NCERT Solutions Chemistry Class XII

UNIT-9: Coordination Compounds

INTEXT QUESTIONS

9.1 Write the formulas for the following coordination compounds: (i) Tetraamminediaquacobalt(III) chloride (ii) Potassium tetracyanidonickelate(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)

ANSWER:

(i) $[Co(NH_3)_4(H_2O)_2]Cl_3$

(ii) $K_2[Ni(CN)_4]$

(iii) $[Pt(en)_3]NO_3$

(iv) $[Pt(NH_3)BrCl(NO_2)]$

(v) $[Pt(Cl)_2(en)_2](NO_3)_2$

(vi) $Fe_4[Fe(CN)_6]_3$

9.2 Write the IUPAC names of the following coordination compounds:
(i) $[Co(NH_3)_6]Cl_3$
(ii) $[Co(NH_3)_5Cl]Cl_2$
(iii) $K_3[Fe(CN)_6]$
(iv) $K_3[Fe(C_2O_4)_3]$
(v) $K_2[PdCl_4]$
(vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]$

ANSWER:

(i) Hexaminecobalt(III)chloride

(ii) Pentaaminechloridecobalt(III)chloride

(iii) Potassium hexacyanoferrate(III)

(iv) Potassium trioxalatoferrate(III)

(v) Potassium tetrachloridopalladate(II)

(vi) Diaminechloride(methylamine)platinum(II)chloride

9.3 Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers: (i) K[Cr(H2O)2 (C2O4)2 (ii) [Co(en)3]Cl3 (iii) [Co(NH3)5 (NO2)](NO3)2
(iv) [Pt(NH3)(H2O)Cl2]

ANSWER:

(i) $K[Cr(H_2O)_2(C_2O_4)_2$ exhibits geometrical isomerism (Cis and trans) and optical isomerism of cis and trans type.

(ii) Optical isomerism exhibiting mirror images.

(iii) Ionisation isomerism- $[Co(NH_3)_5(NO_3)](NO_3)(NO_2)$ and

Linkage isomerism-$[Co(NH_3)_5(ONO)](NO_3)_2$

(iv) Geometrical isomers are seen in $[Pt(NH_3)(H_2O)Cl_2]$

9.4 Give evidence that [Co(NH3)5Cl]SO4 and [Co(NH3)5 (SO4)]Cl are ionisation isomers.

ANSWER:

These compounds give different ions in aqueous solution. This can be tested by using $AgNO_3$ solution and $BaCl_2$

$[Co(NH_3)_5Cl]SO_{4(aq)} + BaCl_{2(aq)} \rightarrow BaSO_{4(ppt)}$

$[Co(NH_3)_5Cl]SO_{4(aq)} + AgNO_{3(aq)} \rightarrow$ no reaction

$[Co(NH_3)_5(SO_4)]Cl_{(aq)} + BaCl_{2(aq)} \rightarrow$ no reaction

$[Co(NH_3)_5(SO_4)]Cl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(ppt)}$

Hence they give different precipitates with different solutions. Thus they are ionisation isomers.

9.5 Explain on the basis of valence bond theory that [Ni(CN)4] 2– ion with square planar structure is diamagnetic and the [NiCl4] 2– ion with tetrahedral geometry is paramagnetic.

ANSWER:

According to the valence band theory , the central metal atom or ion under the influence of ligands can use its (n-1)d , ns, np (inner orbital complex) or ns, np, nd (outer orbital complex)orbitals for hybridisation to form equivalent set of orbitals of definite geometry.

In $[Ni(CN)_4]^{2-}$, oxidation state of Ni can be calculated as :

Using overall charge balance as the whole ion has overall -2 charge:

$x + 4(-1) = -2$ ($\because$ CN^- has -1 negative charge)

$x = +2$

Ni is in + 2 oxidation state.

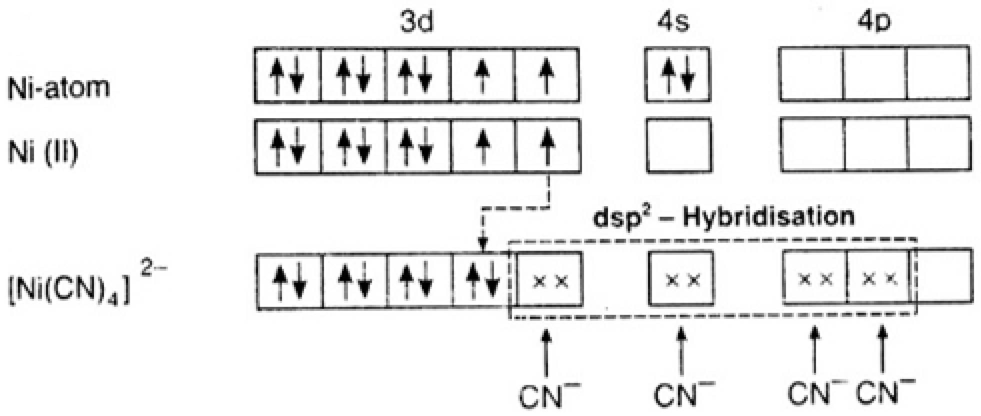
Electronic configuration of Ni is: $[Ar]3d^8 4s^2$

Where, $[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

Electronic configuration of $Ni^{+2} = [Ar]3d^8$

Outer electronic configuration of $Ni^{+2} = 3d^8$

Since there are 4 CN ions so they can either form tetrahedral or square planar geometry. And CN^- is a strong field ligand (according to experimental data of spectro-chemical series) it causes pairing of the 2 unpaired electrons.



It undergoes dsp^2 (one d orbital, one s and two p orbitals used by the ligands) hybridization and forms square planar structure.

Since all the electrons are paired so it is diamagnetic.

Paramagnetic compounds- those compounds which have one or more no. of unpaired electrons in their atomic orbitals.

Diamagnetic compounds-those compounds in which all the electrons in their atomic orbitals are paired.

Co-ordination number	*Type of hybridisation*	*Distribution of hybrid orbitals in space*
4	sp^3	Tetrahedral
4	dsp^3	Square planar
5	sp^{3}d	Trigonalbipyramidal

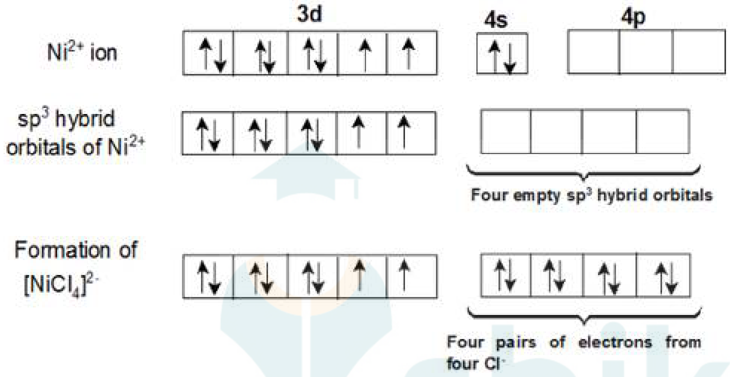
6	sp^3d^2	Octahedral
6	d^2sp^3	octahedral

In case of $[Ni(Cl)_4]^{2-}$ ion, Cl^- is a weak field ligand so it will not pair the unpaired electrons of Ni^{+2} ion. Therefore it undergoes sp^3 hybridization.

Overall charge balance:

X + 4(-1) = -2

X = + 2.



Since there are 2 unpaired electrons in the d orbital so it is a paramagnetic compound.

9.6 $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

ANSWER:

In $[Ni(Cl)_4]^{2-}$ ion, Cl^- is a weak field ligand so it will not pair the unpaired electrons of Ni^{+2} ion.

Electronic configuration of Ni is: $[Ar]3d^8 4s^2$ where $[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

Electronic configuration of $Ni^{+2} = [Ar]3d^8$

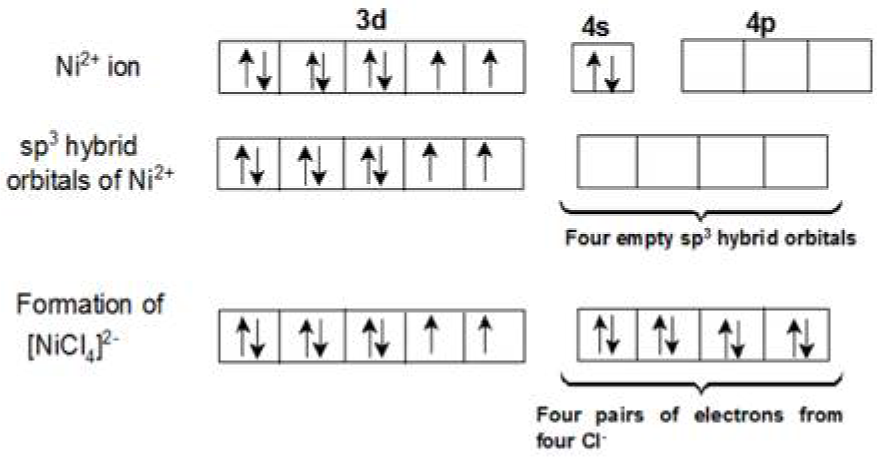
Outer electronic configuration of $Ni^{+2} = 3d^8$

Overall charge balance:

X + 4(-1) = -2

X = + 2.

Therefore it undergoes sp^3 hybridization. So it will have tetrahedral geometry.



Since there are 2 unpaired electrons in the d orbital so it is a paramagnetic compound.

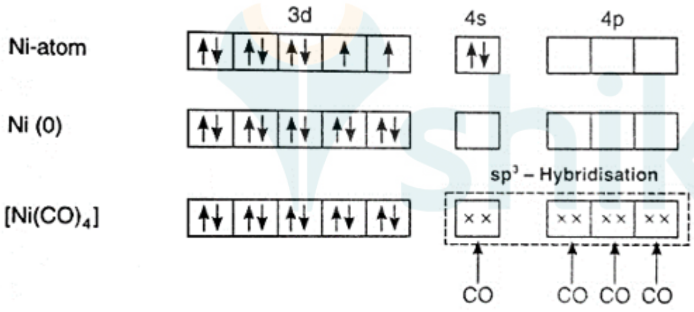
In $[Ni(Co)_4]$:

Overall charge is neutral and oxidation state of Ni can be calculated as:

X + 4(0) = 0

X = 0

Ni is in zero oxidation state.



Co is a strong field ligand it causes pairing of the 4 unpaired electrons in d orbital. Also, it causes the 4s electrons to shift to the 3d orbital, thereby undergoes sp^3 hybridisation forming tetrahedral geometry. Since it has no unpaired electron, therefore it is diamagnetic compound.

9.7 [Fe(H2O)6] 3+ is strongly paramagnetic whereas [Fe(CN)6] 3– is weakly paramagnetic. Explain.

ANSWER:

In $[Fe(H_2O)_6]^{3+}$

Electronic configuration of Fe is: $[Ar]3d^6 4s^2$

$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

Electronic configuration of $Fe^{+3} = [Ar]3d^5$

Outer electronic configuration of $Fe^{+3} = 3d^5$

Overall charge balance:

$X + 6(0) = 3$

$X = +3$

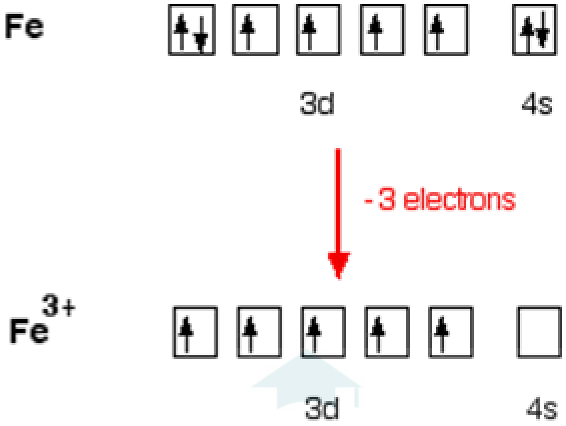
In $[Fe(CN)_6]^{3-}$

Overall charge balance:

$X + 6(-1) = -3$

$X = +3$

In both the compounds Fe is in + 3 oxidation state.



In case of $[Fe(H_2O)_6]^{3+}$

H_2O is weak field ligand so it does not pair the unpaired electron. Total no. of the unpaired electron, n = 5. Spin only magnetic moment is given by:

$\mu = [n(n + 2)]^{1/2}$

$\mu = [5\times7]^{1/2}$

$\mu = 5.916BM$

In case of $[Fe(CN)_6]^{3-}$

CN^- is a strong field ligand so it pairs up the electron.

Total no. of unpaired electrons = 1

Spin only magnetic moment is given by:

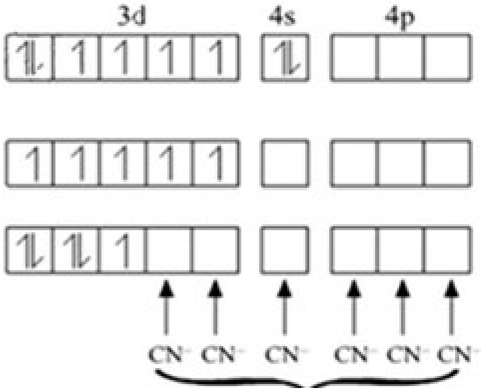
$\mu = [n(n + 2)]^{1/2}$

$\mu = [1\times3]^{1/2}$

$\mu = 1.732BM$

as we can see spin only magnetic moment of $[Fe(H_2O)_6]^{3+}$ is more than $[Fe(CN)_6]^{3-}$.

so, $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^3$ weakly paramagnetic.



Fe in ground state

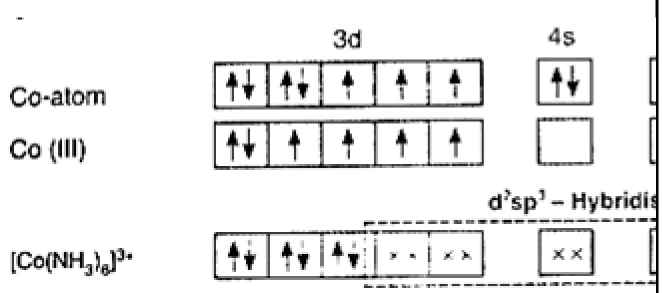
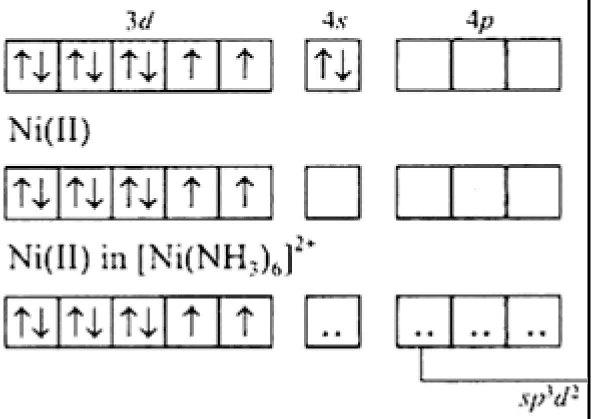
Fe in + 3 oxidation state

Electrons from 5 CN⁻ ligands

9.8 Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

ANSWER:

$[Co(NH_3)_6]^{3+}$	$[Ni(NH_3)_6]^{2+}$
Oxidation state of cobalt: Overall charge balance: X + 6(0) = 3 X = + 3	Oxidation state of nickel: Overall charge balance: X + 6(0) = 2 X = + 2
Outer electronic configuration of cobalt = d^6	Outer electronic configuration of nickel = d^8

	
NH_3 is a strong field ligand so it causes pairing of electron. Therefore cobalt undergoes d^2sp^3 hybridisation. As in the hybridisation d^2 orbitals are used from the (n-1)d orbitals(inner orbitals as n = 4 being quantum number) . hence it is a inner orbital complex.	NH_3 is a strong field ligand so it causes pairing of electron. Therefore nickel undergoes sp^3 d^2 hybridisation. As in the hybridisation d^2 orbitals are used from the nd orbitals (outer orbitals as n = 4 being quantum number) .hence it is a outer orbital complex.

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

ANSWER:

In $Pt[(CN)_4]^{2-}$ ion:

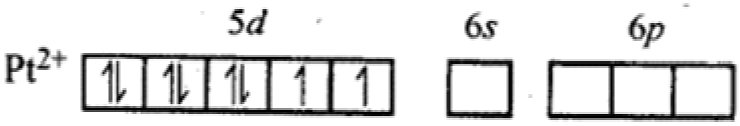
Overall charge balance:

X + 4(-1) = -2

X = + 2.

The oxidation state of Pt is + 2.

Since CN^- is a strong field ligand, it causes pairing of the unpaired electrons.



Therefore, now the 2 unpaired electrons from 5d orbital get paired and it undergoes dsp^2 hybridisation. It forms square planar geometry. Since all the electrons are paired,

No. of unpaired electrons = 0.

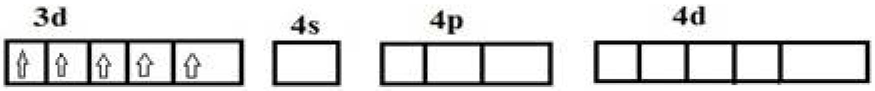
9.10 The hexaquomanganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

ANSWER:

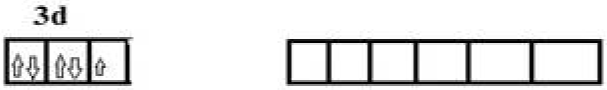
$[Mn(H_2O)_6]^{+2}$	$[Mn(CN)_6]^{4-}$
Oxidation state of manganese: Overall charge balance: $X + 6(0) = 2$ $X = +2$	Oxidation state of manganese: Overall charge balance: $X + 6(-1) = -4$ $X = +2$
Outer electronic configuration of Mn = d^5	Outer electronic configuration of Mn = d^5
H_2O is a weak field ligand so it does not cause pairing of the electron. Therefore Mn undergoes sp^3d^2 hybridization. Geometry is octahedral. Therefore the 5 unpaired electrons from the d orbital remain as it is.	CN is a strong field ligand so it causes pairing of the electron(5 electrons get paired to form 2 pairs and one unpaired electron). Therefore Mn undergoes d^2sp^3 hybridization. Geometry is octahedral.

Mn in + 2 oxidation state:

In presence of CN^- Ligands:



d^2sp^3 hybridisation:



d^2sp^3 hybrid

Electronic configuration of $[Mn(CN)_6]^{4-}$:

EXERCISES

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

ANSWER:

Bonding in coordination compounds in terms of Werner's postulates is explained as:

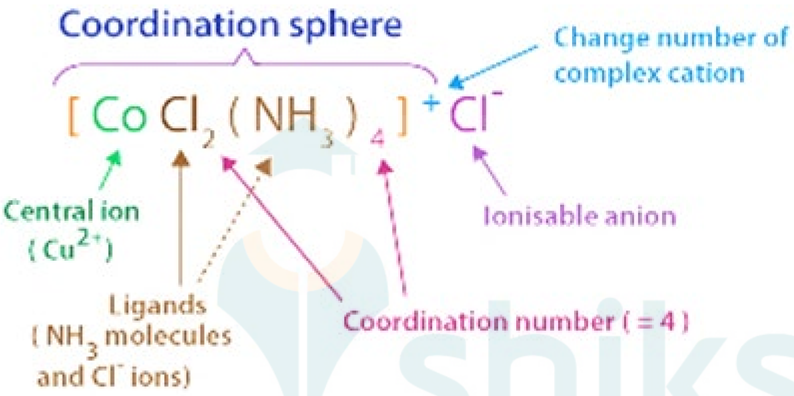
a) Metals can show two types of valencies which are Primary valency and Secondary valency.

1. ***Primary Valency:*** Primary Valency shows Oxidation state. Primary valencies are ionizable.

2. ***Secondary Valency:*** Secondary Valency shows coordination number. These are non-ionizable.

b) Both Primary and secondary valency of the metal are to be satisfied which is done by negative ions in case of primary valency and negative or neutral species in case of secondary valency.

c) Metals have a fixed number of secondary valencies/ Coordination number around the central atom, these secondary valencies are placed in such a way which leads to a specific geometry of the coordination compound.



9.2 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ 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?

ANSWER:

The reaction is given below:

$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \rightarrow FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr Salt)

$FeSO_4$, when reacted with $(NH_4)SO_4$, does not form any complex whereas they form a double salt, $FeSO_4.(NH_4)2SO_4.6H_2O$ - (Mohr salt) which dissociates into ions in the solution. So, it gives the test of Fe^{2+} ions.

$CuSO_4 + 4NH_3 + 5H_2O \rightarrow [Cu(NH_3)_4SO_4].5H_2O$

$CuSO_4$ solution when mixed with aqueous ammonia in 1: 4 molar ratio forms a complex with formula $[Cu(NH_3)]SO_4$ in which the complex ion, $[Cu(NH_3)_4]^{2+}$ does not dissociate to give Cu^{2+} ions. Therefore, it does not give the tests of the Cu^{2+} ion.

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

ANSWER:

1) Coordination Entity: Coordination entity is a charged entity having positive or negative charge in which the central atom is surrounded by molecules which may be neutral/negatively charged called Ligands.

Examples:

i. Cationic Complexes: $[Cu(H_2O)_6]^{2+}$, $[Al(H_2O)_6]^{3+}$

ii. Anionic Complexes: $[CuCl_4]^{2-}$, $[Al(H_2O)_2(OH)_4]^-$

iii. Neutral Complexes: $[Co(NH_3)_4 Cl_2]$,$[Ni(CO)_4]$

2) Ligands: Ligands are the neutral or negatively charged entities surrounding the central metal atom of the coordination complex which possesses at least one unshared pair of electrons

Example: F^-, Cl^-, Br^-, I^-, H_20, and NH_3

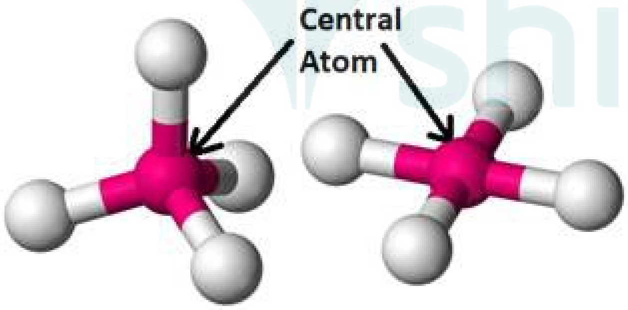
3) Coordination Number: Coordination Number which is also called as Ligancy is the total number of ligands that are attached to the central metal atom of the coordination complex.

Example: $[Cr(NH_3)_2Cl_2Br_2]^-$ has Cr^{3+} as its central cation, and has a coordination number of 6

Al^{3+} has coordination number 4 in $[AlCl_4]^-$ but 6 in $[AlF_6]^{3-}$.

4) Coordination polyhedron: Coordination polyhedron is defined as the spatial arrangement of the ligands around the central atom of a coordination complex.

Example:



A. Tetrahedral B. Square Planar

In the figure: The pink Sphere depicts the central atom of the coordination entity.

5) Homoleptic complexes: Complexes in which the central metal atom is surrounded only by the same kind of donor groups which are the ligands.

Example: $[Ag(CN)_2]^-$,$[Fe(CN_6)]^{4+}$ etc

6) Heteroleptic complexes: Complexes in which the central metal atom is surrounded by more than one kind of donor groups which are the ligands.

Example: $[Co(NH_3)_4 Cl_2]^+$,$[Co(NH_3)_5 Cl]^{2+}$

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

ANSWER:

Ligands are the neutral or negatively charged entities surrounding the central metal atom of the coordination complex which possesses at least one unshared pair of electrons.

Based on the number of donor sites of these ligands, Ligands are classified as:

Unidentate ligands: These Ligands which have only one donor site are called unidentate ligands.

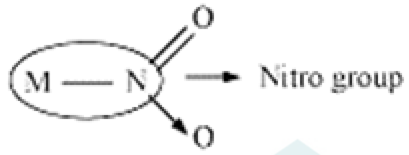
Example: F^-,Cl^- etc

Didentate ligands: These Ligands which have only two donor site are called didentate ligands.

Example: Ethane-1,2-diamine, Oxalate ion etc

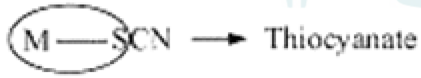
Ambidentate ligands: These ligands which can attach them with the central metal atom by two different atoms are called as ambidentate ligands.

Example:



(The donor atom is N)

(The donor atom is oxygen)
(b)



(The donor atom is S)

(The donor atom is N)

9.5 Specify the oxidation numbers of the metals in the following coordination entities: (i) $[Co(H_2O)(CN)(en)_2]^{2+}$ (iii) $[PtCl_4]^{2-}$ (v) $[Cr(NH_3)_3Cl_3]$ (ii) $[CoBr_2(en)_2]^+$ (iv) $K_3[Fe(CN)_6]$

ANSWER:

(i) Let Oxidation no. of Co be x and charge on the complex is given as + 2

H_2O has Oxidation Number: 0

CN has Oxidation Number: -1

en has Oxidation Number :0

$$\begin{array}{cccccccc} [Co & & (H_2O) & & (CN) & & (en)_2]^{2+} & \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & \\ x & + & 0 & + & (-1) & + & 2(0) & = +2 \end{array}$$

$$x - 1 = +2$$

$$x = +3$$

(ii) Let Oxidation number of Co be x and charge on the complex is given as + 1

Br has Oxidation number: 1

en has oxidation number : 0

$$\begin{array}{cccccc} [Co & & (Br)_2 & & (en)_2]^{2+} & \\ \downarrow & & \downarrow & & \downarrow & \\ x & + & 2(-1) & + & 2(0) & = +1 \end{array}$$

$$x - 2 = +1$$

$$x = +3$$

(iii) Let Oxidation number of Pt be x and charge on the complex is given as -2

Cl has oxidation number : -1

$$\begin{array}{cc} [Pt & (Cl)_4]^{2-} \\ \downarrow & \downarrow \end{array}$$

$$x + 4(-1) = -2$$

$$x = +2$$

(iv) This complex can also be seen as $[Fe(CN)_6]^{3-}$

Let Oxidation number of Fe be x and charge given on the complex is given as -3

CN has oxidation number : -1

$$\begin{array}{cccc} [Fe & & (CN)_6]^{3-} & \\ \downarrow & & \downarrow & \\ x & + & 6(-1) & = -3 \end{array}$$

$$x = +3$$

(v) Let Oxidation number of Cr be x and charge given on the complex is given as 0

NH_3 has oxidation number : 0

Cl has oxidation number: -1

$$\begin{array}{ccc} [\mathrm{Cr} & (\mathrm{NH_3})_3 & \mathrm{Cl_3}] \\ \downarrow & \downarrow & \downarrow \\ x & +\ 3(0) & +\ 3(-1)=0 \end{array}$$

$$x-3=0$$

$$x=+3$$

9.6 Using IUPAC norms write the formulas for the following: (i) Tetrahydroxidozincate(II) (vi) Hexaamminecobalt(III) sulphate (ii) Potassium tetrachloridopalladate(II) (vii) Potassium tri(oxalato)chromate(III) (iii) Diamminedichloridoplatinum(II) (viii) Hexaammineplatinum(IV) (iv) Potassium tetracyanidonickelate(II) (ix) Tetrabromidocuprate(II) (v) Pentaamminenitrito-O-cobalt(III) (x) Pentaamminenitrito-N-cobalt(III)

ANSWER:

(i) Tetrahydroxidozincate (II) = $[Zn(OH)_4]^{-2}$

Tetrahydroxi means 4 hydroxide ions with zinc in + 2 oxidation state. Hydroxide ions have a negative charge of -1 , so balancing the overall charge of the coordination compound to be zero we get the formula as : $[Zn(OH)_4]^{-2}$

(ii) Potassium tetrachloridopalladate(II) = $K_3[PdCl_4]$.

Tetrachlorido means 3 Chloride ions each having a negative charge. Platinum is in + 2 state. Balance overall charge as 0, no. Of potassium ions are 3. Formula: $K_3[PdCl_4]$.

(iii) Diamminedichloridoplatinum(II) = $[Pt(NH_3)Cl_2]^{2+}$

Diammine means 2 ammonia molecules, dichlorido means 2 chloride ions , platinum in + 2 state. Formula: $[Pt(NH_3)Cl_2]^{2+}$

(iv) Potassium tetracyanidonickelate(II) = $K_2[Ni(CN)_4]$.

tetracyanido means 4 cyanide ions each with a unit negative charge and nickel atom with + 2 state. Formula: $K_2[Ni(CN)_4]$.

(v) Pentaamminenitrito-O-cobalt(III) = $[Co(ONO)(NH_3)_5]^{+2}$

penataammine means 5 ammonia molecules, nitrito-O means nitrate ion which is bonded to central atom via oxygen and cobalt in + 3 state. Formula: $[Co(ONO)(NH_3)_5]^{+2}$

(vi) Hexaamminecobalt(III) sulphate = $[Co(NH_3)_6]_2(SO_4)_3$

hexaammine means six ammonia molecules and cobalt in + 3 state. Sulphate have a negative charge of-2. Balance overall charge as 0. Formula: $[Co(NH_3)_6]_2(SO_4)_3$

(vii) Potassium tri(oxalato)chromate(III) = $K_3[Cr(C_2O_4)_3]$.

trioxolato means 3 oxolate ions and chromium in + 3 state. Balance overall charge as 0. Formula: $K_3[Cr(C_2O_4)_3]$.

(viii) Hexaammineplatinum(IV) = $[Pt(NH_3)_6]^{4+}$

hexaammine means 6 neutral ammonia molecules and platinum in + 4 state. Balance overall charge as 0. Formula: $[Pt(NH_3)_6]^{4+}$

(ix) Tetrabromidocuprate(II) = $[Cu(Br)_4]^{2-}$

tetrabromido means 4 bromide ions with a unit negative charge each and copper in + 2 state. Balance overall charge as 0. Formula: $[Cu(Br)_4]^{2-}$

(x) Pentaamminenitrito-N-cobalt(III) = $[Co(NO_2)(NH_3)_5]^{2+}$

pentaammine means 5 neutral ammonia molecules, nitrito-N means nitro group bonded to central atom via the lone pair of electron of nitrogen and cobalt in + 3 state. Balance overall charge as 0. Formula: $[Co(NO_2)(NH_3)_5]^{2+}$

9.7 Using IUPAC norms write the systematic names of the following: (i) $[Co(NH_3)_6]Cl_3$ (iv) $[Co(NH_3)_4Cl(NO_2)]Cl$ (vii) $[Ni(NH_3)_6]Cl_2$ (ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ (v) $[Mn(H_2O)_6]^{2+}$ (viii) $[Co(en)_3]^{3+}$ (iii) $[Ti(H_2O)_6]^{3+}$ (vi) $[NiCl_4]^{2-}$ (ix) $[Ni(CO)_4]$

ANSWER:

(i) Starting with cation , the complex ion contains six ammonia molecules with cobalt in + 3 oxidation state. The name of compound: $[Co(NH_3)_6]Cl_3$ is hexaamminecobalt(III) chloride.

(ii) The complex ion is cation, so there are 2 ammonia molecules, one chloride ion and methyammine molecule qith platinum in + 2 state. Going in alphabetical order, the name of compound: $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ is diamminechloridomethylammineplatinum(II) chloride.

(iii) It is a complex cation with six water molecules and titanium atom in + 3 state. The name of the compound: $[Ti(H_2O)_6]^{3+}$ is hexaaquatitanium(III) ion

(iv) The complex ion is cation with cobalt in + 3 state and with four ammonia molecules i.etetraammine, one chloride ion and nitrate ion. The name of the compound: $[Co(NH_3)_4Cl(NO_2)]Cl$ is tetraamminechloridonitritocobalt(III) chloride.

(v) The complex ion is cation with manganese in + 2 state and six water molecules. The name of compound: $[Mn(H_2O)_6]^{2+}$ is hexaaquamanganese(II) ion.

(vi) The complex is anion with nickel in + 2 state and with four chloride ions. The name of the compound: $[NiCl_4]^{2-}$ is tetrachloridonickeltate(II) ion.

(vii) The complex is cation with nickel in + 2 state and six ammonia molecules. The name of compound: $[Ni(NH_3)_6]Cl_2$ is hexaamminenickel(II) chloride.

(viii) The complex is cationwithcobalt in + 3 stateand there is a bidentate ligand called as ethylenediamine. The name of compound : $[Co(en)_3]^{3+}$ is tris(ethylenediamine)cobalt(III) ion.

(ix) It is neutral complex with four carbonyl molecules and cobalt in 0 state. The name of compound: $[Ni(CO)_4]$ is tetracarbonylcobalt(0).

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

ANSWER:

Isomers are the compounds which have same chemical formula but different arrangement of atoms in space. There are principle two types of isomerism:

(i) Stereo isomerism:

(a) geometrical isomerism

(b) optical isomerism

(ii) structural isomerism

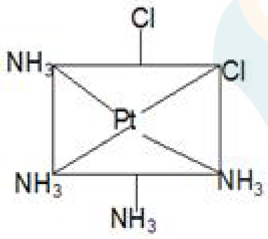
(a) Ionisation isomerism

(b) Linkage isomerism

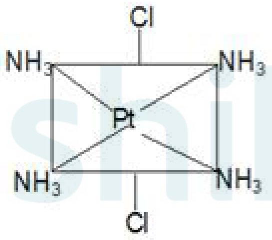
(c) Coordination isomerism

(d) Solvate isomerism

Geometrical isomerism comes into existence by the different spatial arrangement of groups around the central metal atom. Similar groups may either be arranged on the same side or on opposite sides of the central metal atom. This gives rise to two types of isomers called cis and trans isomers. When groups under consideration are arranged on the same side of the central metal atom, isomers are called cis isomers and when the groups under consideration are spatially placed on the opposite sides, isomers are called trans isomer.

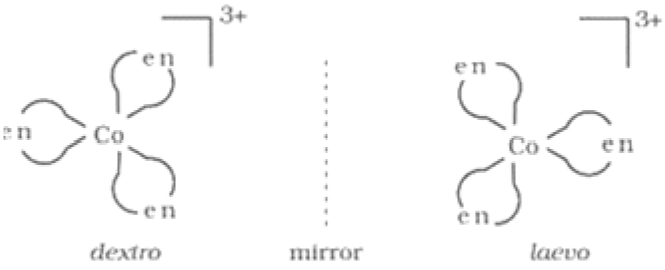


Cis



Trans

Optical isomerism is exhibited by those compounds which possess chirality. The presence of an element of symmetry makes a molecule symmetric and renders it optically inactive. When molecule does not possess any element of symmetry its mirror image is non superimposable with the molecule itself. This makes the molecule optically active. Such an asymmetric molecule can show the phenomenon of optical .The two forms of the molecule which are mirror images of each other are called enantiomers.One form rotates the plane of plane polarized light in clockwise direction, while the other in anticlockwise direction. The former is called the d-form, while the latter is termed as l-form.

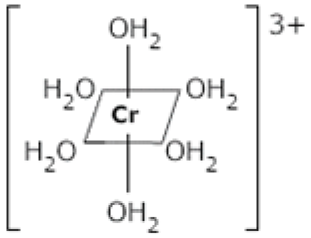


Ionisation isomerism: In ionisation isomerism there is an exchange of ions inside and outside the coordination sphere. Ionisation isomers have the same formula but produce different ions in solution. It is also known as ion-ion exchange isomerism.

Examples:

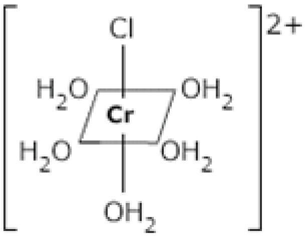
ions present in the solution	Compounds	Colour
$[Co(NH_3)_5\ SO_4]^+ + Br^-$	$[Co(NH_3)_5$ SO4]Br	Red violet
$Co(NH_3)_5Br]^{++} + SO_4^{2-}$	$Co(NH_3)_5Br]SO_4$	Red

In the two isomers (A) and (B), there is an exchange of ions inside and outside the coordination sphere. The aqueous solution of (A) gives the precipitate of AgBr on treatment with $AgNO_3$ as it contains Br, while that of (B) gives precipitate of $BaSO_4$, on treatment with $BaCl_2$.



$3\ Cl^-$

$[Cr(OH_2)_6]Cl_3$

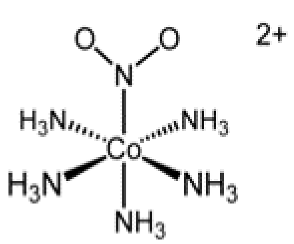


$2\ Cl^-,\ H_2O$

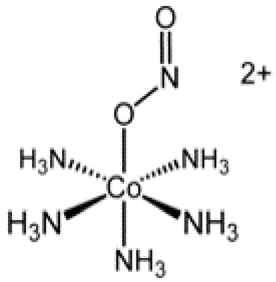
$[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$

Linkage isomerism: In linkage isomerism the same ligand is bonded to central metal atom or ion through different atoms. Linkage isomers have the same molecular formula but differ in the linkage of the ligand to central metal atom.

For example, -NO, ligand can bind to the central metal through nitrogen or oxygen to give two isomers as shown below.



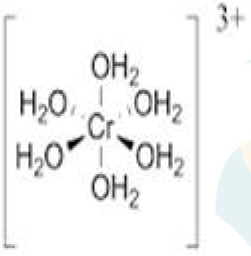
$[Co(NH_3)_5NO_2]Cl_2$
Yellow



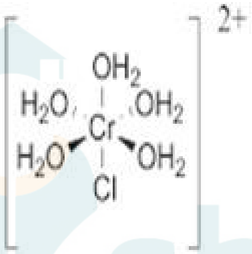
$[Co(NH_3)_5ONO]CI_2$
Red

In isomer A nitro group is bonded to the central metal atom through nitrogen and is known as nitro while in the isomer B it is bonded through Oxygen and is known as nitrito.

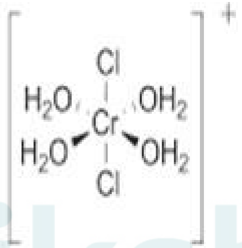
Coordination isomerism: this type of isomerism arises from different Complex ions having same molecular formula. There is interchange of ligands between cationic and anionic entities of different metal ions present in the complex. Example is $[Co(NH_3)_6][Cr(CN)_6]$ in which ammonia ligands are bounded to Cobalt and cyanide ligands to chromium ion. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$ ammonia ligands are bounded to chromium ion and cyanide ligands to Cobalt ion.



$[Cr(OH_2)_6]Cl_3$

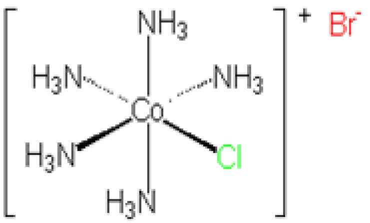


$[Cr(OH_2)_5Cl]Cl_2.H_2O$

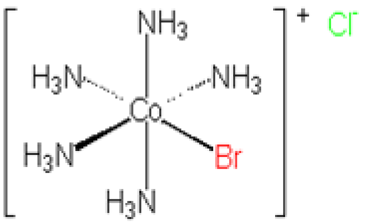


$[Cr(OH_2)_4Cl_2]Cl.2H_2O$

Solvent isomerism or hydrate isomerism: in hydrate isomerism there is an exchange of water molecule inside and outside coordination sphere. Hydrate isomers have the same molecular formula but differ in the number of molecules of water inside and outside the coordination sphere.



$[Co(NH_3)_5Cl]Br$



$[Co(NH_3)_5Br]Cl$

Ex. $CrCl_3.6H_2O$ exists in 3 hydrate isomers:

Compound	Colour	Number of water molecules inside	Number of water molecules outside

		coordination sphere	coordination sphere
$[Cr(H_2O)_6]Cl_3$	Violet	6	0
$[Cr(H_2O)_5Cl]Cl_2H_2O$.	Blue Christmas	5	1
$[Cr(H_2O)_4Cl_2]Cl.H_2O$	Green	4	2

9.9 How many geometrical isomers are possible in the following coordination entities? (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$

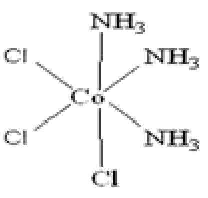
ANSWER:

(i) No geometrical isomer is possible for $[Cr(C2O_4)_3]^{3-}$ because the ligand $C_2O_4^{2-}$ is bidentate ligand(which have two sites of attachment to the central atom) and also in the coordination sphere it is the only ligand bond to it.

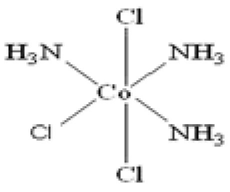
(ii) In the coordination sphere of $[Co(NH_3)_3Cl_3]$ there are two types of ligands present i.e NH_3 and Cl^- . Coordination number is 6. There are 2 isomers possible for the complex:

Facial: In this isomer one type of ligand say NH_3 forms the face of the square bipyramidal (triangular) structure.

Meridional: In this isomer one type of ligand are along the central axis of the pyramidal structure.



fac



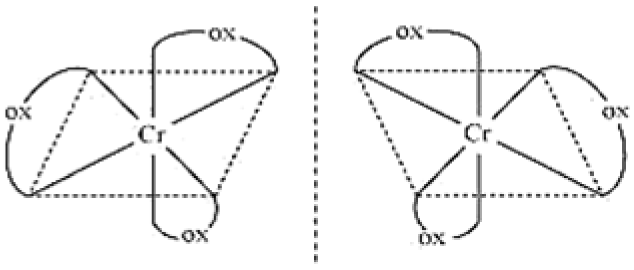
mer

9.10 Draw the structures of optical isomers of: (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[PtCl_2(en)_2]^{2+}$ (iii) $[Cr(NH_3)_2Cl_2(en)]^+$

ANSWER:

Optical isomers are the one which rotate the plane polarized light by a certain angle when passed through them and are mirror images of each other, also called as stereoisomer.

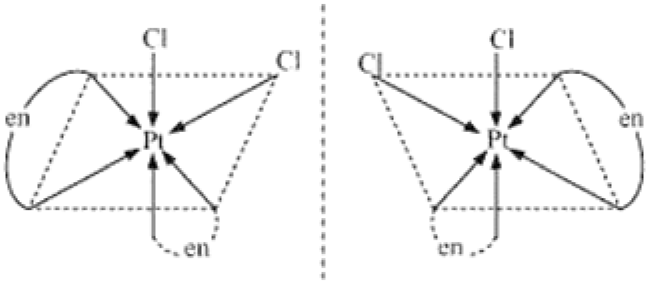
(i) $C_2O_4^{2-}$ is a bidentate ligand so it can attach to central atom at two sites, forming a chelate ring. In the complexes of this type, three symmetrical bidentate chelating ligands AA are coordinated to the central metal atom M. Such complexes do not possess any element of symmetry and are optically active. Moreover, these complexes can be resolved into optical isomers.



$[Cr(ox)_3]^{3+}$ (dextro) Mirror $[Cr(ox)_3]^{3+}$ (Laevo)

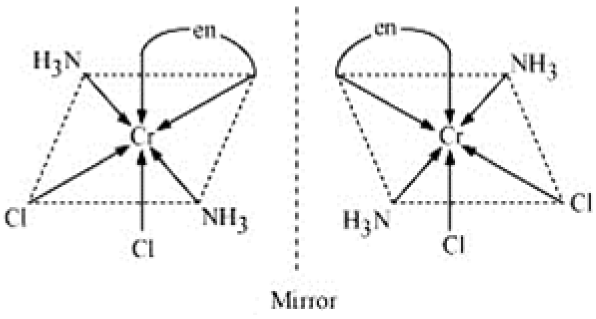
(ii) In this complex Cl is an unidentate ligand with one site of attachment whereas -en(ethylenediamine) is bidentate ligand with two sites of attachment. The complexes in which two symmetrical bidentate chelating ligands AA and two monodentate ligands a, are coordinated to central metal atom M, exhibit the phenomenon of optical isomerism and can be resolved into their optical isomers.

An example of this type of complexes is given as shows both geometrical as well as optical isomerism. Its cis form is unsymmetrical, while the trans form is symmetrical because it contains a plane of symmetry. Hence, optical isomerism is shown by cis form.



Mirror

(iii) In this there are three types of ligands. One is ammonia which is neutral (nitrogen donates the lone pair of electron to metal), Cl^- ligand is unidentate and -en is bidentate ligand. Coordination number is 6. Two optical isomers are possible due to presence of 3 types of ligands.



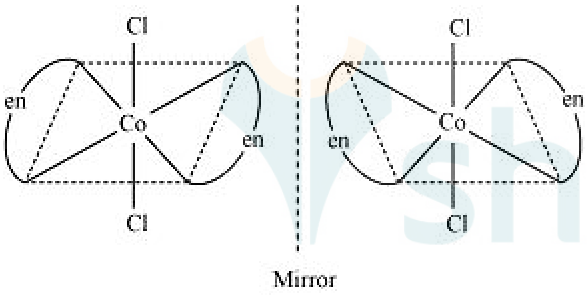
9.11 Draw all the isomers (geometrical and optical) of: (i) $[CoCl_2(en)_2]^+$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$ (iii) $[Co(NH_3)_2Cl_2(en)]^+$

ANSWER:

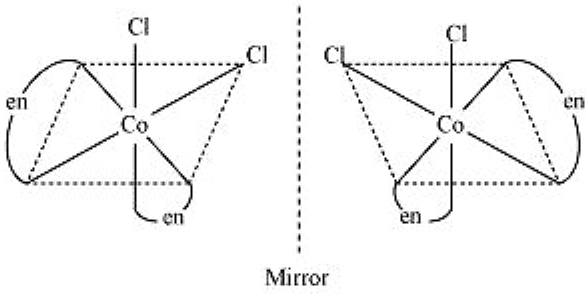
(i) $[CoCl_2(en)_2]^+$

Two types of ligand : chloride ion is unidentate ligand and -en(ethylenediamine) is bidentate ligand with two sites of attachment. The complexes in which two symmetrical bidentate chelating ligands AA and two monodentate ligands a, are coordinated to central metal atom M, exhibit the phenomenon of optical isomerism and can be resolved into their optical isomers.

An example of this type of complexes is given as shows both geometrical as well as optical isomerism. Its cis form is unsymmetrical, while the trans form is symmetrical because it contains a plane of symmetry. Hence, optical isomerism is shown by cis form.



trans- $[CoCl_2(en)_2]^+$

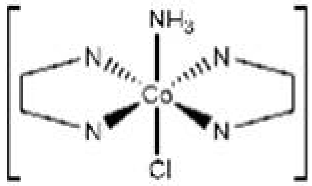


cis- $[CoCl_2(en)_2]^+$

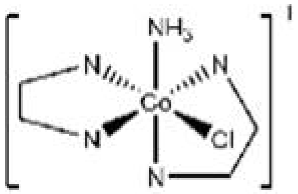
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$

In this there are three types of ligands. One is ammonia which is neutral (nitrogen donates the lone pair of electron to metal), Cl^- ligand is unidentate and -en is bidentate ligand.

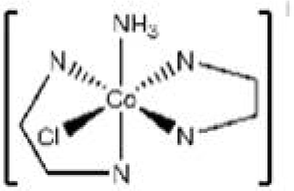
Geometrical isomers are possible because there is no plane of symmetry, so cis and trans geometrical isomers exists. Trans isomer will not show optical isomerism as the mirror image formed is superimposible of each other instead cis isomer show optical isomerism.



(trans)

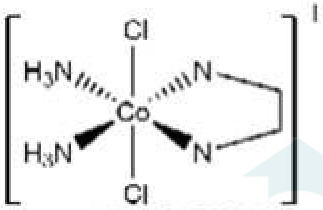


(cis, , Δ)

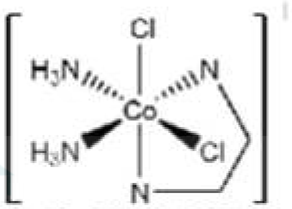


(cis, Λ)

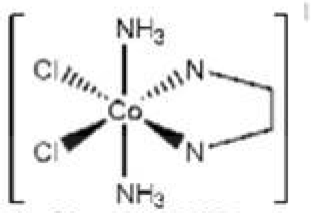
(iii) In this complex there are three types of ligands. There is no axis of symmetry that can divide the whole complex in exactly two equal halves, so there exists geometrical isomers.



(trans Cl, cis NH3)



(cis Cl, cis NH3)

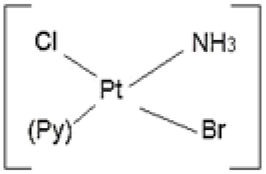


(cis Cl, trans NH3)

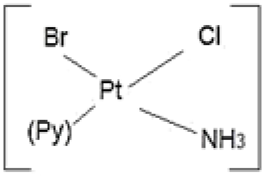
9.12Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

ANSWER:

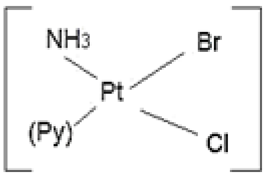
There are four different types of ligands present in the complex. So, by fixing the position of 2 ligands we get 2 geometrical isomers and by changing the position of fixed isomer we get one more geometrical isomer.



trans



Cis



Cis

Since it is tetrahedral complex so it should be optically active . But however it has not been possible to resolve optically active d and l forms of such a complex due to its complicated nature.

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.

ANSWER:

Copper sulphate exists as $[Cu(H_2O)_4]SO_4$. It is blue in colour due to presence of the $[Cu(H_2O)_4]^{2+}$ ions.

When KF is added water is replaced by fluoride ion and green colour is due to $[Cu(F)_4]^{2-}$ ions.

When KCl is added water is replaced by chloride ion and bright green colour is due to presence of $[CuCl_4]^{2-}$ ions.

In both the cases water , weak field ligand is replaced by fluoride and chloride ions.

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 $H_2S(g)$ is passed through this solution?

ANSWER:

$CuSO_4 + KCN \Rightarrow K_2[Cu(CN)_4] + K_2SO_4$

$[Cu(H_2O)_4]^{2+} + 4CN^- \Rightarrow [Cu(CN)_4]^{2-} + 4H_2O$

The coordination entity formed is $K_2[Cu(CN)_4]$.

IUPAC name of the coordination entity is potassium tetracyanocuprate(II). It is a very stable complex. The copper atom present inside the coordination sphere does not separate out to form copper ions and cyanide ions due to strong bond between them.It does not ionize to give Cu^{2+} ions and hence on adding H_2S , since there are no copper ions present so no precipitate of copper sulfide 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) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[CoF_6]^{3-}$

ANSWER:

(i) In the coordination entity iron exists in + 2 oxidation state.

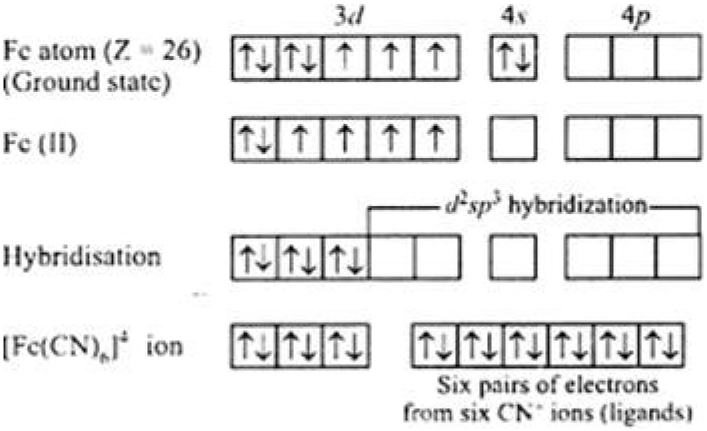
Overall charge balance:

$X + 6(-1) = -4$

$X = +2.$

Its electronic configuration is: $3d^6$

CN^- is strong field ligand so it causes pairing of the unpaired electron and undergoes hybridisation to form 6 d^2sp^3 hybrid orbitals to be filled by the six cyanide ions. It's geometry is octahedral with no unpaired electrons and hence is diamagnetic complex.



(ii) In the coordination entity iron exists in + 3 oxidation state.

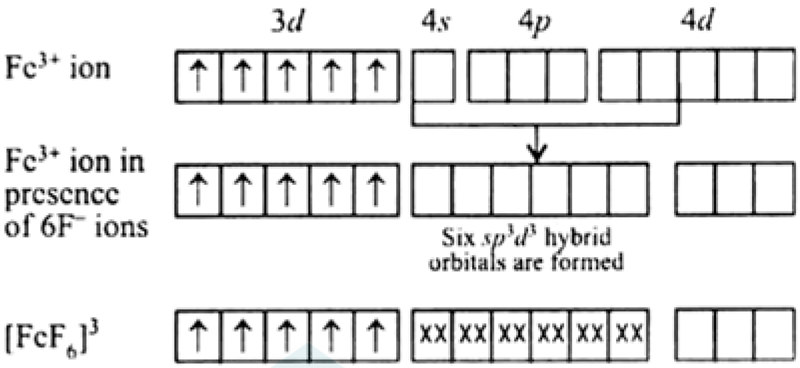
Overall charge balance:

X + 6(-1) = -3

X = + 3.

Its electronic configuration is: $3d^6$

F^- is weak field ligand so it not causes pairing of the unpaired electron and undergoes hybridisation to form 6 sp^3d^2 hybrid orbitals to be filled by the six fluoride ions. It's geometry is octahedral and is paramagnetic.



(iii) In the coordination entity cobalt exists in + 3 oxidation state.

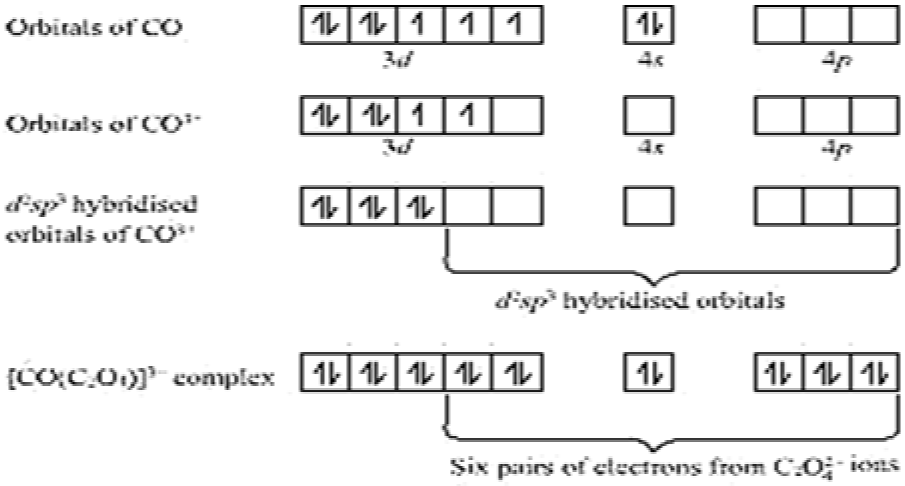
Overall charge balance:

X + 3(-2) = -3

X = + 3.

Its electronic configuration is: $3d^5$

$C_2O_4^-$ is weak-field ligand so it not causes pairing of the unpaired electron and undergoes hybridisation to form 6 sp^3d^2 hybrid orbitals to be filled by the three oxolateions(it is bidentate ligand). It's geometry is octahedral with unpaired electrons and hence is paramagnetic complex.



(iv) In the coordination entity cobalt exists in + 3 oxidation state.

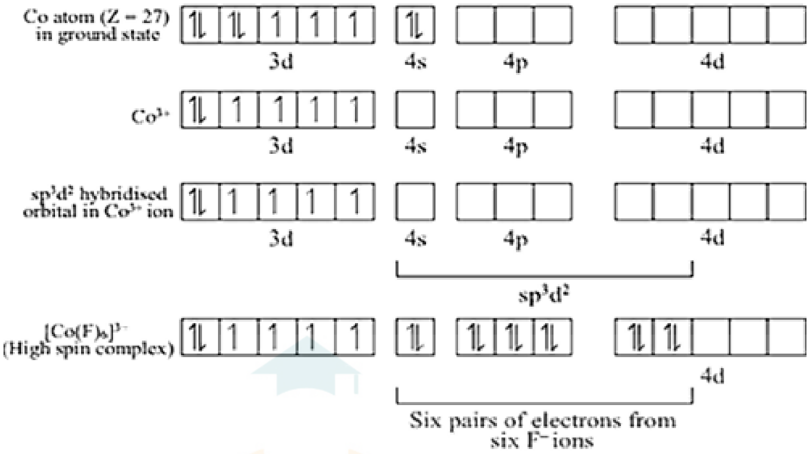
Overall charge balance:

$X + 6(-1) = -3$

$X = +3$.

Its electronic configuration is: $3d^5$

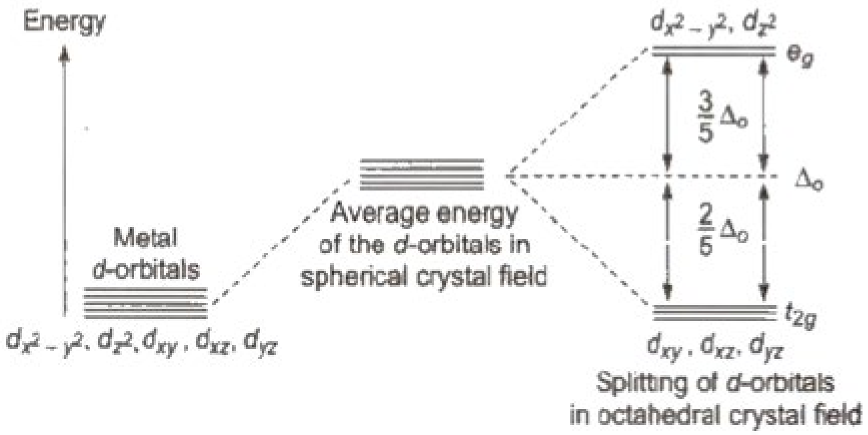
Fluoride ion is weak field ligand so it not causes pairing of the unpaired electron and undergoes hybridisation to form 6 sp^3d^2 hybrid orbitals to be filled by the six fluoride ions. It's geometry is octahedral with unpaired electrons and hence is paramagnetic complex.



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

ANSWER:

In octahedral complex the splitting of the d orbital will be such a way that the $d_{x^2-y^2}$ and d_{z^2} orbitals which face towards the axes along the direction of the ligand will experience more repulsion and will be raised in the energy and the other three orbitals which are directed between the axes are lowered in energy.



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

ANSWER:

The strong ligands have higher splitting power of d orbitals of the central metal ion, whereas weak ligand has relatively lower splitting power of d orbitals of the central metal ion. The energy difference between t_{2g} and e_g sets of d orbitals is CFSE. The strength of the ligands depend on the magnitude of Δ . Strong ligands have larger value of CFSE and in case of weak ligands the CFSE values are smaller. The common ligands can be arranged in a series in the order of their decreasing field strength, as follows.

I–<Br^-< SCN^-<Cl^-< F^-< OH^-< $C_2O_4^{2-}$< H_2O< NCS^-<py< NH_3< en<bipy< o-phen< NO_2^-< CN^-< CO.

This series depends on the power of splitting the d orbitals and is called spectrochemical series, The order of field strength of the common ligands neither depends on the geometry of the complex the nature of central metal ion.

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

ANSWER:

The difference between the energies of the two set of the d orbitals is called as crystal field splitting energy (CFSE). The degenerate d orbitals split into two levels i.e t_{2g} and e_g level due to the presence of the ligands. This splitting of the degenerate orbitals due to the ligand is called as crystal field splitting and the energy difference between the two levels is called as crystal field splitting energy.

After the splitting of the degenerate orbitals has taken place the filling of the electrons takes place. Now first 3 electrons goes into into the lower energy three t_{2g} orbitals. The fourth electron can be filled in two ways:

It can enter the t_{2g} orbitals causing pairing up of the electron (giving rise to $t_{2g}^4e_g^0$ electronic configuration) or it can enter into higher energy e_g orbital (giving rise to $t_{2g}^3e_g^1$ electronic configuration). If the CFSE value of ligand is more than energy required for the pairing up of the electron then it will result in the pairing of electron(2 case) but if the CFSE value of ligand is less than the pairing energy of the electron then it will cause the electron to enter in higher energy e_g orbital.(1 case)

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

ANSWER:

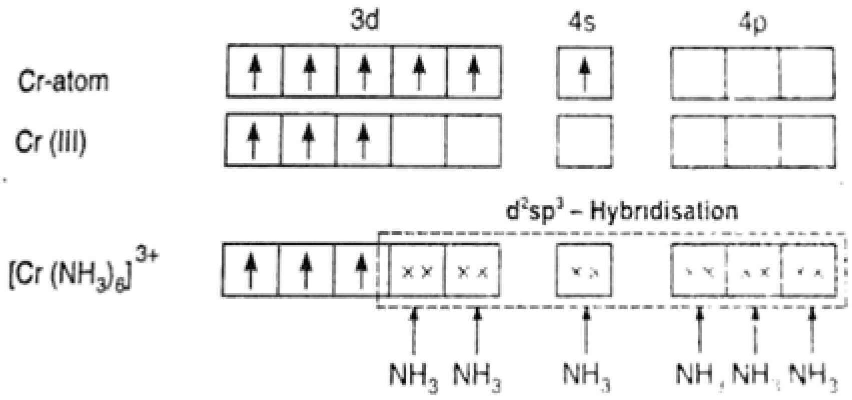
Overall charge balance in $[Cr(NH_3)_6]^{3+}$ complex:

$X + 6(0) = + 3$

$X = + 3$

Cr is in + 3 oxidation state.

Electronic configuration of Cr in + 2 state: $3d^3$. Now ammonia is a weak field ligand so it not causes pairing of the unpaired electron and undergoes hybridisation to form 6 sp^3d^2 hybrid orbitals filled by the six ammonia ligands. It's geometry is octahedral with unpaired electrons and hence is paramagnetic complex.



In case of $[Ni(CN)_4]^{2-}$ ion :

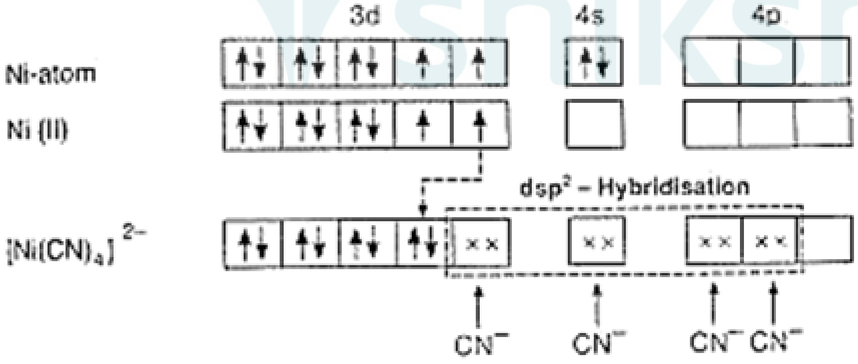
Overall charge balance in $[Ni(CN)_4]^{2-}$complex:

X + 4(-1) = -2

X = + 2

Ni is in + 2 oxidation state.

Electronic configuration of Ni in + 2 state: $3d^8$. Now cyanide ion is a strong field ligand so it causes pairing of the unpaired electron and undergoes hybridisation to form 4 dsp^2 hybrid orbitals filled by the four cyanide ligands. It's geometry is square planar with no unpaired electrons and hence is diamagnetic complex.



9.20 A solution of [Ni(H2O)6] 2+ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

ANSWER:

In case of $[Ni(H_2O)_6]^{2+}$ H_2O is a weak field ligand , so it does not cause the pairing of the unpaired electron of Ni^{2+} ion. Thus there is possibility of the intra d-d transition from the d orbital of lower energy to that of higher energy. Thus the light is absorbed from the visible region and complimentary colour is observed. But in case of $[Ni(CN)_4]^{2-}$ CN^- is strong field ligand.

Therefore it will cause pairing of the unpaired electrons of Ni^{2+} ion. There are no unpaired electrons present, so there is no d-d transition and hence it is colourless.

9.21 $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

ANSWER:

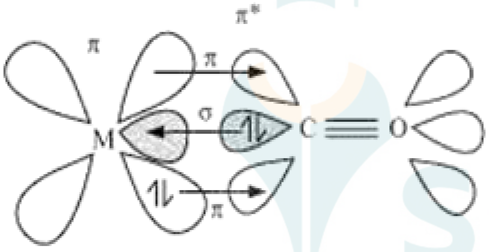
The colour of the particular complex compound depends on the crystal field splitting energy(CFSE). This CFSE depends on the nature of the ligand attached to the metal atom. In case of $[Fe(CN)_6]^{4-}$ and $[Fe(H2O)_6]^{2+}$ the colour differs due to differences in CFSE . CN^- is a strong field ligand so will have high CFSE than H_2O with a low value of CFSE. There is absorption of the energy from the visible region for the d-d transition and corresponding complimentary colour is observed. Thus there is the colour difference.

9.22 Discuss the nature of bonding in metal carbonyls.

ANSWER:

Compounds containing carbonyl

ligands only are known as homoleptic carbonyl. Such types of compounds are formed by most of the transition metals. These metal carbonyls always have simple, well-defined structures. In metal carbonyls the metal - carbonyl bond possess both s and p.character. M-C-bond is sigma bond. It is formed by the donation of lone pair of electrons of the carbonyl carbon into the vacant orbital of the metal. The M-C pi bond is formed by the donation of a pair of electron from a filled d orbital of a metal into the vacant antibonding π orbital of carbon monoxide. Such type of metal to ligand bonding creates a synergic effect which strengthens the bond between CO and metal.



Synergic bonding in metal carbonyls

9.23 Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes: (i) $K_3[Co(C_2O_4)_3]$ (iii) $(NH_4)_2[CoF_4]$ (ii) cis-$[CrCl_2(en)_2]Cl$ (iv) $[Mn(H_2O)_6]SO_4$

ANSWER:

(i) Overall charge balance:

$X + 3(-2) = -3$

$X = +3$

Oxidation state of Co is + 3.

As there are 3 oxolate ion and being bidentate, coordination no. Of complex is 6. So it is octahedral complex.

d orbital occupation: $t_{2g}^6eg^0$(oxolate ion is weak field ligand , does not cause pairing of electron as the energy required for pairing of electron is more than CFSE).

(ii) Overall charge balance:

X + balance4(-1) = -2

X = + 2

Oxidation state of Co is + 2.

As there are 4 fluoride ion , coordination no. Of complex is 4 i.e. Tetrahedral complex.

d orbital occupation: $eg^4t_{2g}^3$(fluoride ion is weak field ligand , does not cause pairing of electron as the energy required for pairing of electron is more than CFSE).

(iii) Overall charge balance:

X + 2(-1) + 2(0) = + 1

X = + 3

Oxidation state of Cr is + 3

Coordination no. Of complex is 6. (-en is a bidentate ligand). Octahedral complex.

d orbital complex: t_{2g}^3

(iv) Ovearll charge balance:

X + 6(0) = + 2

X = + 2

Oxidation state of Mn is + 2.

Coordination no. Of complex is 6. Octahedral complex.

d orbital occupation: $t_{2g}^3e_g^2$(water is weak field ligand, does not cause pairing of the electron).

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) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (iii) $[CrCl_3(py)_3]$ (v) $K_4[Mn(CN)_6]$ (ii) $[Co(NH_3)_5Cl]Cl_2$ (iv) $Cs[FeCl_4]$

ANSWER:

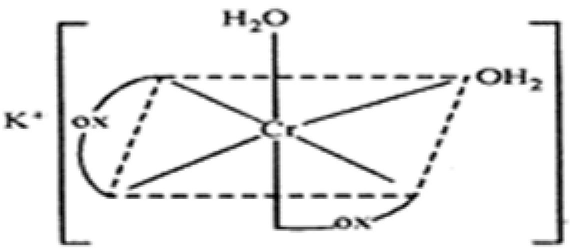
(i) The complex is an anion with chromium as central atom, 2 water molecules and 2 oxolate ions with -2 negative charge each. Balance overall charge as 0, we get oxidation state of Cr as:

X + 2(0) + 2(-2) = -1

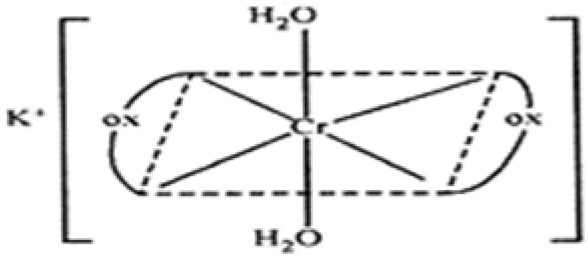
X = + 3.

Name of compound: potassium diaquadioxolatochromate(III) trihydrate.

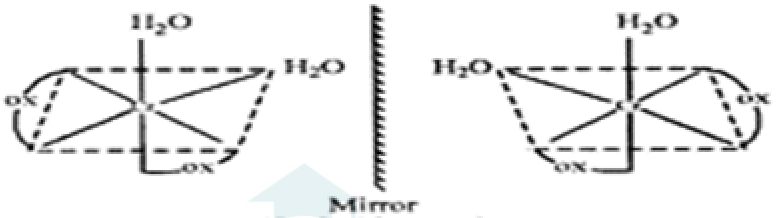
Electronic configuration of Cr: $3d^3$, t_{2g}^3



cis

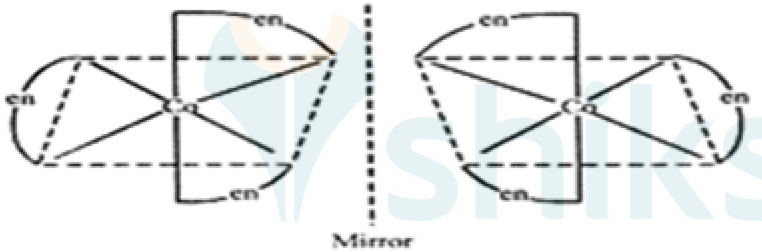


trans



(Optical isomers)

(b) optical isomerism exists



Co-ordination no. Of complex: 6 (as oxolate ion is bidentate ligand)

As both the water molecule and oxolate ion are weak field ligand, so they do not cause pairing up of electron.

$\mu = [n(n + 2)]^{1/2}$

$\mu = [3\times5]^{1/2}$

μ = 4BM.

(ii) The complex is a cation with cobalt as central atom, five neutral ammonia molecules and one chloride ion. Balance overall charge as 0, we get,

X + 5(0) + 1(-1) = + 2

X = + 3.

Oxidation state of cobalt is + 3.

Name of compound is pentaamminechloridocobalt(III) chloride.

Coordination no. is 6.

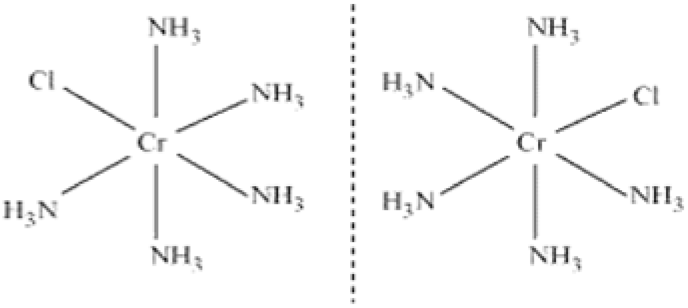
Electronic configuration of cobalt: $3d^6$

As ammonia is a strong field ligand so it causes pairing of the electron. No. Of unpaired electrons:0

$\mu = [n(n + 2)]^{1/2}$

$\mu = [0]^{1/2}$

μ = 0BM.



2 isomers

(iii) The complex is neutral with chromium as central atom, three chloride ions and 3 pyridine molecules which are neutral.

Name of compound is trichloridotripyridinechromium(III).

Balance overall charge as 0.

X + 3(-1) + 3(0) = 0

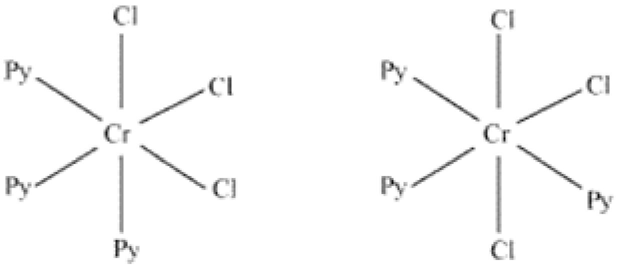
X = + 3.

Oxidation state of chromium is + 3.

Electronic configuration:$3d^3$

Coordination no.Is 6.

As chloride ion and pyridine molecule botha re weak field ligand so they do not cause pairing of electron.



Facial isomer

Meriodional isomer

$\mu = [n(n + 2)]^{1/2}$

$\mu = [3\times5]^{1/2}$

μ = 4BM

(iv) The complex is anion with iron as central atom, and 4 chloride ions. Balance overall charge:

X + 4(-1) = -1

X = + 3

Oxidation state of Fe: + 3.

Electronic configuration:$3d^6$

Name of compound: Caesiumtetrachloridoferrate(III).

Coordination no. is 4.

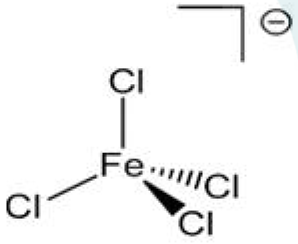
As chloride ion is weak field ligand ,it does not cause pairing of electron.

$\mu = [n(n + 2)]^{1/2}$

$\mu = [4\times6]^{1/2}$

μ = 5BM

Steriochemistry is optically inactive as it is a tetrahedral complex and the relative position of each ligand will be same in all condition.



(v) The complex is anion with manganese as central atom , and six cyanide ions with each unit ngative charge. Balance overall charge

X + 6(-1) = -4

X = + 2

Oxidation state of Mn = + 2

Electronic configuration of Mn:$3d^3$

Name of compound: potassium hexacyanoferrate(III)

Coordination no.Is 6.

As cyanide ions are strong field ligand , they cause pairing of electrons.

No. Of unpaired electrons is 1.

$\mu = [n(n + 2)]^{1/2}$

$\mu = [1\times3]^{1/2}$

$\mu = 1.732$BM.

Steriochemistry: optically inactive .

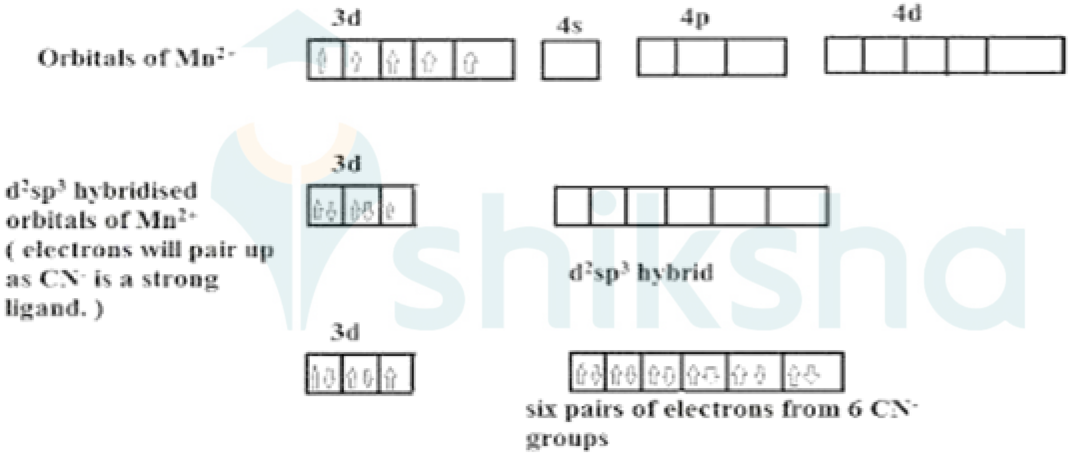
9.25 Explain the violet colour of the complex $[Ti(H_2O)_6]^{3+}$ on the basis of crystal field theory.

ANSWER:

Stability of coordination compounds in a solution refers to the association of the two species i.e coordination sphere and counter ions involved in a state of equilibrium. Stability of complex is expressed in terms of formation constant as:

Stability constant = $[ML_3]/[M][L]^3$

The more will be the value of stability constant, the more will be the amount of $[ML_3]$ in the solution.



Stability can be of 2 types:

Thermodynamics stability (the extent to which complex is formed or will be transformed to other species at point of equilibrium)

Kinetic stability (speed at which the complex is formed)

Stability of complex depends on factors:

(i) Charge on central atom:. More will be the charge on central atom more will be the strong bond between atom and ligand and more will be the stability of the complex.

(ii) Basic nature of ligand: More will be the basic character of ligand , more it will try to donate the electrons to the metal atom, hence greater stability.

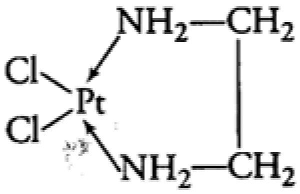
(iii) Presence of chelate ring: The presence of chelate ring give more stability to the complex. (Stronger interaction)

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

ANSWER:

When a ligand bonds with the central metal ion in such a way that it forms a ring, then it is found that the metal - ligand bond is more stable. In other way a compound which forms chelate ring are more stable than the complexes without chelate rings. This effect is known as chelate effect.

In this example we can see that the ligand form a closed ring structure around central atom and increase the stability of complex with forming a strong bond between them.



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

ANSWER:

(i) Role of coordination compounds in biological system: We know that in the process of photosynthesis, sunlight is absorbed by the plants through a green pigment called as chlorophyll. This chlorophyll is a co-ordination compound of magnesium. In our human biological body, coordination compounds play a major role. In our blood the oxygen carrier i.e hemoglobin is a co-ordination compound of iron.

(ii) In medicinal chemistry: A co-ordination compound of platinum called as cis-platin is used in the treatment of stopping the growth of the tumour in our body.

(iii) In analytical chemistry: In the analysis of salt , when different reagents containing ligands are added to different basic radicals they form coordination compounds. These coordination compounds exhibit different colours associated with each of the basic radicals. Thus it can be used in detection of various radicals.

(iv) In extraction or metallurgy of metals: In the extraction of the metals from their ores the ability of the metals to form complexes or coordination comppunds are used. For eg. In aqueous solution, gold combines with the cyanide ions to form a complex. Later gold can be extracted from this complex by treating it with zinc metal.

9.28 How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution? (i) 6 (ii) 4 (iii) 3 (iv) 2

ANSWER:

The given complex can be written as :

Coordination sphere: $[Co(NH_3)_6]^{2+}$

Counter ions: $2Cl^-$ ions. {Considering total overall charge as zero}

Thus we can see that there are total of 1 + 2 ions.

9.29 Amongst the following ions which one has the highest magnetic moment value? (i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Zn(H_2O)_6]^{2+}$

ANSWER:

(i) Overall charge balance :

X + 6(0) = + 3

X = + 3.

Cr is in + 3 oxidation state.

Electronic configuration:$3d^3$

As water is a weak field ligand ,it does not call pairing up of the electrons. Number of unpaired electron is equal to 3.

Spin only magnetic moment is given by:

$\mu = [n(n + 2)]^{1/2}$

$\mu = [3\times5]^{1/2}$

μ = 4BM

(ii) In $[Fe(H_2O)_6]^{3+}$

Electronic configuration of Fe is: $[Ar]3d^64s^2$

$[Ar] = 1s^22s^22p^63s^23p^6$

Electronic configuration of $Fe^{+3} = [Ar]3d^5$

Outer electronic configuration of $Fe^{+3} = 3d^5$

Overall charge balance:

X + 6(0) = 3

X = + 3

H_2O is weak field ligand so it does not pair the unpaired electron. Total no. of unpaired electron, n = 5.

Spin only magnetic moment is given by:

$\mu = [n(n + 2)]^{1/2}$

$\mu = [5\times7]^{1/2}$

μ = 5.916BM

(iii) Overall charge balance:

X + 6(0) = + 2

X = + 2

Electronic configuration:$3d^{10}$

It has completely filled d orbital, so no. Of unpaired electrons is 0.

$\mu = 0$.

Thus, $[Fe(H_2O)_6]^{3+}$ has highest magnetic moment value.

3.30 The oxidation number of cobalt in $K[Co(CO)_4]$ is

(i) + 1 (ii) + 3 (iii) –1 (iv) –3

ANSWER:

$K[Co(CO)_4] = K^+ + [Co(CO)_4]^-$

total overall charge as 0:

$X + 4(0) = -1$

$X = -1$.

Option (iii) is correct.

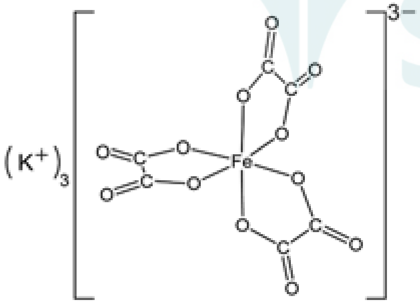
9.31 Amongst the following, the most stable complex is

(i) $[Fe(H_2O)_6]^{3+}$ (ii) $[Fe(NH_3)_6]^{3+}$ (iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[FeCl_6]^{3-}$

ANSWER:

Among all the complex given $[Fe(C_2O_4)_3]^{3-}$ have a bidentate ligand whereas all the other three have unidentated ligand. Now we know that in chelate effect, the bidentate ligand forms a ring like structure and complex so formed is very stable with strong bond between them.

So, $[Fe(C_2O_4)_3]^{3-}$ 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: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

ANSWER:

In all the complex the central metal atom/ion is nickel, Ni. Hence the absorption of wavelength from visible region depends on the ligands attached. The order in which the CFSE energy values of ligands increase according to the spectrochemical series is as follows:

$$H_2O < NH_3 < NO_2^{2-}.$$

So the order of crystal field splitting of d orbitals will also be in the same order because more will be the CFSE energy more will be the energy gap between orbitals. Hence order of wavelength absorption

$$[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$$