}_{3}\right]^{2+}$
(d) $\mathrm{Fe}\left(\mathrm{CH}_{3}\right)_{3}$

Ans. (c)
$\left[\mathrm{Co}(\mathrm{CO})_{5} \mathrm{NH}_{3}\right]^{2+}$. In this complex, Co-atom attached with $\mathrm{NH}_{3}$ through $\sigma$-bonding and with CO through dative $\pi$-bond.

64 Coordination number of Ni in $\left[\mathrm{Ni}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{4}$ is
[CBSE AIPMT 2001]
(a) 3
(b) 6
(c) 4
(d) 2

Ans. (b)
Coordination number of nickel in $\left[\mathrm{Ni}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{4-}$ is 6 because $\mathrm{C}_{2} \mathrm{O}_{4}^{2-}$ is a bidentate ligand.

65 Which statement is incorrect?
[CBSE AIPMT 2001]
(a) $\mathrm{Ni}(\mathrm{CO})_{4}$-tetrahedral, paramagnetic
(b) $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$-square planar, diamagnetic
(c) $\mathrm{Ni}(\mathrm{CO})_{4}$-tetrahedral, diamagnetic
(d) $\left[\mathrm{Ni}(\mathrm{Cl})_{4}\right]^{2-}$ tetrahedral, paramagnetic
Ans. (a)
In $\mathrm{Ni}(\mathrm{CO})_{4}$, Ni has zero oxidation state. It is $s p^{3}$ hybridised.


Hence, it has no unpaired electron so, it shows the property of diamagnetism and has tetrahedral structure.
NOTE The valence shell electronic configuration of ground state Ni atom is $3 d^{8} 4 s^{2}$. The two electrons of $4 s$ are pushed into $3 d$ orbitals and get paired up because of the presentce of strong ligand (CO).

66 Which of the following will exhibit maximum ionic conductivity?
[CBSE AIPMT 2001]
(a) $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
(b) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$
(c) $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}$
(d) $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$

Ans. (a)
Ionic conductivity depends upon the number of ions produced in aqueous solution. $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ produces maximum number of ions, i.e. 5 .

$$
\underbrace{4 \mathrm{~K}^{+}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}}_{\text {Total } 5 \text { ions }}
$$

$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$ produces 3 , $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}$ produces 3 and $\left[\mathrm{Ni}(\mathrm{Co})_{4}\right]$ gives zero ions.

67 In the separation of $\mathrm{Cu}^{2+}$ and $\mathrm{Cd}^{2+}$ of IInd group in qualitative analysis of cations, tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with KCN to form the corresponding cyano complexes, which one of the following pairs of the complexes and their relative stability enables the separation of $\mathrm{Cu}^{2+}$ and $\mathrm{Cd}^{2+}$ ?
[CBSE AIPMT 2000]
(a) $\mathrm{K}_{3}\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]$ : less stable and $\mathrm{K}_{2}\left[\mathrm{Cd}(\mathrm{CN})_{4}\right]$ : more stable
(b) $\mathrm{K}_{3}\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]$ : more stable and $\mathrm{K}_{2}\left[\mathrm{Cd}(\mathrm{CN})_{4}\right]$ : less stable
(c) $\mathrm{K}_{2}\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]$ : less stable and $\mathrm{K}_{2}\left[\mathrm{Cd}(\mathrm{CN})_{4}\right]$ : more stable
(d) $\mathrm{K}_{2}\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]$ : more stable and $\mathrm{K}_{2}\left[\mathrm{Cd}(\mathrm{CN})_{4}\right]$ : less stable
Ans. (b)
$\mathrm{K}_{3}\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]$ is more stable while in $\mathrm{K}_{2}\left[\mathrm{Cd}(\mathrm{CN})_{4}\right]$ is less stable. Here, Cu in + 1oxidation state.

68 Shape of $\mathrm{Fe}(\mathrm{CO})_{5}$ is
[CBSE AIPMT 2000]
(a) octahedral
(b) square planar
(c) trigonal bipyramidal
(d) square pyramidal

Ans. (c)
In $\mathrm{Fe}(\mathrm{CO})_{5}$, the Fe -atom is indsp ${ }^{3}$ hybridised state, therefore the shape of molecule is trigonal bipyramidal. The hybridisation is as follows : ${ }_{26} \mathrm{Fe}=1 s^{2}, 2 s^{2} 2 p^{6}, 3 s^{2} 3 p^{6} 3 d^{6}, 4 s^{2} 4 p^{0}$ In presence of strong field ligand (CO), the electrons of $4 s$ are pushed in3d orbital and get paired up.
$\mathrm{InFe}(\mathrm{CO})_{5}$, the Fe -atom is

$d s p^{3}$ hybridised


69 The coordination number and oxidation state of Cr in $\mathrm{K}_{3}\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$ are respectively
[CBSE AIPMT 1995]
(a) 3 and +3
(b) 3 and 0
(c) 6 and +3
(d) 4 and +2

Ans. (c)
Coordination number of Cr is 6 (oxalate is bidentate ligand) and oxidation state of Cr in $\mathrm{K}_{3}\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$ is calculated below.

$$
\begin{aligned}
3(1)+x+3(-2) & =0 \\
3+x+(-6) & =0 \\
x & =6-3 \\
x & =+3
\end{aligned}
$$

70 In metal carbonyl having general formula $M(C O)_{x}$ where, $M=$ metal, $x=4$ and the metal is bonded to
[CBSE AIPMT 1995]
(a) carbon and oxygen
(b) $\mathrm{C} \equiv 0$
(c) oxygen
(d) carbon

Ans. (d)
In metal carbonyl $\mathrm{M(CO}_{4}$, metal is bonded to the ligand CO through carbon
atoms. These compounds contain both $\sigma$ and $\pi$-bonded complexes.
$\sigma$-bond between metal and carbon atom is formed when a vacant hybrid orbital of the metal atom overlaps with an orbital on C-atom of carbon monooxide containing a low pair of electron.
Formation of $\pi$-bond is occurs when a filled orbital of the metal atom overlaps with a vacant antibonding $\pi$ - orbital of C -atom of Co .

71 Which of the following ligands is expected to be bidentate?
[CBSE AIPMT 1994]
(a) $\mathrm{CH}_{3} \mathrm{NH}_{2}$
(b) $\mathrm{CH}_{3} \mathrm{C} \equiv \mathrm{N}$
(c) Br
(d) $\mathrm{C}_{2} \mathrm{O}_{4}^{2-}$

Ans. (d)
$\mathrm{C}_{2} \mathrm{O}_{4}^{2-}$ is a bidentate ligand because it has two donor atoms(sites) and can coordinate to the central ion at two positions.


72 Which one of the following statements is not correct?
[CBSE AIPMT 1994]
(a) Mercury (II) iodide dissolves in excess of potassium iodide solution
(b) Tin (IV) chloride is made by dissolving tin solution in concentrated hydrochloric acid
(c) Zinc dissolves in sodium hydroxide solution
(d) Carbon monoxide reduces iron (III) oxide to iron
Ans. (b)
$\mathrm{SnCl}_{4}$ is obtained by passing chlorine over tin.
So $\mathrm{Sn}(\mathrm{IV})$ chloride is made by dissolving tin solution in concentrated solution statement is incorrect and answer is (b).

73 The complex ion $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ is formed by $s p^{3} d^{2}$ hybridisation. Hence, the ion should possess
[CBSE AIPMT 1990]
(a) octahedral geometry
(b) tetrahedral geometry
(c) square planar geometry
(d) tetragonal geometry

Ans. (a)
Since the hybridisation of central metal tin $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$ complex ion is $s p^{3} d^{2}$ and coordination number of $\mathrm{Co}^{3+}$ is 6 . So, its geometry is octahedral.

## TOPIC 3

## Importance of Co-ordination Compounds

74 Which of the following complexes is used to be as an anticancer agent?
[CBSE AIPMT 2014]
(a) Mer- $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]$
(b) Cis- $\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]$
(c) $\mathrm{Cis}-\mathrm{K}_{2}\left[\mathrm{PtCl}_{2} \mathrm{Br}_{2}\right]$
(d) $\mathrm{Na}_{2} \mathrm{CoCl}_{4}$

Ans. (b)
Cis-platin is known as anticancer agent. The formula of cis-platin is cis$\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]$. Here, the word cis refers to cis geometrical isomer of
[ $\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{2}$ ]. It is used as an antitumour agent.

75 Which of the following does not have a metal-carbon bond?
(a) $\mathrm{Al}\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{3}$
[CBSE AIPMT 2004]
(b) $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{MgBr}$
(c) $\mathrm{K}\left[\mathrm{Pt}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right) \mathrm{Cl}_{3}\right]$
(d) $\mathrm{Ni}(\mathrm{CO})_{4}$

Ans. (a)
All $\left(\mathrm{OC}_{2} \mathrm{H}_{5}\right)_{3}$ does not have metal-carbon bond, (i.e. it is not an example of organometallic compound)
Structure


76 Which of the following is considered to be an anticancer species?
[CBSE AIPMT 2004]
(a)

(b)

(c)

(d)


Ans. (c)
Cis-platin is the isomer of $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$ which is used as an anticancer drug for treating several types of malignant tumours.


