Q1. Explain the bonding in coordination compounds in terms of Werner's postulates.
Answer:
( 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 ionised, while primary valencies can usually be ionised.
Q2. $\mathrm{FeSO}_{4}$ solution mixed with $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ solution in 1:1 molar ratio gives the test of $\mathrm{Fe}^{2+}$ ion, but $\mathrm{CuSO}_{4}$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of $\mathrm{Cu}^{2+}$ ion. Explain why.

Answer:
$\mathrm{FeSO}_{4}$ solution, when 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 a 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 for each of the following: ligand, coordination entity, coordination number, coordination polyhedron, heteroleptic and homoleptic.

Answer:
( a ) Ligands: They are neutral molecules or negative ions bound to a metal atom in the coordination entity. For example, Cl -, 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.
For 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 $(\mathrm{Ni})$ is 4 .
( d ) Coordination polyhedron: It is the spatial positioning of ligands that are directly connected to the central atom in the coordination sphere. For example,
(i)

(ii)

Tetrahedral
( v ) Heteroleptic: they are complexes with their metal ion being bounded to more than one kind of donor group. For 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 $-\left[\mathrm{PtCl}_{4}\right]^{2-}$, $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$

Q4. What is meant by unidentate, bidentate and ambidentate ligands? Give two examples for each.
Answer:
( i ) Unidentate ligands: These are ligands with one donor site. For 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 $\mathrm{NO}^{-}$or $\mathrm{ONO}^{-}, \mathrm{CN}^{-}$or $\mathrm{NC}^{-}$
( iii ) Bidentate: These are ligands with two donor sites.
For 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) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{CN})(\mathrm{en})_{2}\right]^{2+}$
(ii) $\left[\mathrm{CoBr}_{2}(\mathrm{en})_{2}\right]^{+}$
(iii) $\left[\mathrm{PtCl}_{4}\right]^{2-}$
(iv) $\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
(v) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]$

Answer:
(i ) $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{CN})(\mathrm{en})_{2}\right]^{2+}$
$\Rightarrow x+0+(-1)+2(0)=+2$
$\mathrm{x}-1=+2$
$\mathrm{x}=+3$
(ii) $\left[\mathrm{Co} \mathrm{Br} 2(\mathrm{en})_{2}\right]^{1+}$
$\Rightarrow x+2(-1)+2(0)=+1$
$\mathrm{x}-2=+1$
$\mathrm{x}=+3$
(iii) $\left[\mathrm{PtCl}_{4}\right]^{2-}$
$\Rightarrow x+4(-1)=-2$
$\mathrm{x}=+2$
(iv ) $\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right] \Rightarrow\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$
$\Rightarrow x+6(-1)=-3$
$\mathrm{x}=+3$
( v ) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right] \Rightarrow \mathrm{x}+3(0)+3(-1)=0$
$\mathrm{x}-3=0$
$\mathrm{x}=3$
Q6. Using IUPAC norms, write the formulas for the following:
(i) Tetrahydroxidozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanonickelate(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)

Answer:
( i ) $\left[\mathrm{Zn}(\mathrm{OH})_{4}\right]^{2-}$
( 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) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}$
(ii) $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}\left(\mathrm{NH}_{2} \mathrm{CH}_{3}\right)\right] \mathrm{Cl}$
(iii) $\left[\mathrm{Ti}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
(iv) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}\left(\mathrm{NO}_{2}\right)\right] \mathrm{Cl}$
(v) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
(vi) $\left[\mathrm{NiCl}_{4}\right]^{2-}$
(vii) $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{2}$
(viii) $\left[\mathrm{Co}(\mathrm{en})_{3}\right]^{3+}$
(ix) $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$

Answer:
( 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-diamine) cobalt(III) ion
( ix ) Tetracarbonylnickel(0)
Q8. List various types of isomerism possible for coordination compounds, giving an example of each. Answer:

The various types of isomerism present in coordination compounds are:

(i) Geometrical isomerism:
( ii ) Optical isomerism:


BYJU'S
BYJU'S


(iii) Linkage isomerism: This is found in complexes that have ambidentate ligands. For example, $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5}\left(\mathrm{NO}_{2}\right)\right.$ $] \mathrm{Cl}_{2}$ 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.
For 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 example, $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Br}\right] \mathrm{SO}_{4}$ 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) $\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$
(ii) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}_{3}\right]$

Answer:
(i) 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.


Facial
$\mathrm{NH}_{3}$


Meridional

Q10. Draw the structures of optical isomers of:
(i) $\left[\mathrm{Cr}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$
(ii) $\left[\mathrm{PtCl}_{2}(\text { en })_{2}\right]^{2+}$
(iii) $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}(\text { en })\right]^{+}$

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

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

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


Q11. Draw all the isomers (geometrical and optical) of:
(i) $\left[\mathrm{CoCl}_{2}(\text { en })_{2}\right]^{+}$
(ii) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right) \mathrm{Cl}(\mathrm{en})_{2}\right]^{2+}$
(iii) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2}(\text { en })\right]^{+}$

Answer:
(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 $\left[\operatorname{Pt}\left(\mathrm{NH}_{3}\right)(\mathrm{Br})(\mathrm{Cl})(\mathrm{py})\right]$, and how many of these will exhibit optical isomers?
Answer:
[ $\mathrm{Pt}\left(\mathrm{NH}_{3}\right)(\mathrm{Br})(\mathrm{Cl})($ py $\left.)\right]$


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.

Answer:

The blue colour of the 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-coloured [ $\left.\mathrm{CuF}_{4}\right]^{2+}$ 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 coloured $\left[\mathrm{CuCl}_{4}\right]^{2+}$ 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 an excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_{2} S(g)$ is passed through this solution?

Answer:

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

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 ionise 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) $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$
(ii) $\left[\mathrm{FeF}_{6}\right]^{3-}$
(iii) $\left[\mathrm{Co}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$
(iv) $\left[\mathrm{CoF}_{6}\right]^{3-}$

Answer:
(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 hybridisation is $\mathrm{d}^{2} \mathrm{sp}^{3 ;} \mathrm{d}^{2} \mathrm{sp}^{3}$ hybridised 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 ) $\left[\mathrm{FeF}_{6}\right]^{3-}$
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 $\mathrm{sp}^{3} \mathrm{~d}^{2}$ hybridisation.
Since $\mathrm{F}^{-}$is a weak field ligand, it does not cause the pairing of the electrons in the 3 d orbital. Thus, the most practical hybridisation is $\mathrm{sp}^{3} \mathrm{~d}^{2} . \mathrm{sp}^{3} \mathrm{~d}^{2}$ hybridised 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 :


3d


4s

$4 p$


4d

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


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

The Learring Apo


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:

The Learring App


3d

$4 s$


4d

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


Thus, the complex has a geometric configuration of an octahedral, and it is paramagnetic.
Q16. Draw a figure to show the splitting of d orbitals in an octahedral crystal field.
Answer:


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

Answer:
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 $\Delta o$ decide the actual configuration of $d$ orbitals in a coordination entity?

Answer:
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 symbolised as $\Delta \mathrm{o}$.
Once the orbitals split up, electrons start filling the vacant spaces. An electron each goes into the three $t_{28}$ orbitals, the fourth electron, however, can enter either of the two orbitals:
(1) It can go to the $\mathrm{e}_{8}$ orbital ( producing $\mathrm{t}_{28}{ }^{3} \mathrm{e}_{8}{ }^{1}$ like electronic configuration), or
( 2 ) it can go to the $\mathrm{t}_{28}$ orbitals (producing $\mathrm{t}_{28}{ }^{4} \mathrm{e}_{\mathrm{g}}{ }^{0}$ like electronic configuration).
This filling of the fourth electron is based on the energy level of $\Delta \mathrm{o}$. If a ligand has an $\Delta \mathrm{o}$ value smaller than the pairing energy, then the fourth electron enters the $e_{8}$ orbital. However, if the value of $\Delta \mathrm{o}$ is greater than the value of pairing energy, the electron enters $\mathrm{t}_{28}$ orbital.

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

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

$\mathrm{dsp}^{2}$ hybridisation.

Since all the electrons are paired, it is diamagnetic in nature.
Cr has an oxidation state of +3 . Thus, it has a $\mathrm{d}^{3}$ configuration. 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 $d^{2} s p^{3}$ hybridisation, 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 $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ is green, but a solution of $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$ is colourless. Explain

Answer:
[ $\left.\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ 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 emits a green light, thereby giving a green colour to the solution. [ $\left.\mathrm{Ni}(\mathrm{CN})_{4}\right]{ }^{2-}$ consists of $\mathrm{Ni}^{+2}$ ion with $3 \mathrm{~d}^{8}$ electronic configuration. But CN - is present here as a strong ligand, and in its presence, the unpaired electrons pair up. Thus, there is no d-d transition, so there is no colour.
Q21. $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{+-}$and $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ are of different colours in dilute solutions. Why?
Answer:
[ $\left.\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ 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 colours in a solution.

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

Answer:
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 are donated to the empty orbital of the metal by the carbonyl carbon. A $\pi$ bond forms when a pair of electrons are donated to the empty antibonding $\pi^{*}$ orbital by the filled d orbital of the metal. This, in its entirety, stabilises and strengthens the metal-ligand bonding.
The above two types of bonding are represented as :

$\sigma$-overlap : Donation of lone pair of electrons on carbon into a vacant orbital on the metals.

$\pi$-overlap : Donation of electrons from a filled metal d-orbital into a vacant antibonding $\pi$-orbital of CO

Q23. Give the oxidation state, $d$ orbital occupation and coordination number of the central metal ion in the following complexes:
(i) $\mathrm{K}_{3}\left[\mathrm{Co}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]$
(ii) $\mathrm{cis}-\left[\mathrm{CrCl}_{2}(\text { en })_{2}\right] \mathrm{Cl}$
(iii) $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{CoF}_{4}\right]$
(iv) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{SO}_{4}$

Answer:
(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,
The oxidation state is:
$x-6=-3$
$\mathrm{x}=+3$
The d orbital occupation: $\mathrm{t}_{28}{ }^{6}{ }_{8}{ }_{8}{ }^{0}$.
(ii ) cis - [ $\left.\mathrm{Cr}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right] \mathrm{Cl}$
Central metal ion : Cr.
Coordination number $=6$.
We know,
The oxidation state is:
$\mathrm{x}+2(0)+2(-1)=+1$
$x-2=-1$
$\mathrm{x}=+3$
The d orbital occupation: $\mathrm{t}_{2 \mathrm{z}}{ }^{3}$.
( iii ) ( $\left.\mathrm{NH}_{4}\right)_{2}\left[\mathrm{CoF}_{4}\right]$ Central metal ion: Co.
Coordination number $=4$.
We know,

The oxidation state is :
$x-4=-2$
$\mathrm{x}=+2$
The d orbital occupation: $\mathrm{e}_{\mathrm{g}} \mathrm{t}_{2 \mathrm{~g}}{ }^{3}$.
(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,
The oxidation state is :
$\mathrm{x}+0=2$
$\mathrm{x}=+2$
The d orbital occupation: $\mathrm{t}_{2 \mathrm{~g}}{ }^{3} \mathrm{e}_{\mathrm{g}}{ }^{2}$.
Q24. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also, give the stereochemistry and magnetic moment of the complex:
(i) $\mathrm{K}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O}$
(ii) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2}$
(iii) $\left[\mathrm{CrCl}_{3}(\mathrm{py})_{3}\right]$
(iv) $\mathrm{Cs}\left[\mathrm{FeCl}_{4}\right]$
(v) $K_{4}\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]$

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

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


Magnetic moment, $\mu=$

$$
\begin{aligned}
& \sqrt{n(n+2)} \\
& \quad[\mathrm{n}=\text { unpaired electrons }]= \\
& \sqrt{3(3+2)} \\
& = \\
& \sqrt{15} \\
& \approx 4 \mathrm{BM}
\end{aligned}
$$

( ii ) IUPAC name $=$ Pentaamminechloridocobalt(III) chloride
Coordination number $=6$
The oxidation state of Co:
$\mathrm{x}+0-1=+2$
$\mathrm{x}=3$
Electronic configuration: $3 \mathrm{~d}^{6}=\mathrm{t}_{28}{ }^{6}$
Shape: Octahedral
Stereochemistry:
BYJU'S

$\mathrm{n}=0$.
Thus, Magnetic moment $=0$
( iii ) IUPAC name $=$ Trichloridotripyridinechromium (III)
Coordination number $=6$
The oxidation state of Cr :
$\mathrm{x}-3+0=0$
$\mathrm{x}=3$
Electronic configuration: $3 \mathrm{~d}^{3}=\mathrm{t}_{28^{3}}$
Shape: Octahedral
Stereochemistry:


Facial isomer


Meridional isomer
$\mathrm{n}=3$

$$
\begin{aligned}
& \sqrt{n(n+2)} \\
& = \\
& \sqrt{3(3+2)} \\
& = \\
& \sqrt{15} \\
& \approx 4 \mathrm{BM}
\end{aligned}
$$

( iv ) IUPAC name $=$ Caesiumtetrachloroferrate (III)
Coordination number $=4$
The oxidation state of Fe :
$x-4=-1$
$\mathrm{x}=3$
Electronic configuration: $\mathrm{d}^{6}=\mathrm{e}_{\mathrm{g}}{ }^{2} \mathrm{t}_{2 \mathrm{~g}}{ }^{3}$
Shape: Tetrahedral
Stereochemistry:- optically inactive
$\mathrm{n}=5$
Magnetic moment, $\mu=$

$$
\begin{aligned}
& \sqrt{n(n+2)} \\
& = \\
& \sqrt{5(5+2)} \\
& = \\
& \sqrt{35} \\
& \approx 6 \text { BM } \\
& \text { (v) IUPAC name }=\text { Potassium hexacyanomanganate }(\text { II }) \\
& \text { Coordination number }=6 \\
& \text { The oxidation state of Mn: } \\
& \mathrm{x}-6=-4 \\
& \mathrm{x}=+2
\end{aligned}
$$

Electronic configuration: $3 \mathrm{~d}^{5}=\mathrm{t}_{2 \mathrm{~g}}{ }^{5}$
Shape: Octahedral
Stereochemistry: optically inactive
$\mathrm{n}=1$
Magnetic moment, $\mu=$

$$
\begin{aligned}
& \sqrt{n(n+2)} \\
& = \\
& \sqrt{1(1+2)} \\
& = \\
& \sqrt{3}
\end{aligned}
$$

$$
=1.732 \mathrm{BM}
$$

## Q25. Explain the violet colour of the complex $\left[\mathrm{Ti}\left(\mathrm{H}_{2} \mathrm{O}\right)_{\sigma^{3+}}\right.$ on the basis of crystal field theory

Answer:
The 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.
$\mathrm{M}+3 \mathrm{~L} \quad \Leftrightarrow \quad \mathrm{ML}_{3}$
Stability constant, $\beta=$

$$
\frac{\left[M L_{3}\right]}{[M][L]^{3}}
$$

The greater the value of $\beta$, the stronger the metal-ligand bond is.
Factors responsible for the stability of a complex:
( 1 ) Charge on the central metal ion - the bigger the charge, the more stable the complex is.
( 2 ) Nature of ligand - chelating ligand produces a more stable complex.
( 3 ) The basic strength of ligand - the more basic a ligand, the more stable its complex.
Q26. What is meant by the chelate effect? Give an example.

## Answer:

When a polydentate or a bidentate ligand fastens itself to a 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.
$\mathrm{Ni}^{2+}(\mathrm{aq})+6 \mathrm{NH}_{3} \leftrightarrow \quad\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}(\mathrm{aq})$
$\log \beta=7.99$
$\mathrm{Ni}^{2+}(\mathrm{aq})+3 \mathrm{en}(\mathrm{aq}) \quad \leftrightarrow \quad \begin{gathered}{\left[\mathrm{Ni}(\mathrm{en})_{3}\right]^{2+}(\mathrm{aq})} \\ \log \beta=18.1(\text { more stable })\end{gathered}$


B BYJU'S

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

Answer:
( i ) Role in biological systems:
In the body of animals, there are several very important coordination compounds. For example, haemoglobin 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 example, a coordination compound of platinum, cisplatin, is used to check the growth of tumours.
( iii ) Role in analytical chemistry:
Determination of the hardness of the water.
(iv) Role in metallurgy or extraction:

During metal extraction from ores, complexes are formed. For example, 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 $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6} \mathrm{Cl}_{2}$ in the solution?
(i) 6 (ii) 4 (iii) 3 (iv) 2

Answer:
(iii) 3

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

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

$$
\begin{aligned}
& \sqrt{3(3+2)} \\
& \sqrt{3(3+2)} \\
& = \\
& \sqrt{15} \\
& =4 \mathrm{BM}
\end{aligned}
$$

(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, $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ has the highest magnetic moment value.

Q30. What is the oxidation number of cobalt in $\mathrm{K}\left[\mathrm{Co}(\mathrm{CO})_{4}\right]$ ?
Answer:
$\mathrm{K}\left[\mathrm{Co}(\mathrm{CO})_{4}\right]=\mathrm{K}^{+}\left[\mathrm{Co}(\mathrm{CO})_{4}\right]$
We know,
$\Rightarrow \mathrm{x}+0=-1$ [Where x is the oxidation number.] $\mathrm{x}=-1$
Q31. Amongst the following, the most stable complex is
(i) $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
(ii) $\left[\mathrm{Fe}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(iii) $\left[\mathrm{Fe}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$
(iv) $\left[\mathrm{FeCl}_{6}\right]^{3-}$

Answer:
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.

## NCERT Solutions for Class 12 Chemistry Chapter 9 -

 Coordination CompoundsQ32. What will be the correct order for the wavelengths of absorption in the visible region for the following: $\left[\mathrm{Ni}\left(\mathrm{NO}_{2}\right)_{6}\right]^{+},\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+},\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{++}$?

Answer:
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
$\mathrm{E}=\mathrm{hc} / \lambda$
$=>E \propto 1 / \lambda$
Therefore, the values of the absorbed wavelength in ascending order would be:
$\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}<\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}<\left[\mathrm{Ni}\left(\mathrm{NO}_{2}\right)_{6}\right]^{4-}$

