

CH9 – COORDINATION COMPOUNDS

9.1. Write the formulas for the following coordination compounds:

- (i) Tetraamminediaquacobalt(III) chloride
- (ii) Potassium tetracyanonickelate(II)
- (iii) Tris(ethane-1,2-diamine) chromium(III) chloride
- (iv) Amminebromidochloridonitrito-N-platinate(II)
- (v) Dichloridobis(ethane-1,2-diamine) platinum(IV) nitrate
- (vi) Iron(III) hexacyanidoferrate(II)

Ans: (i) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$.

(ii) $\text{K}_2[\text{Ni}(\text{CN})_4]$

(iii) $[\text{Cr}(\text{en})_3]\text{Cl}_3$

(iv) $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{NO}_2)]^-$

(v) $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$

(vi) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

9.2. Write IUPAC names of following co-ordination compounds :

(a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

(b) $[\text{Co}(\text{NH}_3)\text{Cl}]\text{Cl}_2$

(c) $\text{K}_3[\text{Fe}(\text{CN})_6]$

(d) $[\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]]$

(e) $\text{K}_2[\text{PdCl}_4]$

(f) $[\text{Pt}(\text{NH}_3)_2\text{ClNH}_2\text{CH}_3]\text{Cl}$. (C. B. S. E. Delhi 2013)

Ans:

(a) hexaamminecobalt(III) chloride

(b) pentaamminechloridocobalt(III) chloride

(c) potassium hexacyanoferrate(III)

(d) potassium trioxalatoferrate(III)

(e) potassium tetrachloridoplatinum(II)

(f) diamminechlorido(methylamine)platinum(II) chloride.

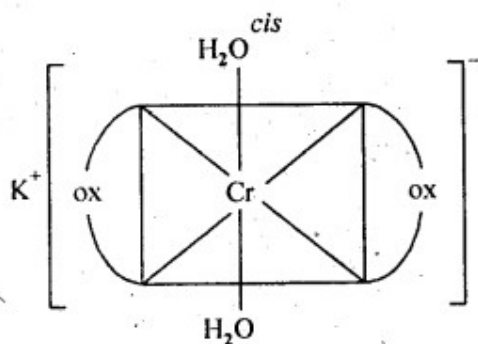
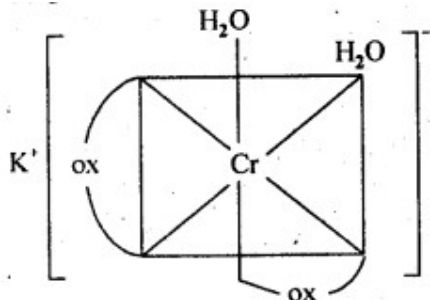
9.3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(i) $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$

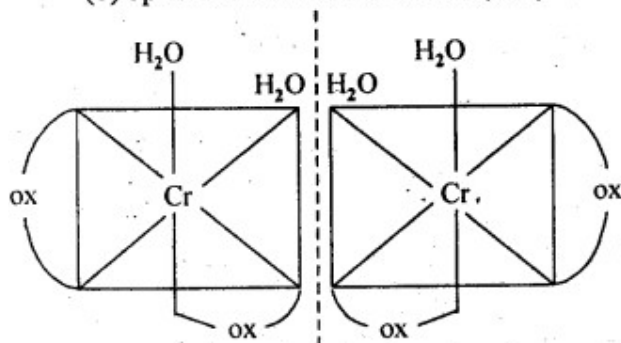
(ii) $[\text{Co}(\text{en})_3]\text{Cl}_3$

(iii) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)(\text{NO}_3)_2]$, .(iv) $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$

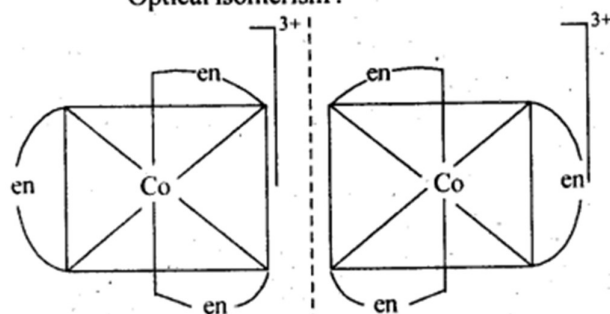
Ans: (i)(a) geometrical isomerism (cis and tram)



(b) optical isomerism of cis-form, i.e.,



Mirror images

(ii) $[\text{Co}(\text{en})_3]\text{Cl}_3$
Optical isomerism :

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(iii) $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$

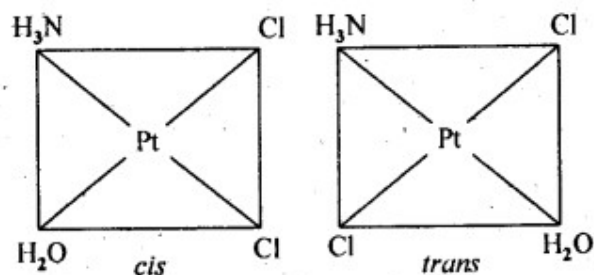
– Ionisation isomerism :

 $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ and $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_2)(\text{NO}_3)$

– Linkage isomerism :

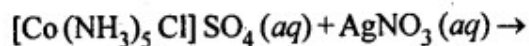
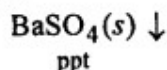
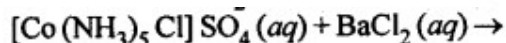
 $[(\text{Co}(\text{NH}_3)_5(\text{NO}_2))](\text{NO}_3)_2$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})](\text{NO}_3)_2$ (iv) $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$

Geometrical isomerism :

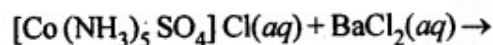


9.4. Give evidence that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ are ionisation isomers.

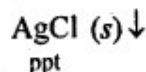
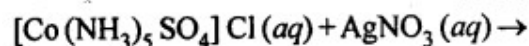
Ans: When dissolved in water, they give different ions in solution which can be tested by adding AgNO_3 solution and BaCl_2 solution, i.e.,



No reaction



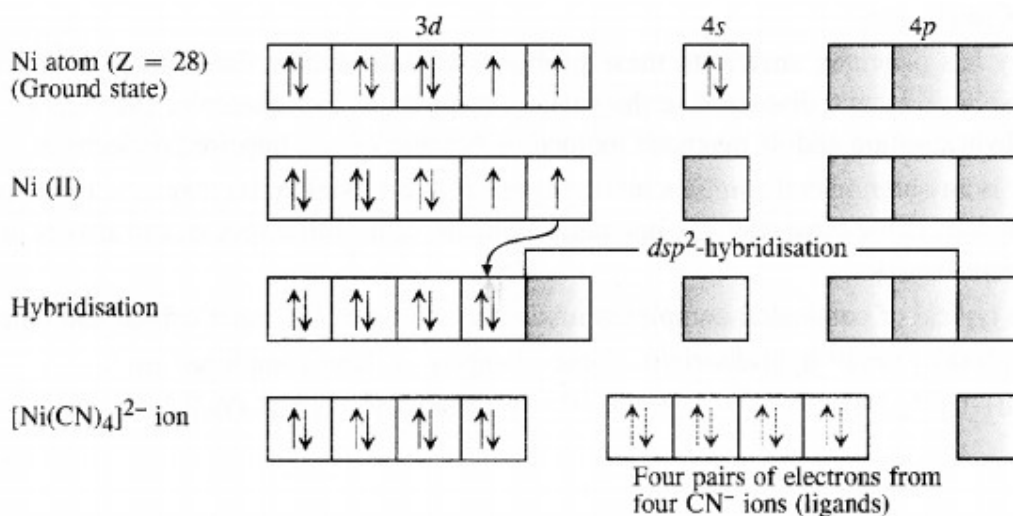
No reaction



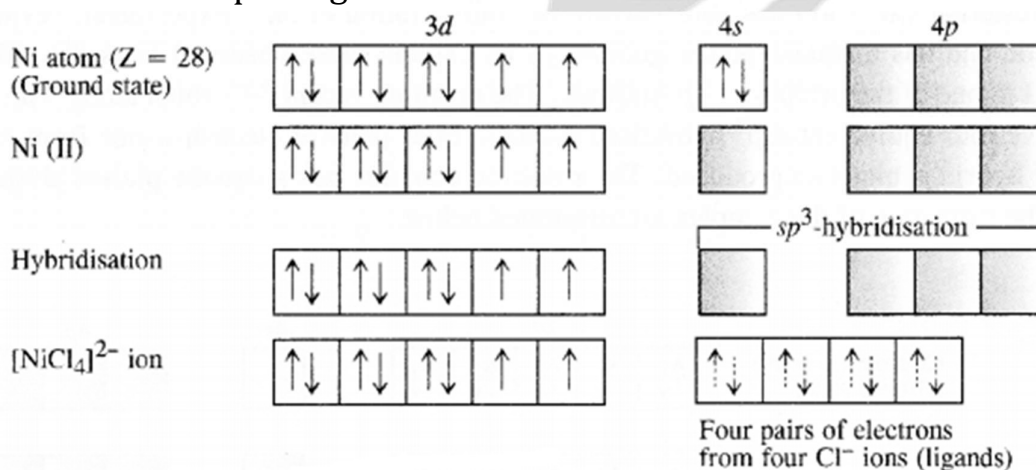
Hence, the two are ionisation isomers.

9.5. Explain on the basis of valence bond theory that $[\text{Ni}(\text{CN})_4]^{2-}$ ion with square planar structure is diamagnetic and $[\text{NiCl}_4]^{2-}$ ion with tetrahedral geometry is paramagnetic. (Rajasthan Board 2012)

Ans: Outer electronic configuration of nickel ($Z = 28$) in ground state is $3d^8 4s^2$. Nickel in this complex is in + 2 oxidation state. It achieves + 2 oxidation state by the loss of the two 4s-electrons. The resulting Ni^{2+} ion has outer electronic configuration of $3d^8$. Since CN^- ion is a strong field, under its attacking influence, two unpaired electrons in the 3d orbitals pair up.

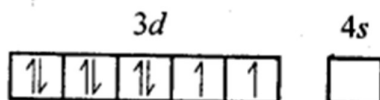


Outer electronic configuration of nickel ($Z = 28$) in ground state is $3d^8 4s^2$. Nickel in this complex is in + 2 oxidation state. Nickel achieves + 2 oxidation state by the loss of two 4s-electrons. The resulting Ni^{2+} ion has outer electronic configuration of $3d^8$. Since CN^- ion is a weak field ligand, it is not in a position to cause electron pairing.

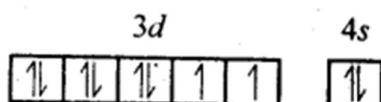


9.6. $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?

Ans:

In $[\text{NiCl}_4]^{2-}$, Ni is in +2 oxidation stateNi (28) : $3d^8 4s^2$ Ni^{2+} : $3d^8 4s^0$  Cl^- is weak field ligand. It does not pair up e^- s.

Hence, it is paramagnetic

In $[\text{Ni}(\text{CO})_4]$, Ni is in 0 O.S.Ni (28) : $3d^8 4s^2$ 

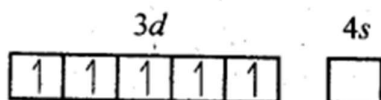
CO is strong field ligand, as it pairs the $4s e^-$ s with $3d e^-$ s to give $3d^{10} 4s^0$. So, no unpaired e^- and hence, the complex is diamagnetic.

9.7. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic. Explain.

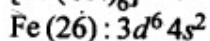
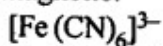
Ans:

 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ Fe (26) : $3d^6 4s^2$

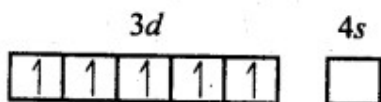
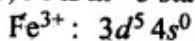
Here, Fe is in +3 state. Thus,

 Fe^{3+} : $3d^5 4s^0$  H_2O being a weak field ligand does not pair up

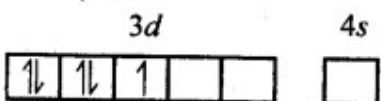
the e^- s and hence the complex is strongly paramagnetic.



Here, Fe is in +3 state, So



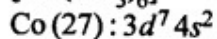
CN^- being a strong field ligand pairs up the e^- s so that we have



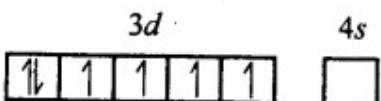
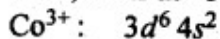
Due to only one unpaired e^- , the complex is weakly paramagnetic

9.8. Explain $[\text{Co}(\text{NH}_3)_6]^{2+}$ is an inner orbital complex, whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex.

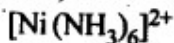
Ans:



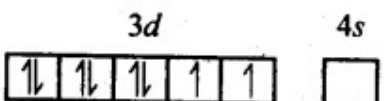
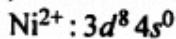
Here, Co is in +3 state, so



In presence of NH_3 , two d e^- s pair up leaving two d -orbitals empty. Hence, hybridisation is d^2sp^3 i.e., inner orbital complex.



Here, Ni is in +2 state. Thus,



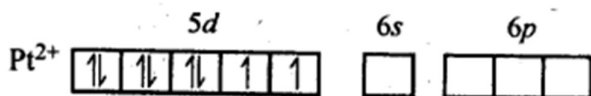
In presence of NH_3 , d e^- s do not pair up. The hybridisation is sp^3d^2 i.e., outer orbital complex.

9.9. Predict the number of unpaired electrons in the square planar $[\text{Pt}(\text{CN})_4]^{2-}$ ion.

Ans:

$[\text{Pt}(\text{CN})_4]^{2-}$: The outer shell electronic configuration of Pt is $5d^9 6s^1$.

In +2 state of Pt, it is $5d^8$, i.e.,



For square planar geometry, hybridisation is dsp^2 .

Hence, the two $d e^{-}$'s pair up to make one d -orbital empty. So, there is no unpaired e^{-} .

9.10. The hexaaquamanganese (II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

Ans: Mn(II) ion has $3d^5$ configuration. In the presence of H_2O molecules acting as weak field ligands, the distribution of these five electrons is $t_{2g}^3 e_g^2$ i. e., all the electrons remain unpaired to form a high spin complex. However, in the presence of CN^- acting as strong field ligands, the distribution of these electrons is $t_{2g}^5 e_g^0$ i.e., two t_{2g} orbitals contain paired electrons while the third t_{2g} orbital contains one unpaired electron. The complex formed is a low spin complex.

9.11. Calculate the overall complex dissociation equilibrium constant for the $\text{Cu}(\text{NH}_3)_4^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13} .

Ans: Overall stability constant (β_4) = 2.1×10^{13} .

Thus, the overall dissociation constant is

$$= \frac{1}{\beta_4} = \frac{1}{2.1 \times 10^{13}} = 4.7 \times 10^{-14}.$$

NCERT EXERCISES

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

Ans: The main postulates of Werner's theory of coordination compounds are as follows:

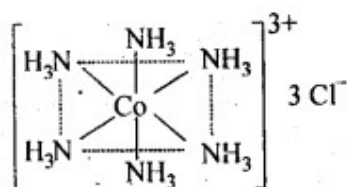
(a) Metals possess two types of valencies called

(i) primary valency which are ionisable; (ii) secondary valency which are non-ionisable

(b) Primary valency is satisfied by the negative ions and it is that which a metal

exhibits in the formation of its simple salts.

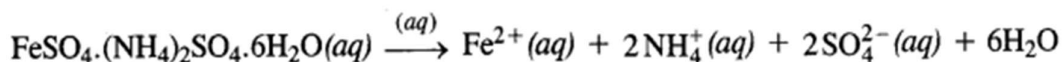
(c) Secondary valencies are satisfied by neutral ligand or negative ligand and are those which metal exercises in the formation of its complex ions. Every cation has a fixed number of secondary valencies which are directed in space about central metal ion in certain fixed directions, e.g., In $\text{CoCl}_3 \cdot 6\text{NH}_3$, valencies between Co and Cl are primary valencies and valencies between Co and NH_3 are secondary. In $\text{CoCl}_3 \cdot 6\text{NH}_3$, six ammonia molecules linked to Co by secondary valencies are directed to six corners of a regular octahedron and thus account for structure of $\text{CoCl}_3 \cdot 6\text{NH}_3$ as follows:



In modern theory, it is now referred as coordination number of central metal atom or ion.

9.2. FeSO_4 solution mixed with $(\text{NH}_4)_2\text{SO}_4$ solution in 1 : 1 molar ratio gives the test of Fe^{2+} ion but CuSO_4 solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

Ans: When FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$ solutions are mixed in 1 : 1 molar ratio, a double salt known as Mohr's salt is formed. It has the formula $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. In aqueous solution, the salt dissociates as :



The solution gives the tests for all the ions including Fe^{2+} ions. On the other hand, when CuSO_4 and NH_3 are mixed in the molar ratio of 1 : 4 in solution, a complex $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ is formed. Since the Cu^{2+} ions are a part of the complex entity (enclosed in square bracket), it will not give their characteristic tests as are given by Fe^{2+} ions.

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

Ans: Coordination entity: It constitutes of a central atom/ion bonded to fixed number of ions or molecules by coordinate bonds e.g. $[\text{CoCl}_3(\text{NH}_3)_3]$, $[\text{Ni}(\text{CO})_4]$ etc.

Ligand : The ions/molecules bound to central atom/ion in coordination entity are

called ligands. Ligands in above examples are Cl^- , NH_3 , CO Coordination number : This is the number of bond formed by central atom/ion with ligands.

Coordination polyhedron : Spatial arrangement of ligands defining the shape of complex. In above cases Co and Ni polyhedron are octahedral and tetrahedral in $[\text{CoCl}_3(\text{NH}_3)_3]$ and $[\text{Ni}(\text{CO})_4]$ respectively.

Homoleptic : Metal is bound to only one kind of ligands eg Ni in $[\text{Ni}(\text{CO})_4]$

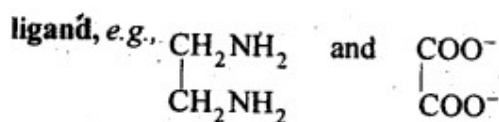
Heteroleptic Metal is bound to more than one kind of ligand eg Co in

$[\text{CoCl}_3(\text{NH}_3)_3]$

9.4. What is meant by unidentate didentate and ambidentate ligands? Give two examples for each.

Ans: A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called unidentate ligand, e.g., Cl^- and NH_3 .

A molecule or ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called didentate



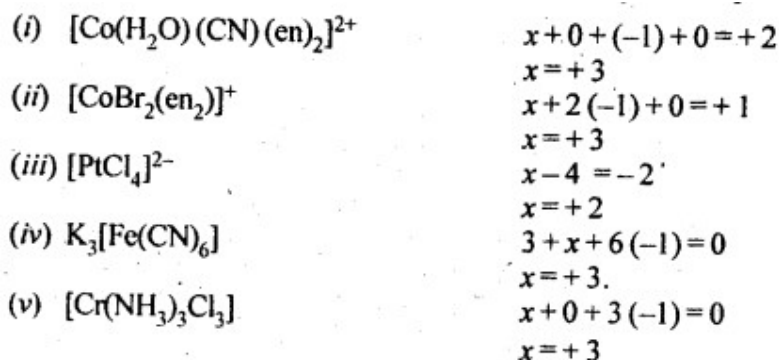
A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called

ambidentate ligand, e.g., CN^- or NC^- and NO_2^- or ONO^-

9.5. Specify the oxidation numbers of the metals in the following coordination entities:

(i) $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$ (ii) $[\text{CoBr}_2(\text{en})_2]^+$ (iii) $[\text{PtCl}_4]^{2-}$ (iv) $\text{K}_3[\text{Fe}(\text{CN})_6]$ (v) $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$

Ans:



9.6. Using IUPAC norms, write the formulae for the following : (C.B.S.E. Foreign 2015)

- (a) tetrahydroxozincate(II)
- (b) hexaammineplatinum (TV)
- (c) potassiumtetrachloridopalladate(II)
- (d) tetrabromidocuprate (II)
- (e) hexaaminecobalt(III) sulphate
- (f) potassiumtetracyanonicklate (II)
- (g) potassiumtrioxalatochromate(III)
- (h) pentaamminenitrito-O-cobalt(III)
- (i) diamminedichloridoplatinum(II)
- (j) pentaamminenitrito-N-cobalt (III). (C.B.S.E. Delhi 2012)

Ans: (a) $[\text{Zn}(\text{OH})_4]^{2-}$

(b) $[\text{Pt}(\text{NH}_3)_6]^{4+}$

(c) $\text{K}_2[\text{PdCl}_4]$

(d) $[\text{Cu}(\text{Br})_4]^{2-}$

(e) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$

(f) $\text{K}_2[\text{Ni}(\text{CN})_4]$

(g) $\text{K}_3[\text{Cr}(\text{OX})_3]$

(h) $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$

(i) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(j) $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$.

9.7. Using IUPAC norms write the systematic names of the following:

(i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$,

(ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)] \text{Cl}$

(iii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

(iv) $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl}$

(v) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

(vi) $[\text{NiCl}_4]^{2-}$

(vii) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$

(viii) $[\text{Co}(\text{en})_3]^{3+}$

(ix) $[\text{Ni}(\text{CO})_4]$

Ans: (i) Hexaammine cobalt (III) chloride.

(ii) Diammine chlorido (methylamine) platinum (II) chloride.

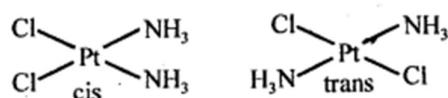
- (iii) Hexaaquatitanium (III) ion.
- (iv) Tetraammine chlorido nitrito-N-cobalt (IV) chloride.
- (v) Hexaaquamanganese (II) ion.
- (vi) Tetrachloridonickelate (II) ion.
- (vii) Hexaammine nickel (II) chloride.
- (viii) Tris (ethane -1,2-diamine) cobalt (III) ion.
- (ix) Tetra carbonyl nickel (0).

9.8. List various types of isomerism possible for coordination compounds, giving an example of each.

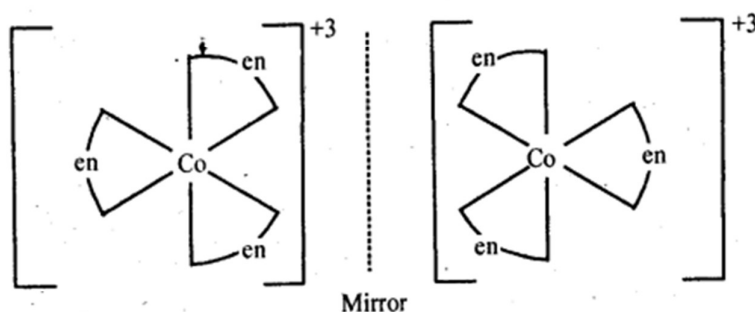
Ans: Coordination compounds exhibit stereo isomerism and structural isomerism.

Two types of stereoisomerism and their examples are as follows.

- (i) Geometrical isomerism



- (ii) Optical isomerism.



Four types of structural isomerism are as follows:

- (i) Linkage isomerism $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$
- (ii) Coordination isomerism $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- (iii) Ionisation isomerism $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
- (iv) Solvate or hydrate isomerism $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl} \cdot \text{H}_2\text{O}$

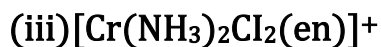
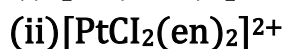
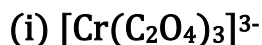
9.9. How many geometrical isomers are possible in the following coordination entities?

- (i) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ (ii) $[\text{CoCl}_3(\text{NH}_3)_3]$

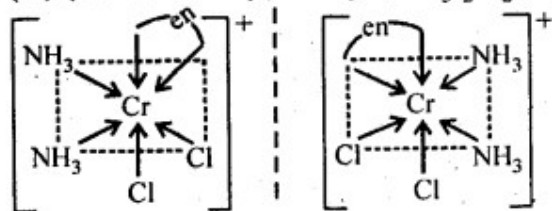
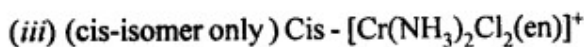
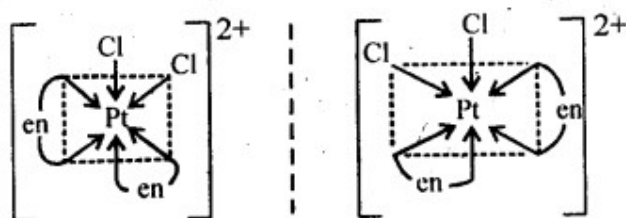
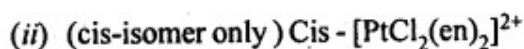
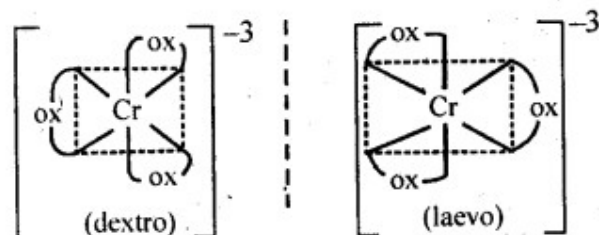
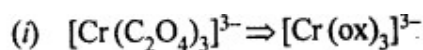
Ans: (i) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-} \Rightarrow$ No geometrical isomers are possible in this coordination entity.

(ii) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \Rightarrow$ Two geometrical isomers are possible (fac and mer) in this coordination entity.

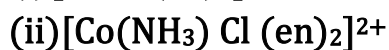
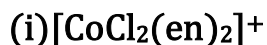
9.10. Draw the structures of optical isomers of



Ans:



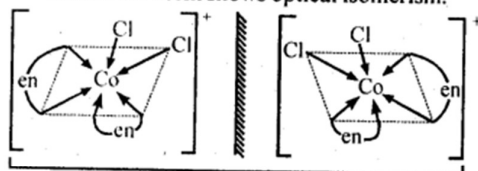
9.11. Draw all the isomers (geometrical and optical) of



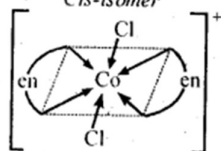
Ans:

(i) $[\text{CoCl}_2(\text{en})_2]^+$ has 2 geometrical isomers.

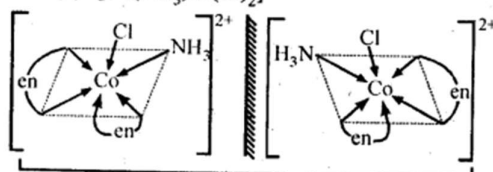
Further cis-form shows optical isomerism.



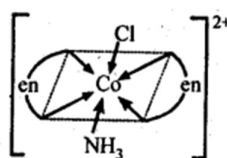
Cis-isomer



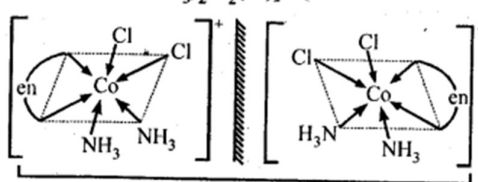
Trans-isomer

(ii) $[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$ 

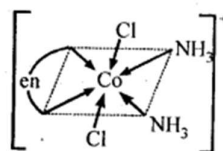
Cis-isomer



Trans-isomer

(iii) $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$ 

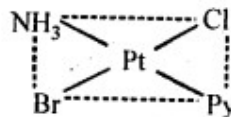
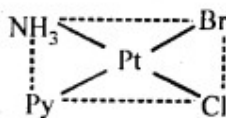
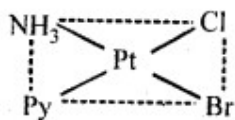
Cis-isomer



Trans-isomer

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.

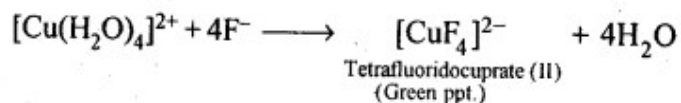


These are obtained by keeping the position of one of the ligand, say NH_3 fixed and rotating the positions of others. This type of isomers do not show any optical isomerism. Optical isomerism only rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

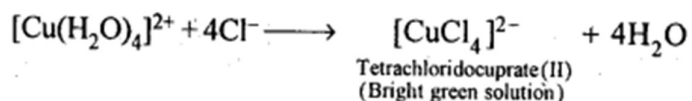
9.13. Aqueous copper sulphate solution (blue in colour) gives: (i) a green precipitate with aqueous potassium fluoride and (ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

Ans: Aqueous 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 KF is added, the weak H_2O ligands are replaced by F^- ligands forming $[\text{CuF}_4]^{2-}$ ions which is a green precipitate.

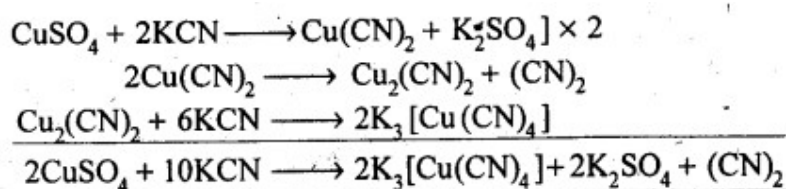


(ii) When KCl is added, Cl⁻ ligands replace the weak H₂O ligands forming [CuCl₄]²⁻ ion which has bright green colour.



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 H₂S (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, K₃[Cu(CN)₄],



Thus, coordination entity formed in the above reaction is [Cu(CN)₄]³⁻. As CN⁻ is a strong ligand, the complex ion is highly stable and does not dissociate/ionize to give Cu²⁺ ions. Hence, no precipitate, with H₂S is formed.

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

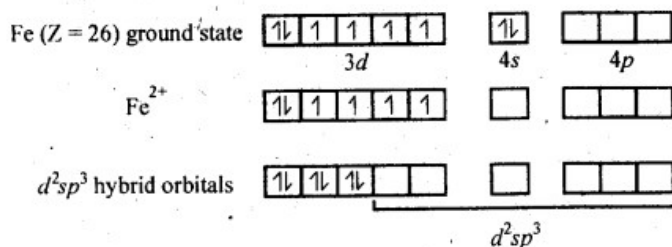
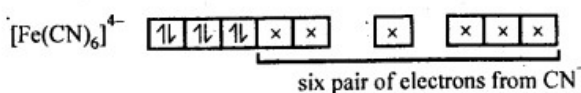
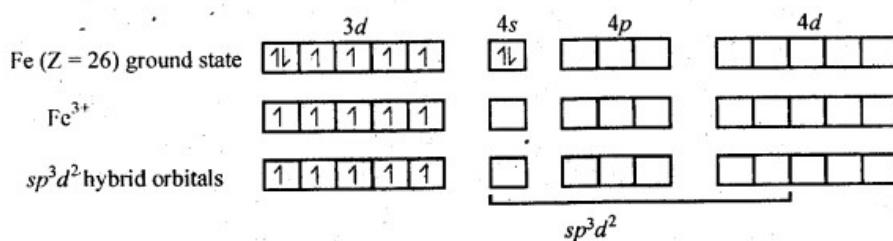
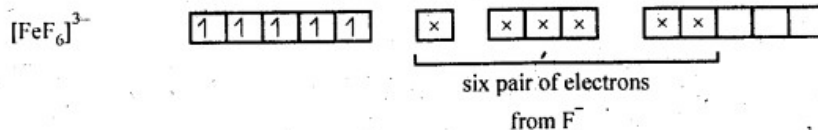
(i) [Fe(CN)₆]⁴⁻

(ii) [FeF₆]³⁻

(iii) [Co(C₂O₄)₃]³⁻

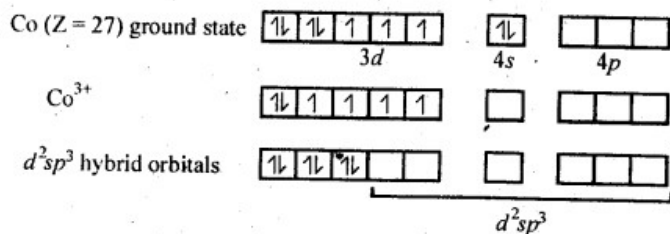
(iv) [CoF₆]³⁻

Ans:

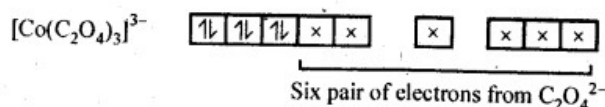
(i) $[\text{Fe}(\text{CN})_6]^{4-}$ is d^2sp^3 hybridised, octahedral in shape and diamagnetic in nature.Pairing of electrons takes place because of strong CN^- ligand(ii) $[\text{FeF}_6]^{3-}$ is sp^3d^2 hybridised, octahedral in shape and paramagnetic in nature.As F^- ions are weak ligands, no pairing of electrons occurs

<https://loyaleducation.org>

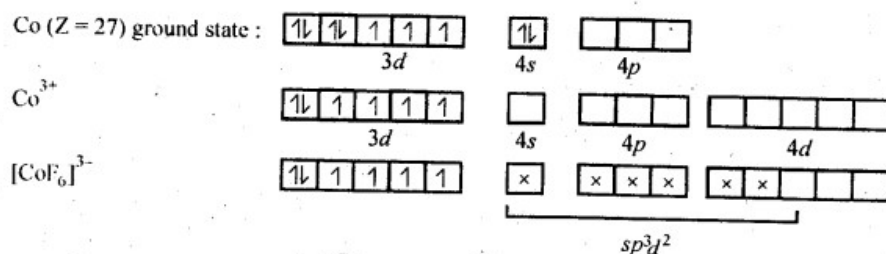
(iii) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ is d^2sp^3 hybridised, octahedral in shape and diamagnetic in nature.



Pairing of electrons occurs due to strong $\text{C}_2\text{O}_4^{2-}$ ligands



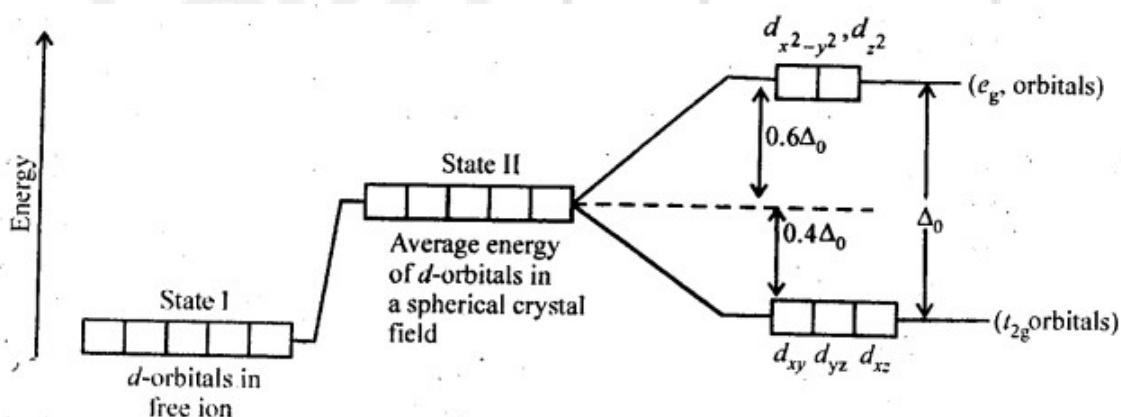
(iv) $[\text{CoF}_6]^{3-}$ is sp^3d^2 hybridised, octahedral in shape and paramagnetic in nature.



As F^- ions are weak ligands, pairing of electrons does not take place.

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

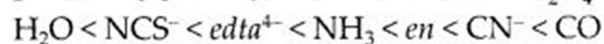
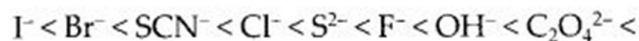
Ans:



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

Ans: The crystal field splitting, Δ_0 , depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d-orbitals. In general, ligands can be

arranged in a series in the order of increasing field strength as given below :



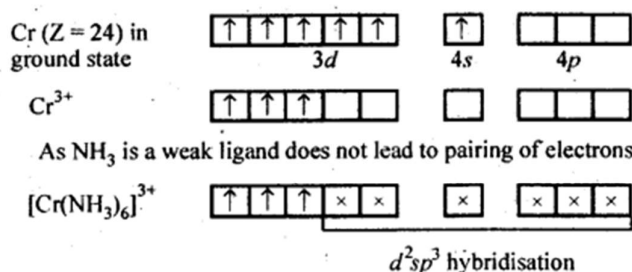
9.18. What is crystal field splitting energy? How does the magnitude of Δ_0 decide the actual configuration of d-orbitals in a coordination entity?

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 (Δ_0 for octahedral field). If $\Delta_0 < P$ (pairing energy), the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$, 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 $t_{2g}^4 e_g^1$ thereby forming low spin complexes. Such ligands for which $\Delta_0 > P$ are called strong field ligands.

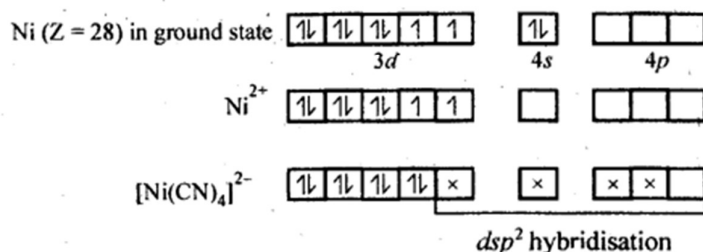
9.19. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

Ans:

The presence of three unpaired electrons in $[Cr(NH_3)_6]^{3+}$ explains its paramagnetic character.



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



Pairing of electrons occurs due to strong CN⁻ ligand

9.20. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

Ans: In $[Ni(H_2O)_6]^{2+}$, Ni is in + 2 oxidation state and having 3d⁸ electronic

configuration, in which there are two unpaired electrons which do not pair in the presence of the weak H_2O 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 $3d^8$ electronic configuration. But in presence of strong ligand CN^- the two unpaired electrons in the 3d orbitals pair up. Thus, there is no unpaired electron present. Hence, it is colourless.

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?

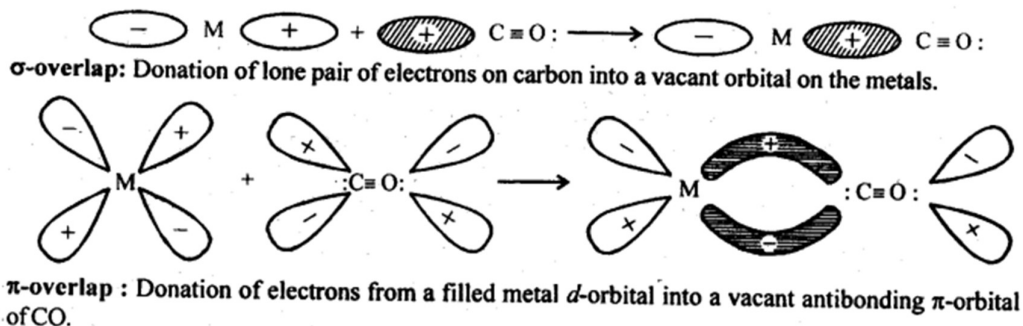
Ans: In both the complexes, Fe is in + 2 oxidation state with d^6 configuration. This means that it has four unpaired electrons. Both CN^- ion and H_2O molecules which act as ligands occupy different relative positions in the spectrochemical series. They differ in crystal field splitting energy (Δ_0). Quite obviously, they absorb radiations corresponding to different wavelengths/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) $K_3[Co(C_2O_4)_3]$ (ii) $cis-[Cr(en)_2Cl_2]Cl$ (iii) $(NH_4)_2[CoF_4]$ (iv) $[Mn(H_2O)_6]SO_4$

Ans: (i) $K_3[Co(C_2O_4)_3] \Rightarrow [Co(C_2O_4)_3]^{3-}$. $x + 3(-2) = -3$. Oxidation state, $x = +3$
Coordination number is also 6 as $C_2O_4^{2-}$ is didentate. Co^{+3} is a case in which all electrons are paired

(ii) $cis-[Cr(en)_2Cl_2] + Cl^-$

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

Oxidation state, $x = +3$

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

(iii) $(NH_4)_2[CoF_4] = (NH_4)_2^{2+}[CoF_4]^{2-}$

$$x - 4 = -2.$$

Oxidation state, $x = +2$

Coordination number = 4.

Co^{2+} is a d^5 case, paramagnetic

(iv) $[Mn(H_2O)_6]^{2+}SO_4^{2-}$

$$x + 0 + 2$$

•. 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:

(i) $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 3H_2O$ (ii) $[Co(NH_3)_5Cl]Cl_2$ (iii) $CrCl_3(Py)_3$

(iv) $Cs[FeCl_4]$ (v) $K_4[Mn(CN)_6]$

Ans: (i) $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 3H_2O$ IUPAC name is
potassiumdiaquadioxalatochromate (III) hydrate.

Coordination number = 6

$$\text{Oxidation state of Cr: } x + 0 + 2(-2) = -1$$

$$\therefore x = +3$$

Shape is octahedral Electronic configuration of $Cr^{3+} = 3d^3 = t_{2g}^3 e_g^0$.

Magnetic moment,

$$\mu = n(n+2) = \sqrt{3 \times 5} = \sqrt{15} = 3.87 \text{ BM}$$

$$= 3.87 \text{ BM}$$

(ii) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 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 $\text{Co}^{3+} = 3d^6 = t_{2g}^4 e_g^2$ $n=0, \mu=0$.

(iii) $\text{CrCl}_3(\text{Py})_3$. 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

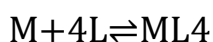
$\text{Mn}^{2+} = 3d^5 = t_{2g}^3 e_g^2$

$$n = 5$$

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

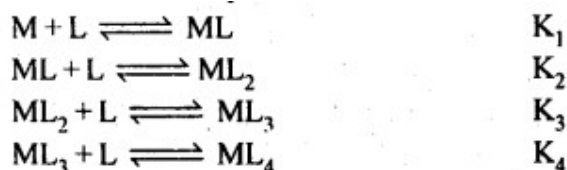
9.25. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

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



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

$$\beta_4 = K_1 K_2 K_3 K_4$$

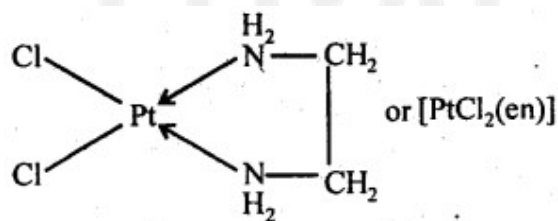
Greater the stability constant, stronger is the metal-ligand bond.

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 :

- (a) biological systems,
- (b) analytical chemistry,
- (c) medicinal chemistry, and
- (d) extraction/metallurgy of metals.

Ans:

(i) Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment 1 of blood which acts as oxygen

carrier is a coordination compound of iron. Vitamin B₁₂, cyanocobalamine, the anti- pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

(ii) There is growing Interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D-penicillamine and desferrioxime B via the formation of coordination compounds.

EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: ds-platin and related compounds.

(iii) Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α -nitroso- β -naphthol, cupron, etc.

(iv) Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[\text{Au}(\text{CN})_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc.

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

(i) 6

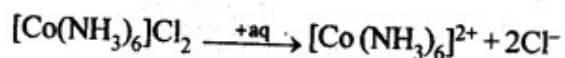
(ii) 4

(iii) 3

(iv) 2

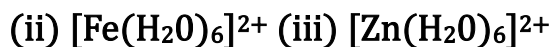
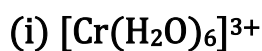
Ans: Coordination number of cobalt = 6

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

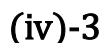
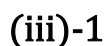
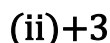
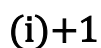
Electronic configuration of $\text{Fe}^{2+} = 3d^6$, unpaired electron = 4

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

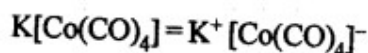
$$\mu = n(n+2) \text{ --- } \sqrt{\quad}$$

where V 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



Ans:

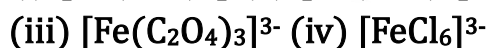
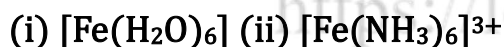


$$\therefore x + 0 = -1$$

$$x = -1$$

Hence, (iii) is the correct option.

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

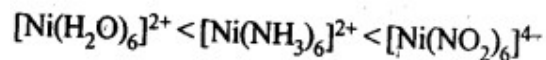


Ans: In each of the given complex, Fe is in + 3 oxidation state. As $\text{C}_2\text{O}_4^{2-}$ is didentate chelating ligand, it forms chelate rings and hence (iii) out of complexes given above is the most stable complex.

9.32. What will be the correct order for the wavelengths of absorption in the visible region for the following: $[\text{Ni}(\text{NO}_2)_6]^{4-}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$?

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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