Class - XII_Chemistry

## Ch. 9 - Coordination Compounds NCERT Solutions

## Q1. Explain the bonding in coordination compounds in terms of Werner's postulates.

Ans:
(a)A metal shows two kinds of valencies viz primary valency and secondary valency. Negative ions satisfy primary valencies and secondary valencies are filled by both neutral ions and negative ions.
(b)A metal ion has a fixed amount of secondary valencies about the central atom. These valencies also orient themselves in a particular direction in the space provided to the definite geometry of the coordination compound.
(c) Secondary valencies cannot be ionized, while primary valencies can usually be ionized.

Q2. FeSO4 solution mixed with (NH4)2SO4 solution in 1:1 molar ratio gives the test of Fe2+ ion but CuSO4 solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu2+ ion. Explain why?

Ans:
$\mathrm{FeSO}_{4}$ solutionwhen mixed with $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ in 1 : 1 molar ratio produces a double salt $\mathrm{FeSO}_{4}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ $6 \mathrm{H}_{2} \mathrm{O}$. This salt is responsible for giving the $\mathrm{Fe}^{2+}$.
$\mathrm{CuSO}_{4}$ mixed with aqueous ammonia in the ratio of $1: 4$ gives a complex salt. The complex salt does not ionize to give $\mathrm{Cu}^{2+}$, hence failing the test.

## Q3. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Ans:
( a ) Ligands - they are neutral molecules or negative ions bound to a metal atom in the coordination entity. Example- $\mathrm{Cl}^{-},{ }^{-} \mathrm{OH}$
(b) Coordination entity - they are electrically charged radicals or species. They constitute a central ion or atom surrounded by neutral molecules or ions. Example - [ $\left.\mathrm{Ni}(\mathrm{CO})_{4}\right]$, $\left[\mathrm{COCL}_{3}\left(\mathrm{NH}_{3}\right)_{3}\right]$
( c ) Coordination number- it is the number of bonds formed between ligands and central atom/ion. Example: (i) In $\mathrm{K}_{2}\left[\mathrm{PtCl}_{6}\right]$, 6 chloride ions are attached to Pt in the coordinate sphere. Thus, 6 is the coordination number of Pt.
(ii) In $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}$, the coordination number of the central metal ion ( Ni ) is 4 .
(d) Coordination polyhedron - it is the spatial positioning of ligands that are directly connected to the central atom in the coordination sphere. Example -
(1)

(ii)

( v ) Heteroleptic: they are complexes with their metal ion being bounded to more than one kind of donor group. Example - [ $\left.\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}\right]^{+}$, $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$
( vi ) Homoleptic: they are complexes with their metal ion being bounded to only one type of donor.
Example - $\left[\mathrm{PtCl}_{4}\right]^{2 \cdot},\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
Q4. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

Ans:
(i) Unidentate ligands: these are ligands with one donor site. Example $\mathrm{Cl}^{-}, \mathrm{NH}_{3}$
(ii) Ambidentate ligands: these are ligands that fasten themselves to the central metal ion/ atom via two different atoms.
Example $\mathrm{NO}^{-}{ }_{2}$ or $\mathrm{ONO}^{-}, \mathrm{CN}^{-}$or $\mathrm{NC}^{-}$
( iii) Didentate - these are ligands with two donor sites.
Example - Ethane-1,2-diamine , Oxalate ion ( $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ )
Q5. Specify the oxidation numbers of the metals in the following coordination entities:
(i) $[\mathrm{Co}(\mathrm{H} 2 \mathrm{O})(\mathrm{CN})(\mathrm{en}) 2] 2+$
(ii) $[\mathrm{CoBr} 2(e n) 2]+$
(iii) [PtCl4]2-
(iv) $\mathrm{K} 3[\mathrm{Fe}(\mathrm{CN}) 6]$
(v) $[\mathrm{Cr}(\mathrm{NH} 3) 3 \mathrm{Cl} 3]$

Ans:
(i) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{CN})(\mathrm{en})_{2}\right]^{2+}$
$\Rightarrow x+0+(-1)+2(0)=+2$
$x-1=+2$
$x=+3$
(ii) $\left[\mathrm{CoBr} 2(\mathrm{en})_{2}\right]^{2+}$
$\Rightarrow x+2(-1)+2(0)=+1$
$x-2=+1$
$x=+3$
(iii) $\left[\mathrm{PtCl}_{4}\right]^{2-}$
$\Rightarrow x+4(-1)=-2 x$
$x=+2$
(iv) $\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
$\Rightarrow\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$
$\Rightarrow x+6(-1)=-3$
$x=+3$
( v ) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]$
$\Rightarrow x+3(0)+3(-1)=0$
$x-3=0$
$x=3$
Q6. Using IUPAC norms write the formulas for the following:
(i) Tetrahydroxidozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanidonickelate(II)
(v) Pentaamminenitrito-O-cobalt(III)
(vi) Hexaamminecobalt(III) sulphate
(vii) Potassium tri(oxalato)chromate(III)
(viii) Hexaammineplatinum(IV)
(ix) Tetrabromidocuprate(II)
(x) Pentaamminenitrito-N-cobalt(III)

Ans:
(i) $[\mathrm{Zn}(\mathrm{OH}) 4] 2$ -
(ii) $\mathrm{K}_{2}\left[\mathrm{Pd} \mathrm{Cl}_{4}\right]$
( iii ) $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}\right]$
(iv) $\mathrm{K}_{2}\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]$
(v) $\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)\left(\mathrm{NH}_{3}\right)_{5}\right]^{2+}$
(vi) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{2}\left(\mathrm{SO}_{4}\right)_{3}$
(vii) $\mathrm{K}_{3}\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$
( viii ) $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{6}\right]^{4+}$
(ix ) $\left[\mathrm{Cu}(\mathrm{Br})_{4}\right]^{2-}$
( x ) $\left[\mathrm{Co}(\mathrm{ONO})\left(\mathrm{NH}_{3}\right)_{5}\right]^{2+}$
Q7. Using IUPAC norms write the systematic names of the following:
(i) [ $\mathrm{Co}(\mathrm{NH} 3) 6] \mathrm{Cl} 3$
(ii) [Pt(NH3)2Cl(NH2CH3)]Cl
(iii) [Ti(H2O)6]3+
(iv) $[\mathrm{Co}(\mathrm{NH} 3) 4 \mathrm{Cl}(\mathrm{NO} 2)] \mathrm{Cl}$
(v) $[\mathrm{Mn}(\mathrm{H} 2 \mathrm{O}) 6] 2+$
(vi) [NiCl4]2-
(vii) $[\mathrm{Ni}(\mathrm{NH} 3) 6] \mathrm{Cl} 2$
(viii) [Co(en)3]3+
(ix) [Ni(CO)4]

Ans:
(i) Hexaamminecobalt(III) chloride
( ii ) Diamminechlorido(methylamine) platinum(II) chloride
(iii) Hexaquatitanium(III) ion
(iv ) Tetraamminichloridonitrito-N-Cobalt(III) chloride
( v ) Hexaquamanganese(II) ion
( vi ) Tetrachloridonickelate(II) ion
( vii) Hexaamminenickel(II) chloride
( viii ) Tris(ethane-1, 2-diammine) cobalt(III) ion
(ix ) Tetracarbonylnickel(0)
Q8. List various types of isomerism possible for coordination compounds, giving an example of each. Ans :

The various types of isomerism present in coordination compounds are :
(i) Geometrical isomerism :

(ii) Optical isomerism :

(iii) Linkage isomerism : This is found in complexes that have ambidentate ligands. For e.g. :
$\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{NO}_{2}\right)\right] \mathrm{Cl}_{2}$ and $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}(\mathrm{ONO})\right] \mathrm{Cl}_{2}$
(iv) Coordination isomerism:

This kind of isomerism comes up when ligands are interchanged between anionic and cationic entities of different metal ions present in the complex.
Example - [ $\left.\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right]\left[\mathrm{Co}(\mathrm{CN})_{6}\right]$
( v ) Ionisation isomerism :
This is the kind of isomerism where a counter ion takes the place of a ligand inside the coordination sphere.. For e.g., $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Br}\right] \mathrm{SO}_{4}$ and $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{SO}_{4}\right] \mathrm{Br}$
( vi ) Solvate isomerism :
$\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl} . \mathrm{H}_{2} \mathrm{O}$
Q9. How many geometrical isomers are possible in the following coordination entities?
(i) $[\mathrm{Cr}(\mathrm{C2O4}) 3] 3-$
(ii) $[\mathrm{Co}(\mathrm{NH} 3) 3 \mathrm{Cl} 3]$

Ans:
(ii) In $\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$ no geometric isomers are present because it is a bidentate ligand.

(ii) In $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]$ two isomers are possible.



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Q10. Draw the structures of optical isomers of: (i) $[\mathrm{Cr}(\mathrm{C} 2 \mathrm{O} 4) 3] 3-$

## (ii) $[\mathrm{PtCl} 2(e n) 2] 2+$

(iii) $[\mathrm{Cr}(\mathrm{NH} 3) 2 \mathrm{Cl} 2(e n)]+$

Ans:
(i) $\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$

(ii) $\left[\mathrm{PtCl}_{2}(\mathrm{en})_{2}\right]^{2+}$

(iii) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}(\text { en })\right]^{+}$


Q11. Draw all the isomers (geometrical and optical) of: (i) [CoCl2(en)2]+
(ii) $[\mathrm{Co}(\mathrm{NH} 3) \mathrm{Cl}($ en)2] $2+$
(iii) $[\mathrm{Co}(\mathrm{NH} 3) 2 \mathrm{Cl} 2(e n)]+$

Ans:
(i) $\left[\mathrm{CoCl}_{2}(\mathrm{en})_{2}\right]^{+}$

(ii ) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right) \mathrm{Cl}(\mathrm{en})_{2}\right]^{2+}$

(iii) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}(\mathrm{en})\right]^{+}$


Q12. Write all the geometrical isomers of [ $\mathrm{Pt}(\mathrm{NH} 3)(\mathrm{Br})(\mathrm{Cl})(\mathrm{py})]$ and how many of these will exhibit optical isomers?

Ans:
[ Pt( $\mathrm{NH}_{3}$ )( Br )(Cl)(py )]


None of the above isomers will exhibit optical isomerism.
Q13. Aqueous copper sulphate solution (blue in colour) gives:
(i) a green precipitate with aqueous potassium fluoride and
(ii) a bright green solution with aqueous potassium chloride. Explain these experimental results

Ans:
The blue color of aqueous $\mathrm{CuSO}_{4}$ solution is because of the presence of $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{2+}$ ions.
(i) So when KF is added, $\mathrm{H}_{2} \mathrm{O}$ ligands are replaced by $\mathrm{F}^{-}$ligands which yield green colored $\left[\mathrm{CuF}_{4}\right]^{2+}$ ions.

$$
\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{2+}+4 \mathrm{~F}^{-} \rightarrow\left[\mathrm{CuF}_{4}\right]^{2-}+4 \mathrm{H}_{2} \mathrm{O}
$$

(ii ) So when KCL is added, $\mathrm{H}_{2} \mathrm{O}$ ligands are replaced by $\mathrm{Cl}^{-}$ligands which yield bright green colored $\quad\left[\mathrm{CuCl}_{4}\right]^{2+}$ ions.

$$
\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{2+}+4 \mathrm{Cl}^{-} \rightarrow\left[\mathrm{CuCl}_{4}\right]^{2-}+4 \mathrm{H}_{2} \mathrm{O}
$$

Q14. 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 $\mathrm{H} 2 \mathrm{~S}(\mathrm{~g})$ is passed through this solution?
Ans:

$$
2\left[\mathrm{CuSO}_{4}\right](a q)+10 \mathrm{KCN}(a q) \rightarrow 2 \mathrm{~K}_{2}\left[\mathrm{Cu}(C N)_{4}\right](a q)+2 \mathrm{~K}_{2} \mathrm{SO}_{4}(a q)+(C N)_{2}
$$

Therefore, the coordination entity obtained in the above process is $\mathrm{K}_{2}\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]$.
As the above coordination entity is highly stable it does not ionize to yield $\mathrm{Cu}^{2+}$ ions. Thus, no precipitate is obtained when hydrogen Sulphide gas is bubbled through it.
Q15. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:
(i) $[\mathrm{Fe}(\mathrm{CN}) 6] 4-$
(ii) [FeF6]3-
(iii) $[\mathrm{Co}(\mathrm{C2O4}) 3] 3-$
(iv) $[$ CoF6]3

Ans:
(i) $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$

In this coordination complex, the oxidation state of Fe is +3 .
$\mathrm{Fe}^{2+}$ : Electronic configuration is $3 \mathrm{~d}^{6}$
Orbitals of $\mathrm{Fe}^{2+}$ ion :


Since $\mathrm{CN}^{-}$is a strong field ligand, it causes the unpaired 3d electrons to pair up:


As there are six ligands around the central metal ion, the most practical hybridization is $\mathrm{d}^{2} \mathrm{sp}^{3}, \mathrm{~d}^{2} \mathrm{sp}^{3}$ hybridized orbitals of $\mathrm{Fe}^{2+}$ are:


6 electron pairs from $\mathrm{CN}^{-}$ions take the place of the six hybrid $\mathrm{d}^{2} \mathrm{sp}^{3}$ orbitals.
Then,

Thus, the geometry of the complex is octahedral and it is a diamagnetic complex ( since all the electrons are paired ).
(ii) $[\mathrm{FeF} 6]^{3-}$

In this coordinate entity the oxidation state of iron is +3 .
Orbitals of $\mathrm{Fe}^{+3}$ ion:

## 

There are $6 \mathrm{~F}^{-}$ions. Hence, it will go through $\mathrm{d}^{2} \mathrm{sp}^{3}$ or $\mathrm{sp}^{3} \mathrm{~d}^{2}$ hybridization.
Since $F^{-}$is a weak field ligand, it does not cause the pairing of the electrons in the 3d orbital. Thus, the most practical hybridization is $s p^{3} d^{2} . \mathrm{sp}^{3} \mathrm{~d}^{2}$ hybridized orbitals of Fe are :


Thus, the geometry of this coordinate entity is octahedral.
(iii) $\left[\mathrm{Co}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$

In this complex, the oxidation state of cobalt is +3 .
Orbitals of $\mathrm{Co}^{3+}$ ion:

$$
\frac{\square 1 T 11 T]}{3} a_{4}^{\square} \underbrace{\square}_{4} \frac{\square T T}{\square}
$$

Oxalate is a weak field ligand. Thus, it will not cause the pairing of the 3d orbital electrons.
As there are 6 ligands, hybridization has to be either $s p^{3} d^{2}$ or $d^{2} s p^{3}$ hybridization.
$\mathrm{sp}^{3} \mathrm{~d}^{2}$ hybridization of $\mathrm{Co}^{3+}$ :

The 6 electron pairs from the 3 oxalate ions (oxalate anionis a bidentate ligand) occupy these $\mathrm{sp}^{3} \mathrm{~d}^{2}$ orbitals :

6drearn pers from
jondatic
Thus, the complex shows octahedral geometry.
(iv )) $\left[\mathrm{CoF}_{6}\right]^{3-}$
In this complex Cobalt has an oxidation state of +3 .
Orbitals of $\mathrm{Co}^{3+}$ ion:


As, fluoride ion is a weak field ligand it will not cause the 3d electrons to pair. Hence, the $\mathrm{Co}^{3+}$ ion will go through $\mathrm{sp}^{3} \mathrm{~d}^{2}$ hybridization.
$\mathrm{sp}^{3} \mathrm{~d}^{2}$ hybridized orbitals of $\mathrm{Co}^{3+}$ ion are :


Thus, the complex has a geometric configuration of an octahedral and it is paramagnetic.

## Q16. Draw figure to show the splitting of $d$ orbitals in an octahedral crystal field.

Ans:


Q17. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

## Ans:

A series of common ligands in ascending order of their crystal-field splitting energy (CFSE) is termed as the Spectrochemical series.
Strong field ligands have larger values of CFSE. Whereas, weak field ligands have smaller values of CFSE.

Q18. What is crystal field splitting energy? How does the magnitude of $\Delta 0$ decide the actual configuration of $d$ orbitals in a coordination entity?

Ans:
Crystal-field splitting energy is the difference in the energy between the two levels (i.e., $\mathrm{t}_{2 \mathrm{~g}}$ and $\mathrm{e}_{\mathrm{g}}$ ) that have split from a degenerated d orbital because of the presence of a ligand. It is symbolized as $\Delta \mathrm{o}$. Once the orbitals split up, electrons start filling the vacant spaces. An electron each goes into the three $t_{2 g}$ orbitals, the fourth electron, however, can enter either of the two orbitals:
(1) It can go to the $e_{g}$ orbital ( producing $t_{2 g}{ }^{3}{ }_{g}{ }^{1}$ like electronic configuration), or
(2) it can go to the $\mathrm{t}_{2 g}$ orbitals (producing $\mathrm{t}_{2 g}{ }^{4} \mathrm{e}_{\mathrm{g}}{ }^{0}$ like electronic configuration).

This filling of the fourth electron is based on the energy level of $\Delta \mathrm{o}$. If a ligand has a $\Delta \mathrm{o}$ value smaller than the pairing energy, then the fourth electron enters the $\mathrm{e}_{\mathrm{g}}$ orbital. However, if the value of $\Delta \mathrm{o}$ is greater than the value of pairing energy, the electron enters $t_{2 g}$ orbital.

Q19. $[\mathrm{Cr}(\mathrm{NH} 3) 6] 3+$ is paramagnetic while $[\mathrm{Ni}(\mathrm{CN}) 4] 2$ - is diamagnetic. Explain why?
Ans:
$\ln \left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$, Ni has an oxidation state of +2 . Thus, it has $\mathrm{d}^{8}$ configuration. $\mathrm{Ni}^{2+}$.

$\mathrm{CN}{ }^{-}$being a strong field ligand causes the electrons in 3d orbitals to pair. This causes, $\mathrm{Ni}^{2+}$ to undergo dsp ${ }^{2}$ hybridization.


Since all the electrons are paired, it is diamagneticin nature.
Cr has an oxidation state of +3 . Thus, it has a $\mathrm{d}^{3}$ configuration. $\mathrm{As}, \mathrm{NH}_{3}$ is not a strong field ligand it does not cause the electrons in the 3d orbital to pair.
$\mathrm{Cr}^{3+}$ :


It undergoes $\mathrm{d}^{2} \mathrm{sp}^{3}$ hybridization and the 3 d orbital electrons remain unpaired. Thus, $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ is paramagnetic in nature.

## Q20. A solution of [ $\mathrm{Ni}(\mathrm{H} 2 \mathrm{O}) 6] 2+$ is green but a solution of $[\mathrm{Ni}(\mathrm{CN}) 4] 2-$ is colourless. Explain

Ans:
[ $\left.\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ consists of $\mathrm{Ni}^{+2}$ ion with $3 \mathrm{~d}^{8}$ electronic configuration. In this configuration, there are two unpaired electrons which cannot pair up because $\mathrm{H}_{2} \mathrm{O}$ is a weak ligand. Thus, the $d-d$ transition absorbs
the incoming light and it emits a green light. Thereby, giving a green color to the solution.
$\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2 \cdot}$ consists of $\mathrm{Ni}^{+2}$ ion with $3 \mathrm{~d}^{8}$ electronic confıguration. But, $\mathrm{CN}^{-}$is present here, which is a strong ligand and in its presence, the unpaired electrons pair up. Thus, there is no $d-d$ transition so no color.

## Q21. [ $\mathrm{Fe}(\mathrm{CN}) 6] 4$ - and $[\mathrm{Fe}(\mathrm{H} 2 \mathrm{O}) 6] 2+$ are of different colours in dilute solutions. Why?

Ans:
[ $\left.\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ and $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$ have two different ligands $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CN}^{-}$. $\mathrm{CN}^{-}$being a strong field ligand has a higher value of CFSE ( crystal field splitting energy ) than water. As a result, the d-d transitions absorb and give back different wavelengths of light. Thus, they have different colors in a solution.

## Q22. Discuss the nature of bonding in metal carbonyls.

Ans:
In metal carbonyls, the metal-carbon bond contains both the $\sigma$ and $\pi$ bond characters.A $\sigma$ bond forms when a lone pair of electrons is donated to the empty orbital of the metal by the carbonyl carbon. A $\pi$ bond forms when a pair of electrons is donated to the empty antibonding $\pi^{\star}$ orbital by the filled d orbital of the metal. This in entirety stabilizes and strengthens the metal-ligand bonding.
The above two types of bonding is represented as:


Q23. Give the oxidation state, $d$ orbital occupation and coordination number of the central metal ion in the following complexes:
(i) K3[Co(C2O4)3] (iii) (NH4)2[CoF4]
(ii) cis-[CrCl2(en)2]Cl (iv) [Mn(H2O)6]SO4

Ans:
(i) $\mathrm{K}_{3}\left[\mathrm{Co}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$

Central metal ion: Co.
Coordination number $=6$
We know,
Oxidation state is :
$x-6=-3$
$x=+3$
The d orbital occupation : $\mathrm{t}_{2 \mathrm{~g}}{ }^{6} \mathrm{e}_{\mathrm{g}}{ }^{0}$.
(ii ) cis - [ $\left.\mathrm{Cr}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right] \mathrm{Cl}$
Central metal ion : Cr.
Coordination number $=6$.
We know,
Oxidation state is :
$x+2(0)+2(-1)=+1$
$x-2=-1$
$x=+3$
The d orbital occupation : $\mathrm{t}_{2 \mathrm{~g}}{ }^{3}$.
(iii) $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{CoF}_{4}\right]$

Central metal ion: Co.
Coordination number $=4$.
We know,
Oxidation state is:
$x-4=-2$
$x=+2$
The d orbital occupation: $\mathrm{eg}^{4} \mathrm{t}_{2 \mathrm{~g}}{ }^{3}$.
(iv) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SO}_{4}$

Central metal ion : Mn.
Coordination number $=6$.
We know,
Oxidation state is :
$x+0=2$
$x=+2$
The d orbital occupation : $\mathrm{t}_{2 \mathrm{~g}}{ }^{3} \mathrm{e}_{\mathrm{g}}{ }^{4}$.
Q24. 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) $\mathrm{K}[\mathrm{Cr}(\mathrm{H} 2 \mathrm{O}) 2(\mathrm{C} 2 \mathrm{O} 4) 2] .3 \mathrm{H} 2 \mathrm{O}$
(ii) [ $\mathrm{Co}(\mathrm{NH} 3) 5 \mathrm{Cl}-] \mathrm{Cl} 2$
(iii) [CrCl3(py)3]
(iv) $\mathrm{Cs}[\mathrm{FeCl} 4]$
(v) $\mathrm{K} 4[\mathrm{Mn}(\mathrm{CN}) 6]$

Ans:
(i) IUPAC name = Potassium diaquadioxalatochromate (III) trihydrate.

Coordination number $=6$
Oxidation state of chromium :
$x+0+2(-2)=-1$
$x=3$
Electronic configuration: $3 \mathrm{~d}^{3}=\mathrm{t}_{2 \mathrm{~g}}{ }^{3}$
Shape: Octahedral
Stereochemistry :


Magnetic moment, $\mu=\sqrt{n(n+2)} \quad[\mathrm{n}=$ unpaired electrons ]
$=\sqrt{3(3+2)}$
$=\sqrt{15} \approx 4 \mathrm{BM}$
(ii ) IUPAC name = Pentaamminechloridocobalt(III) chloride

Coordination number = 6
Oxidation state of Co :
$x+0-1=+2$
$x=3$
Electronic configuration: $3 d^{6}=t_{2 g}{ }^{6}$
Shape: Octahedral
Stereochemistry:

$\mathrm{n}=0$.
Thus, Magnetic moment $=0$
( iii ) IUPAC name = Trichloridotripyridinechromium (III)
Coordination number $=6$
Oxidation state of Cr :
$x-3+0=0$
$x=3$
Electronic configuration: $3 \mathrm{~d}^{3}=\mathrm{t}_{2 \mathrm{~g}}{ }^{3}$
Shape: Octahedral
Stereochemistry :
$n=3$
Magnetic moment, $\mu=\sqrt{n(n+2)}$
$=\sqrt{3(3+2)}$
$=\sqrt{15} \approx 4 \mathrm{BM}$
(iv) IUPAC name = Caesiumtetrachloroferrate (III)

Coordination number $=4$
Oxidation state of Fe :
$x-4=-1$
$x=3$
Electronic configuration: $d^{6}=e_{g}{ }^{2} t_{2 g}{ }^{3}$
Shape : Tetrahedral
Stereochemistry :- optically inactive
$\mathrm{n}=5$
Magnetic moment, $\mu=\sqrt{n(n+2)}$
$=\sqrt{5(5+2)}$
$=\sqrt{35} \approx 6 \mathrm{BM}$
( v ) IUPAC name = Potassium hexacyanomanganate(II)
Coordination number $=6$
Oxidation state of Mn :
$x-6=-4$
$x=+2$
Electronic configuration: $3 d^{5}=t_{2 g}{ }^{5}$
Shape: Octahedral
Stereochemistry :- optically inactive
n = 1
Magnetic moment, $\mu=\sqrt{n(n+2)}$
$=\sqrt{1(1+2)}$
$=\sqrt{3}=1.732 \mathrm{BM}$

## Q25. Explain the violet colour of the complex [Ti(H2O)6]3+ on the basis of crystal field theory

 Ans:Stability of a coordination compound in a solution is the degree/level of association among the species involved in a state of equilibrium.
Stability can also be written quantitatively in terms of formation constant or stability constant.
$M+3 L \quad M L_{3}$
Stability constant, $\beta=\frac{\left[M L_{3}\right]}{[M][L]^{3}}$
Greater the value of $\beta$, stronger is the metal-ligand bond.
Factors responsible for the stability of a complex:
(1) Charge on the central metal ion - bigger the charge, more stable is the complex.
( 2 ) Nature of ligand - chelating ligand produces a more stable complex.
( 3 ) The basic strength of ligand- more basic aligand, more stable its complex.
Q26. What is meant by the chelate effect? Give an example.
Ans:
When a polydentate or a bidentate ligand fastens itself toa metal ion in such a way that it assumes the shape of a ring, the metal-ligand bond becomes more stable. These rings are called chelate rings.
From here we can infer that complexes with chelate rings are more stable than complexes without the rings. This phenomenon is termed the chelate effect.

$$
\left.\begin{array}{lr}
\mathrm{Ni}^{2+}(\mathrm{aq})+6 \mathrm{NH}_{3} \\
\log \beta=7.99 & {\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}(\mathrm{aq})} \\
\mathrm{Ni}^{2+}(\mathrm{aq})+\text { 3en }(\mathrm{aq}) & {\left[\mathrm{Ni}(\mathrm{en})_{3}\right]^{2+}(\mathrm{aq})}
\end{array}\right)
$$



Q27. Discuss briefly giving an example in each case the role of coordination compounds in: (i) biological systems (iii) analytical chemistry (ii) medicinal chemistry and (iv) extraction/metallurgy of metals.

Ans:
(i) Role in biological systems:

In the body of animals, there are several very important coordination compounds e.g. hemoglobin is a coordination compound of iron.
In plants, chlorophyll pigment is a coordination compound of magnesium.
( ii ) Role in medicinal chemistry:
So many coordinate compounds are used for curing purposes. For e.g., a coordination compound of platinum, cis-platin is used for checking the growth of tumors.
( iii ) Role in analytical chemistry:
Determination of hardness of the water.
( iv) Role in metallurgy or extraction:
During metal extraction from ores, complexes are formed. For e.g. gold combines with cyanide ions in an aqueous solution. Gold is then extracted from this complex using zinc.
Q28. How many ions are produced from the complex $\mathrm{Co}(\mathrm{NH} 3) 6 \mathrm{Cl} 2$ in solution?
(i) 6 (ii) 4 (iii) 3 (iv) 2

Ans:
(iii) 3

The given complex $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{2}$ ionizes to give three ions,viz one $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{+}$and two $\mathrm{Cl}^{-}$ions.
Q29. Amongst the following ions which one has the highest magnetic moment value?
(i) $[\mathrm{Cr}(\mathrm{H} 2 \mathrm{O}) 6] 3+$
(ii) $[\mathrm{Fe}(\mathrm{H} 2 \mathrm{O}) 6] 2+$
(iii) $[\mathrm{Zn}(\mathrm{H} 2 \mathrm{O}) 6] 2+$

Ans:
(i) $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ number of unpaired electrons, $n=3$

Magnetic moment, $\mu=\sqrt{3(3+2)}$

$$
=\sqrt{3(3+2)}
$$

$=\sqrt{15} \approx 4 \mathrm{BM}$
(ii) $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
number of unpaired electrons, $n=4$
Magnetic moment, $\mu=\sqrt{4(4+2)}$

$$
=\sqrt{4(4+2)}
$$

$=\sqrt{24} \approx 5 \mathrm{BM}$
(iii) $\left[\mathrm{Zn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2}$
$\mathrm{n}=0$
Thus, $\left[\mathrm{Zn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2}$ has the highest magnetic moment value.

Ans:
$\mathrm{K}\left[\mathrm{Co}(\mathrm{CO})_{4}\right]=\mathrm{K}^{+}\left[\mathrm{Co}(\mathrm{CO})_{4}\right]^{-}$
We know,
$\Rightarrow x+0=-1$ [Where $x$ is the oxidation number.]
$x=-1$

Q31. Amongst the following, the most stable complex is
(i) $[\mathrm{Fe}(\mathrm{H} 2 \mathrm{O}) 6] 3+$
(ii) $[\mathrm{Fe}(\mathrm{NH} 3) 6] 3+$
(iii) $[\mathrm{Fe}(\mathrm{C} 2 \mathrm{O} 4) 3] 3-$
(iv) [FeCl6]3-

Ans:
In all the cases Fe has an oxidation state of $+3 .\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}$ is a bidentate chelating ligand and it forms chelating rings. Thus, ( iii ) is the most stable complex.

Q32. What will be the correct order for the wavelengths of absorption in the visible region for the following:
[ $\mathrm{Ni}(\mathrm{NO} 2) 6] 4-$, $[\mathrm{Ni}(\mathrm{NH} 3) 6] 2+$, $[\mathrm{Ni}(\mathrm{H} 2 \mathrm{O}) 6] 2+$ ?
Ans:
All of the complexes have the same metal ion, so the energy absorption depends upon the CFSE values of the ligands. According to the spectro-chemical series, the CFSE values of the ligands are in the order of :
$\mathrm{H}_{2} \mathrm{O}<\mathrm{NH}_{3}<\mathrm{NO}_{2}{ }^{-}$
As,
$\mathrm{E}=\mathrm{hc} / \lambda$
$\Rightarrow E \propto 1 / \lambda$
Therefore, the values of the absorbed wavelength in ascending order would be :
$\left[\mathrm{Ni}\left(\mathrm{NO}_{2}\right)_{6}\right]^{4-}<\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}<\left[\mathrm{Ni}\left(\mathrm{NO}_{2}\right)_{6}\right]^{4-}$

