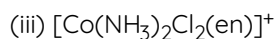
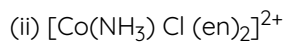
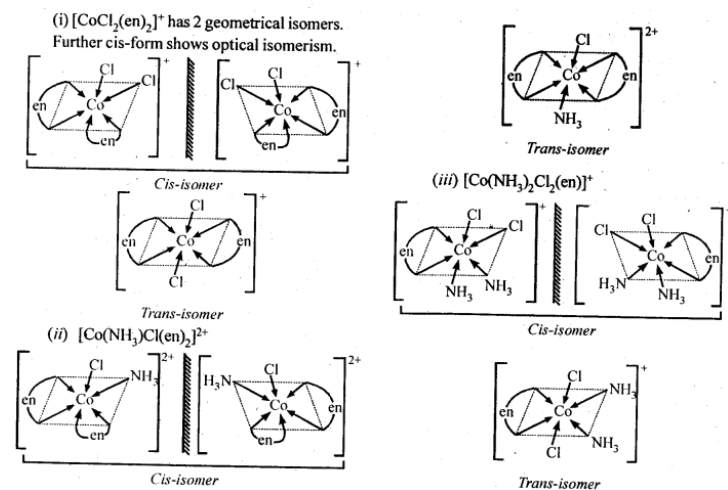




9.11. Draw all the isomers (geometrical and optical) of

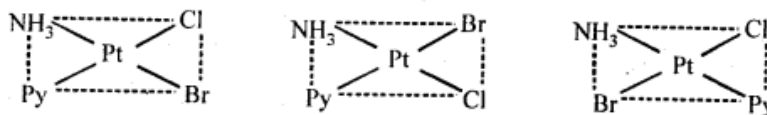


Ans:



9.12. Write all the geometrical isomers of  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$  and how many of these will exhibit optical isomerism?

Ans: Three isomers of  $[\text{Pt}(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$  are possible.



These are obtained by keeping the position of one of the ligand, say  $\text{NH}_3$  fixed and rotating the positions of others. This type of isomers do not show any optical isomerism. Optical isomerism only rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

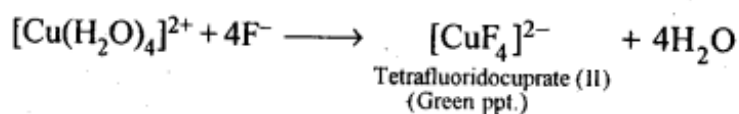
9.13. Aqueous copper sulphate solution (blue in colour) gives:

(i) a green precipitate with aqueous potassium fluoride and

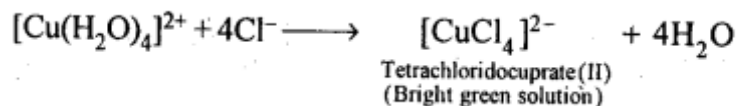
(ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

Ans: Aqueous  $\text{CuSO}_4$  solution exists as  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$  which has blue colour due to  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  ions.

(i) When  $\text{KF}$  is added, the weak  $\text{H}_2\text{O}$  ligands are replaced by  $\text{F}^-$  ligands forming  $[\text{CuF}_4]^{2-}$  ions which is a green precipitate.

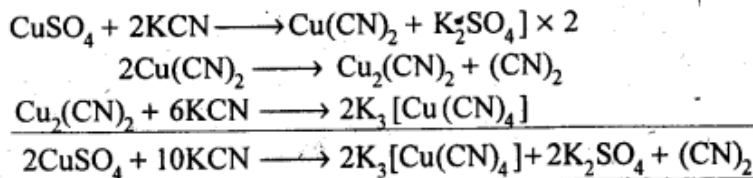


(ii) When  $\text{KCl}$  is added,  $\text{Cl}^-$  ligands replace the weak  $\text{H}_2\text{O}$  ligands forming  $[\text{CuCl}_4]^{2-}$  ion which has bright green colour.



9.14. 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  $\text{H}_2\text{S}$  (g) is passed through this solution?

Ans: First cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form the complex,  $\text{K}_3[\text{Cu}(\text{CN})_4]$ .



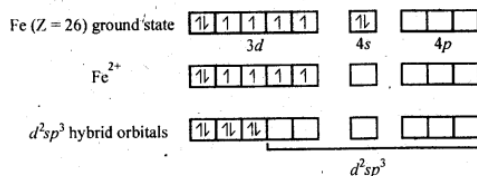
Thus, coordination entity formed in the above reaction is  $[\text{Cu}(\text{CN})_4]^{3-}$ . As  $\text{CN}^-$  is a strong ligand, the complex ion is highly stable and does not dissociate/ionize to give  $\text{Cu}^{2+}$  ions. Hence, no precipitate, with  $\text{H}_2\text{S}$  is formed.

9.15. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

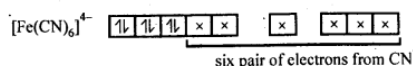
- (i)  $[\text{Fe}(\text{CN})_6]^{4-}$
- (ii)  $[\text{FeF}_6]^{3-}$
- (iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
- (iv)  $[\text{CoF}_6]^{3-}$

Ans:

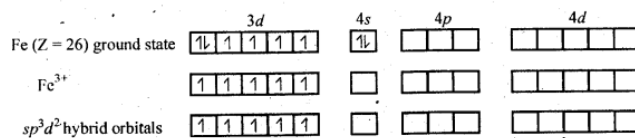
(i)  $[\text{Fe}(\text{CN})_6]^{4-}$  is  $d^2sp^3$  hybridised, octahedral in shape and diamagnetic in nature.



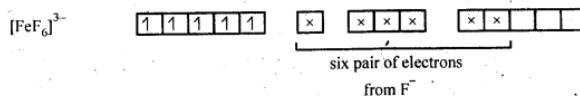
Pairing of electrons takes place because of strong  $\text{CN}^-$  ligand



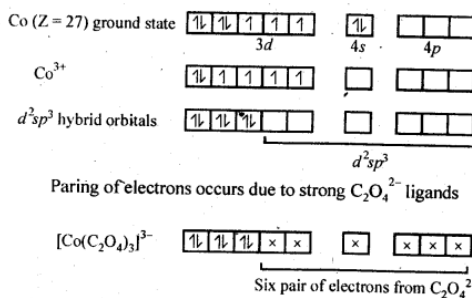
(ii)  $[\text{FeF}_6]^{3-}$  is  $sp^3d^2$  hybridised, octahedral in shape and paramagnetic in nature.



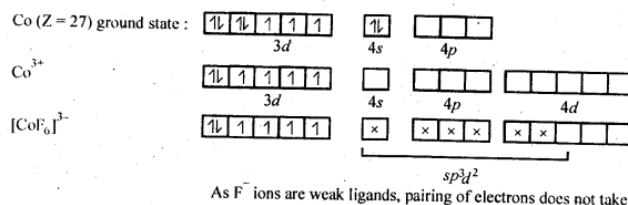
As  $\text{F}^-$  ions are weak ligands, no pairing of electrons occurs



(iii)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$  is  $d^2sp^3$  hybridised, octahedral in shape and diamagnetic in nature.

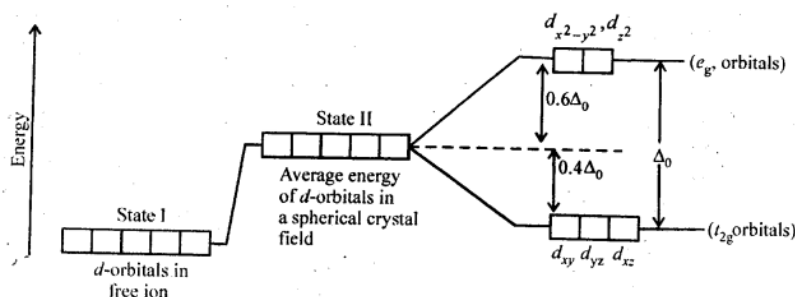


(iv)  $[\text{CoF}_6]^{3-}$  is  $sp^3d^2$  hybridised, octahedral in shape and paramagnetic in nature.



9.16. Draw figure to show the splitting of d-orbitals in an octahedral crystal field.

Ans:



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

Ans: The arrangement of ligands in order of their increasing field strengths, i.e., increasing crystal field splitting energy (CFSE) values is called spectrochemical series.

The ligands with small value of CFSE ( $\Delta_0$ ) are called weak field ligands whereas those with large value of CFSE ( $\Delta_0$ ) are called strong field ligands.

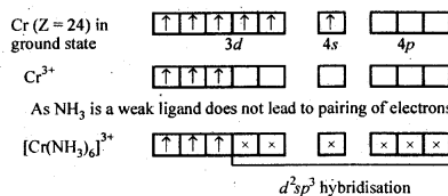
9.18. What is crystal field splitting energy? How does the magnitude of  $\Delta_0$  decide the actual configuration of d-orbitals in a coordination entity?

Ans: When the ligands approach a transition metal ion, the d-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy ( $\Delta_0$  for octahedral field). If  $\Delta_0 < P$  (pairing energy), the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3e_g^1$ , thus forming high spin complexes. Such ligands for which  $\Delta_0 < P$  are called weak field ligands. If  $\Delta_0 > P$ , the fourth electron pairs up in one of the  $t_{2g}$  orbitals giving the configuration  $t_{2g}^4e_g^1$  thereby forming low spin complexes. Such ligands for which  $\Delta_0 > P$  are called strong field ligands.

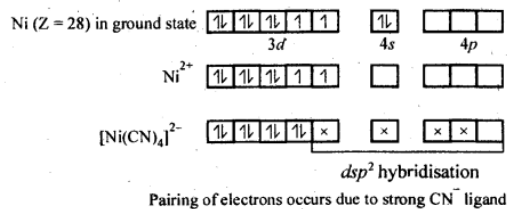
9.19.  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  is paramagnetic while  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Explain why?

Ans:

The presence of three unpaired electrons in  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  explains its paramagnetic character.



$[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic, since there is no unpaired electrons.



9.20. A solution of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is green but a solution of  $[\text{Ni}(\text{CN})_4]^{2-}$  is colourless. Explain.

Ans: In  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , Ni is in +2 oxidation state and having 3d<sup>8</sup> electronic configuration, in which there are two unpaired electrons which do not pair in the presence of the weak H<sub>2</sub>O ligand. Hence, it is coloured. The d-d transition absorbs red light and the complementary light emitted is green.

In  $[\text{Ni}(\text{CN})_4]^{2-}$  Ni is also in +2 oxidation state and having 3d<sup>8</sup> electronic configuration. But in presence of strong ligand CN<sup>-</sup> the two unpaired electrons in the 3d orbitals pair up. Thus, there is no unpaired electron present. Hence, it is colourless.

\*\*\*\*\* END \*\*\*\*\*