



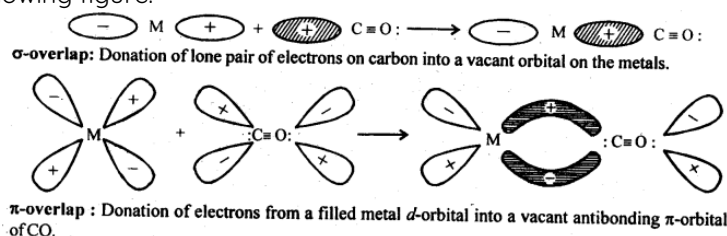
9.21. $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different colours in dilute solutions. Why?

Ans: In both the complexes, Fe is in +2 oxidation state with d^6 configuration. This means that it has four unpaired electrons: Both CN^- ion and H_2O molecules act as ligands occupy different relative positions in the spectrochemical series. They differ in crystal field splitting energy (Δ_0). Quite obviously, they absorb radiations corresponding to different wavelengths and frequencies from the visible region of light, (VIBGYOR) and the transmitted colours are also different. This means that the complexes have different colours in solutions.

9.22. Discuss the nature of bonding in metal carbonyls.

Ans: In metal carbonyl, the metal carbon bond (M - C) possess both the σ and π -bond character. The bond are formed by overlap of atomic orbital of metal with that of C-atom of carbon monoxide in following sequence:

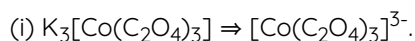
(a) σ -bond is first formed between metal and carbon when a vacant d-orbital of metal atom overlaps with an orbital containing lone pair of electrons on C-atom of carbon monoxide ($\text{C} \equiv \text{O}$)
 (b) In addition to σ -bond in metal carbonyl, the electrons from filled d-orbitals of a transition metal atom/ ion are back donated into anti bonding π -orbitals of carbon monoxide. This stabilises the metal ligand bonding. The above two concepts are shown in following figure:



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

- (i) $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$
- (ii) $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$
- (iii) $(\text{NH}_4)_2[\text{CoF}_4]$
- (iv) $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$

Ans:



$$x + 3(-2) = -3.$$

Oxidation state, $x=+3$ Coordination number is also 6 as $\text{C}_2\text{O}_4^{2-}$ is didentate.

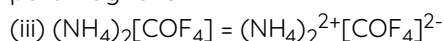
Co^{+3} is a case in which all electrons are paired.



$$x + 0 - 2 = +1$$

Oxidation state, $x=+3$

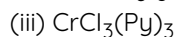
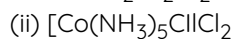
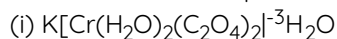
Coordination number is 6 as 'en' is didentate. Cr^{3+} is a cfi case, paramagnetic.



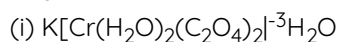
$$x - 4 = -2.$$

Oxidation state, $x = +2$
 Coordination number = 4.
 Co^{2+} is a d^5 case, paramagnetic
 (iv) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}\text{SO}_4^{2-}$
 $x + 0 + 2 = +2$
 \therefore Oxidation state, $x = +2$
 Coordination number is 6.
 Mn^{+2} is a d^5 case, paramagnetic

9.24. 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:



Ans:



IUPAC name is potassiumdiaquadioxalatochromate (III) hydrate.

Coordination number = 6

Oxidation state of Cr: $x + 0 + 2(-2) = -1$

$\therefore x = +3$

Shape is octahedral Electronic configuration of $\text{Cr}^{3+} = 3d^3 = t^3_{2g}e^0_g$.

Magnetic moment,

$$= \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$$

= 3.87 BM



IUPAC name is pentaamminechloridocobalt (III) chloride.

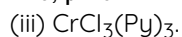
Coordination number of Co = 6 Shape is octahedral.

Oxidation state of Co, $x + 0 - 1 = +2$

$\therefore x = +3$

Electronic configuration of $\text{Co}^{3+} = 3d^6 = t^6_{2g}e^0_g$

$n=0, \mu=0$.



IUPAC name is trichloridotripyridine chromium (III).

Coordination number of Cr = 6

Oxidation state of Cr, $x - 3 + 0 = 0$

$$x = 3$$

Electronic configuration of $\text{Cr}^{3+} = 3d^3 = t_{2g}^3 e_g^0$

Unpaired electrons (n) = 3

$$\mu = 3.87 \text{ BM.}$$

(iv) $\text{Cs}[\text{FeCl}_4]$

IUPAC name is

cesium tetrachloridoferrate (III)

Coordination number of Fe is 4

Shape is tetrahedral

Oxidation number of Fe, $x - 4 = -1$

$$\Rightarrow x = +3$$

Electronic configuration of $\text{Fe}^{3+} = t_{2g}^3 e_g^2$

$$n = 5$$

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM.}$$

(v) $\text{K}_4[\text{Mn}(\text{CN})_6]$

IUPAC name is

potassium hexacyanomanganate (II)

Coordination number of Mn = 6

Shape is octahedral

Oxidation state of Mn is $x - 6 = -4$

$$x = +2$$

Electronic configuration of

$\text{Mn}^{2+} = 3d^5 = t_{2g}^5 e_g^0$

$$n = 1$$

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM.}$$

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

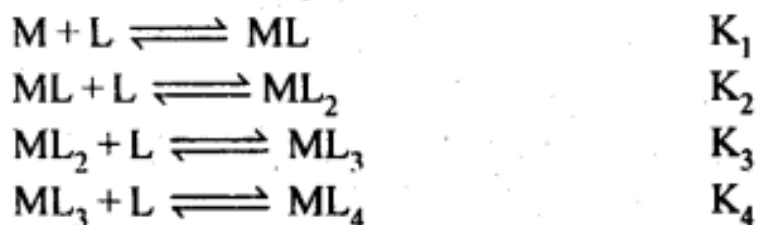
Ans: Formation of a complex in solution is an equilibrium reaction. It may be represented as



$$\text{Stability constant, } \beta = \frac{[\text{ML}_3]}{[\text{M}][\text{L}]^3}$$

The equilibrium constant of this reaction is the measure of stability of the complex. Hence the equilibrium constant is also called as stability constant or Instability constant may be defined as

equilibrium constant for reverse reaction. The formation of above complex may also be written in successive steps:



Stability constant is written as

$$\beta_4 = K_1 K_2 K_3 K_4$$

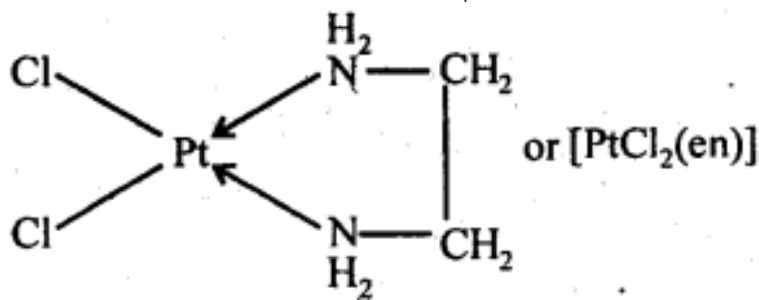
Greater the stability constant, stronger is the metal-ligand bond.

The stability of complex will depend on

- (a) Nature of metal
- (b) Oxidation state of metal
- (c) Nature of ligand e.g. chelating ligand form stabler complexes
- (d) Greater the basic strength of the ligand, more will be the stability.

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

Ans: When a didentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six membered ring is formed, the effect is called chelate effect. For example,



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

- (i) biological systems
- (ii) analytical chemistry
- (iii) medicinal chemistry and
- (iv) extraction/ metallurgy of metals.

Ans: Application of coordination compounds.

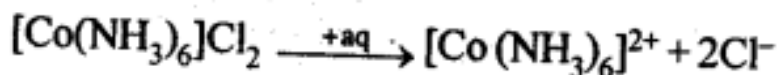
- (a) Used in qualitative and quantitative analysis.
- (b) Determination of hardness of water
- (c) Extraction of Au and Ag through complex formation
- (d) Refining of Ni through complex formation
- (e) Use of Rhodium complex in hydrogenation of alkene.
- (f) Use of EDTA in lead poisoning etc.

9.28 How many ions are produced from the complex $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ in solution?

- (i) 6
- (ii) 4
- (iii) 3
- (iv) 2

Ans: Coordination number of cobalt = 6

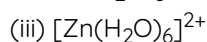
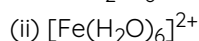
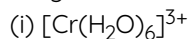
Hence, the complex is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$. It ionizes in the solution as follows:



Thus, three ions are produced. Hence, the correct option is (iii).

9.29. Amongst the following ions? Which one has the highest

magnetic moment value:



Ans:

The oxidation states are: Cr (III), Fe (II) and Zn (II).

Electronic configuration of $\text{Cr}^{3+} = 3d^3$, unpaired electron = 3

Electronic configuration of $\text{Fe}^{2+} = 3d^6$, unpaired electron = 4

Electronic configuration of $\text{Zn}^{2+} = 3d^{10}$, unpaired electrons = 0
 $= \sqrt{n(n+2)}$

where n is number of unpaired electrons Hence, (ii) has highest value of magnetic moment.

9.30 The oxidation number of cobalt in $\text{K}[\text{Co}(\text{CO})_4]$ is

(i) +1

(ii) +3

(iii) -1

(iv) -3

Ans:

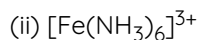
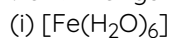


$$\therefore x + 0 = -1$$

$$x = -1$$

Hence, (iii) is the correct option.

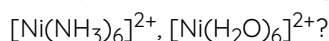
9.31. Amongst the following, the most stable complex is:



Ans: In each of the given complex, Fe is in +3 oxidation state.

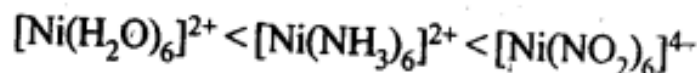
As $\text{C}_2\text{O}_4^{2-}$ is didentate chelating ligand, it forms chelate rings and hence (iii) out of complexes given above is the most stable complex.

9.32. What will be the correct order for the wavelengths of absorption in the visible region for the following: $[\text{Ni}(\text{NO}_2)_6]^{4-}$,



Ans: As metal ion is fixed, the increasing field strengths, i.e., the CFSE values of the ligands from the spectro-chemical series are in the order: $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^-$;

Thus, the energies absorbed for excitation will be in the order:



As $E = \frac{hc}{\lambda}$ the wavelengths absorbed will be in the opposite order.

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