

# Coordination Compounds

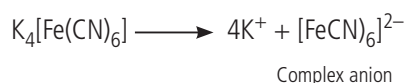
## TRY YOURSELF

## ANSWERS

1. Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts dissociate into simple ions completely when dissolved in water, and complex ions do not dissociate into all constituent ions.

For example, Mohr's salt,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  when dissolved in water, dissociates completely into its constituent ions  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions and gives test of respective ions.

While a coordination compound,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , does not dissociate into  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions.



2.  $\text{CoCl}_3 \cdot 6\text{NH}_3 \longrightarrow 3$  moles of  $\text{AgCl}$  precipitated means it has  $3\text{Cl}^-$  ions outside the coordination sphere.

$\text{CoCl}_3 \cdot 6\text{NH}_3$  has formula  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , thus, its secondary valency or C.No. is 6.

$\text{PtCl}_2 \cdot 3\text{NH}_3 \longrightarrow 1$  mole of  $\text{AgCl}$  precipitated means it has 1  $\text{Cl}^-$  ion outside the coordination sphere thus, it is formulated as  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$ , hence its secondary valency is 4.

$\text{CrCl}_3 \cdot 3\text{NH}_3 \cdot 3\text{H}_2\text{O} \longrightarrow 3$  moles of  $\text{AgCl}$  precipitated means it has  $3\text{Cl}^-$  ions outside the coordination sphere, thus, it is formulated as  $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$  hence its secondary valency is 6.

$\text{NiCl}_2 \cdot 6\text{NH}_3 \longrightarrow 2$  moles of  $\text{AgCl}$  precipitated mean it has  $2\text{Cl}^-$  ions outside the coordination sphere thus, it is formulated as  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ , hence it has secondary valency 6.

3. Molar conductivity of these coordination compounds in aqueous solution depends on the number of ions they produce.

$[\text{Ni}(\text{CO})_4]$  does not produce any ion so it has zero molar conductivity.

$[\text{Co}(\text{NH}_3)_6]\text{Br}_3 \longrightarrow [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Br}^-$  i.e., 4 ions

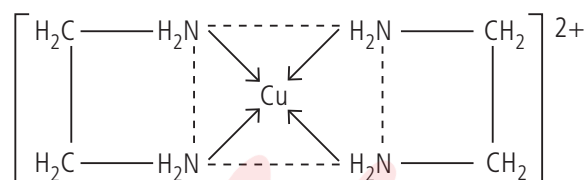
$\text{K}_2[\text{Zn}(\text{OH})_4] \longrightarrow 2\text{K}^+ + [\text{Zn}(\text{OH})_4]^{2-}$  i.e., 3 ions

$[\text{Ag}(\text{CN})_2]\text{Cl} \longrightarrow [\text{Ag}(\text{CN})_2]^+ + \text{Cl}^-$  i.e., 2 ions

Thus, the increasing order of molar conductivity is

$[\text{Ni}(\text{CO})_4] < [\text{Ag}(\text{CN})_2]\text{Cl} < \text{K}_2[\text{Zn}(\text{OH})_4] < [\text{Co}(\text{NH}_3)_6]\text{Br}_3$

4. (i) A chelate results from the attachment of multidentate ligands to a metal ion. It is a five or six-membered ring that includes the central metal ion and atoms of the ligand. For example,  $[\text{Cu}(\text{en})_2]^{2+}$



(ii) A chelating agent is a multidentate ligand. It simultaneously attaches to two or more positions in the coordination sphere of a central metal ion e.g., en, ethylenediamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) and ox, oxalate,  $\text{C}_2\text{O}_4^{2-}$  ion.

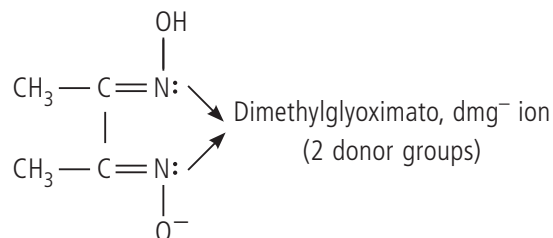
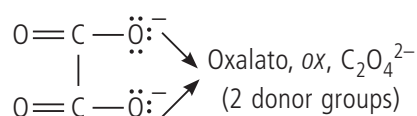
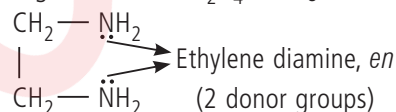
5. The two constituents of the complex are :

(i) The central metal cation or atom i.e.,  $\text{Pt}^{4+}$

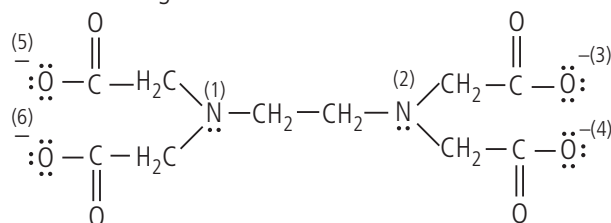
(ii) The ligands which are  $\text{NH}_3$  molecules here.

6. Monodentate ligands :  $\text{NCS}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$

Bidentate ligands : en and  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{dmg}^-$



Hexadentate ligand:  $\text{EDTA}^{4-}$



7. (i) In  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ , the C.N. of Mn is 6 as  $\text{H}_2\text{O}$  is a monodentate ligand. Its IUPAC nomenclature is hexaaquamanganese(II) ion.

(ii) In  $\text{Na}[\text{PtBrCl}(\text{NO}_2)(\text{NH}_3)]$ , the C.N. of Pt is 4 as all  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_3$  are monodentate ligands.

Let x be the oxidation no. of Pt then,

$$+x + 1(-1) + 1(-1) + 1(-1) + 0 = -1$$

$$\Rightarrow x = -1 + 3 = +2$$

Thus, its IUPAC nomenclature is

sodium amminebromidochloridonitrito-N-platinate(II).

(iii) In  $\text{Hg}[\text{Co}(\text{SCN})_4]$ , the C.N. of Co is 4 as  $\text{SCN}^-$  is a monodentate ligand.

Let  $x$  be the oxidation no. of Co then,

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

Thus, its name is mercury tetrathiocyanatocobaltate(II).

(iv)  $[\text{Rh}((\text{C}_6\text{H}_5)_3\text{P})_3]\text{Cl}$  the C.N. of Rh is 3 as  $(\text{C}_6\text{H}_5)_3\text{P}$  is a monodentate ligand. Let  $x$  be the oxidation no. of Rh then

$$+x + 3(0) = +1 \Rightarrow x = +1$$

Thus, name will be *tris*(triphenylphosphine)rhodium(I) chloride

(v) In  $[\text{Zn}(\text{OH})_4]^{2-}$ , the C.N. of Zn is 4 as  $\text{OH}^-$  ion is a monodentate ligand. Let  $x$  be the oxidation state of Zn then,

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

Its IUPAC name is tetrahydroxozincate(II) ion.

(vi) In  $[\text{Cu}(\text{Br})_2(\text{H}_2\text{O})(\text{NH}_3)]$ , the C.N. of Cu is 4. Let  $x$  be the oxidation state of Cu then,

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

$$\Rightarrow x = +2$$

Its name will be ammineaquadibromidocopper(II).

8. (a)  $[\text{Pt} \text{BrCl} (\text{py})(\text{NH}_3)]^x$

Let us find out the charge on the complex.

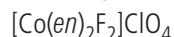
$$+2 - 1 - 1 + 0 + 0 = x \text{ (as pyridine (py), } \text{C}_5\text{H}_5\text{N is a neutral ligand)}$$

$$\Rightarrow x = 0$$

Thus, this is a neutral complex,  $[\text{PtBrCl}(\text{py})(\text{NH}_3)]$ .

(b)  $[\text{Co}(\text{en})_2\text{F}_2]^{+1}\text{ClO}_4^{-1}$

Thus, the charges are balanced. So the formula is



(c)  $[\text{Co}(\text{NH}_3)_4(\text{Cl})_2]^x [\text{Cr}(\text{CN})_6]^y$

Let us find the charges over this cationic and anionic complexes.

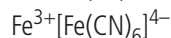
$$+3 + 4(0) + 2(-1) = x; \quad +3 + 6(-1) = y$$

$$\Rightarrow x = +1 \quad y = -3$$

Thus, the formula is  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]_3[\text{Cr}(\text{CN})_6]$

(d)  $\text{Fe}^{3+}[\text{Fe}(\text{CN})_6]^x$ , let us first find out the charge on the anionic complex.

$$+2 + 6(-1) = x \Rightarrow x = -4$$



Now, to balance the total charge on cation and anion, we write  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  which is the formula of the complex.

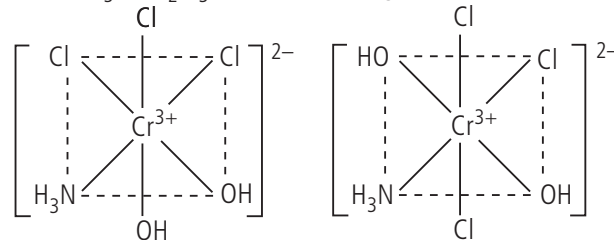
(e)  $[\text{Cr}(\text{CO})_5(\text{Ph}_3\text{P})]$  is the formula of the complex as CO and  $\text{Ph}_3\text{P}$  both are neutral ligands.

(f)  $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$  is the formula of the complex.

9. (i) All the possible isomers of  $[\text{Pt}(\text{SCN})(\text{NH}_3)_3]\text{SCN}$  are  $[\text{Pt}(\text{SCN})(\text{NH}_3)_3]\text{SCN}$ ,  $[\text{Pt}(\text{SCN})(\text{NH}_3)_3]\text{NCS}$ ,  $[\text{Pt}(\text{NCS})(\text{NH}_3)_3]\text{SCN}$

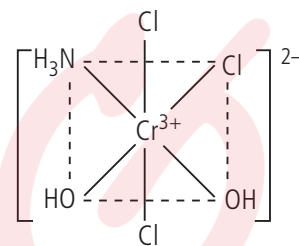
and  $[\text{Pt}(\text{NCS})(\text{NH}_3)_3]\text{NCS}$ .

(ii)  $[\text{Cr}(\text{NH}_3)(\text{OH})_2\text{Cl}_3]^{2-}$  ion has three geometrical isomers.



(a) Cl-Cl *cis*, OH-OH *cis*

(b) Cl-Cl *trans*, OH-OH *trans*



(c) Cl-Cl *trans*, OH-OH *cis*

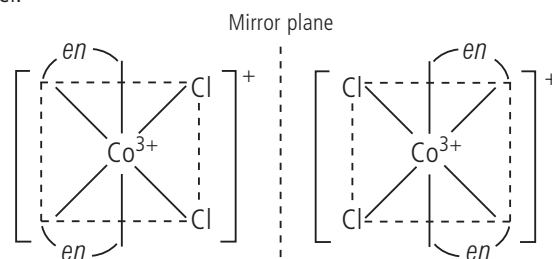
10. The formula of complex compound is  $\text{Co}(\text{en})_2\text{Cl}_2\text{NO}_2$ . As the complex is octahedral it may be represented by any of the two structural formulae.

$[\text{Co}(\text{en})_2\text{Cl}_2]\text{NO}_2$  and  $[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]\text{Cl}$  which are ionisation isomers.

$[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]\text{Cl}$  has linkage isomer, *bis* (ethylenediamine) chloridonitrito-N-cobalt (III) chloride and  $[\text{Co}(\text{en})_2\text{Cl}(\text{ONO})]\text{Cl}$  *bis*(ethylenediamine) chloridonitrito-O-cobalt(III) chloride

$[\text{Co}(\text{en})_2\text{Cl}_2]\text{NO}_2$ -*bis* (ethylene diamine)dichloridocobalt(III) nitrite has geometrical and optical isomers.

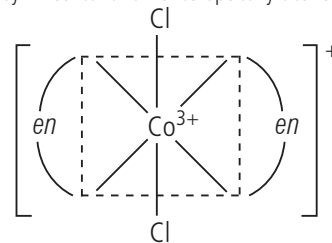
$[\text{Co}(\text{en})_2\text{Cl}_2]^+$  ions is an octahedral complex ion of  $[M(\text{AA})_2a_2]$  type has total three isomers *d*- and *l*-forms of *cis*-isomer and *trans*-isomer.



*cis-d*-isomer

*cis-l*-isomer

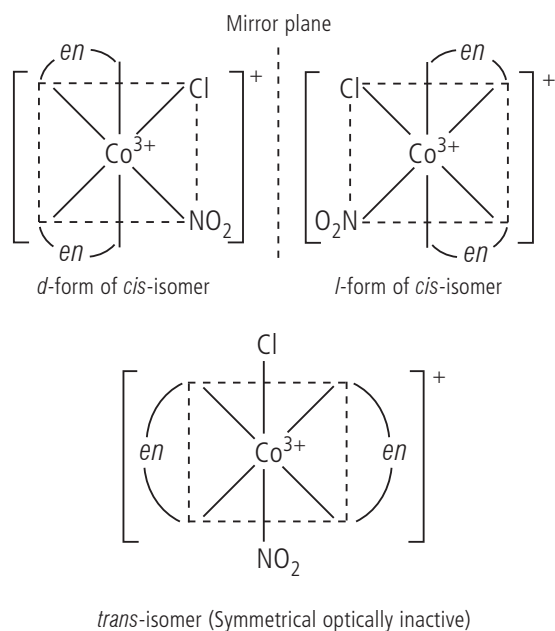
(Unsymmetrical and hence optically active form)



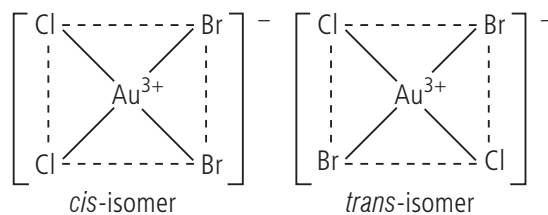
*trans-meso* form (Symmetrical and hence optically inactive form)

$[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]^+$  ion is an octahedral complex ion of  $[M(\text{AA})_2ab]$

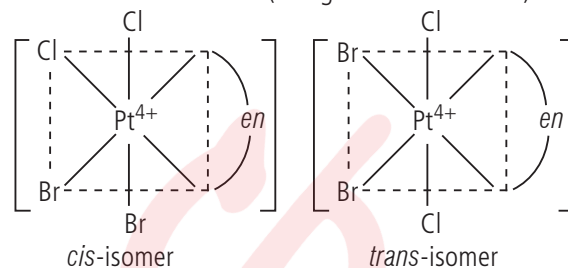
type also has three isomers viz; *d*- and *l*-forms of *cis*-isomer and *trans*-isomer.



11. (a) A square planar complex,  $[\text{AuCl}_2\text{Br}_2]^-$  has two geometrical isomers viz. *cis* and *trans*-isomers.

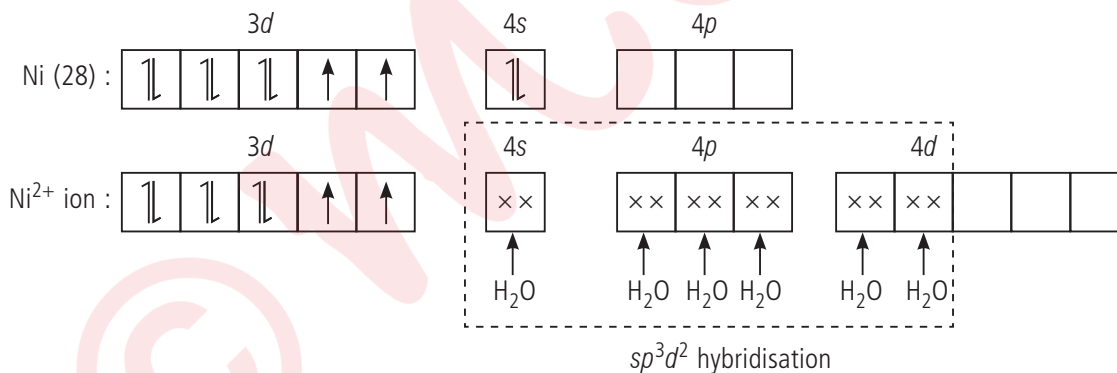


(b)  $[\text{Pt}(\text{en})\text{Cl}_2\text{Br}_2]$  is an octahedral compound of  $[\text{M}(\text{AA})\text{a}_2\text{b}_2]$  type and has *cis*- and *trans*-isomers (two geometrical isomers).



(c) Since  $[\text{CoCl}_2\text{Br}_2]^{2-}$  ion is a tetrahedral complex ion, it has no geometrical isomer.

12. (i) The valence shell configuration of  $\text{Ni}^{2+}$  ion is  $3d^8 4s^0 4p^0$  which shows that two  $3d$ -orbitals cannot be made vacant for  $d^2sp^3$  hybridisation. Thus,  $\text{Ni}^{2+}$  ion cannot form inner orbital octahedral complexes. Hence, all octahedral complexes of  $\text{Ni}^{2+}$  ion involve  $sp^3d^2$  hybridisation by using one  $4s$ , three  $4p$  and two  $4d$ -orbitals so, these are outer orbital octahedral complexes. For example,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion,



(ii) In the complex ions,  $[\text{Co}(\text{NH}_3)_6]^{2+}$  and  $[\text{Co}(\text{NO}_2)_6]^{4-}$ ,  $\text{Co}$  is in +2 oxidation state.  $\text{Co}^{2+}$  has valence shell configuration of  $3d^7$ . These complex ions are formed by  $sp^3d^2$  hybridisation of  $\text{Co}^{2+}$  ion with 3 unpaired electrons, since pairing of  $3d$  electrons is not possible.

Now, when  $[\text{Co}(\text{NH}_3)_6]^{2+}$  ion is oxidised,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  ion is formed and  $[\text{Co}(\text{NO}_2)_6]^{4-}$  ion is oxidised to  $[\text{Co}(\text{NO}_2)_6]^{3-}$  ion.

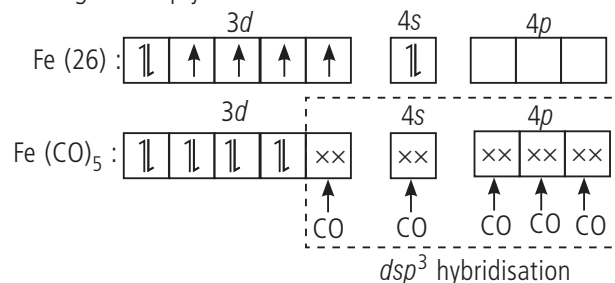
The new complex ions have  $\text{Co}^{3+}$  ion having  $3d^6$  configuration. These complex ions formed inner orbital octahedral complexes involving  $d^2sp^3$  hybridisation.

Since in  $d^2sp^3$  hybridisation, inner  $3d$ -orbitals are used, stronger bonds are formed in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{NO}_2)_6]^{3-}$  ions and hence, these ions are more stable.

Thus,  $[\text{Co}(\text{NH}_3)_6]^{2+}$  and  $[\text{Co}(\text{NO}_2)_6]^{4-}$  ions are easily oxidisable.

13. In  $[\text{Fe}(\text{CO})_5]$ :  $\text{Fe}$  is in zero oxidation state.

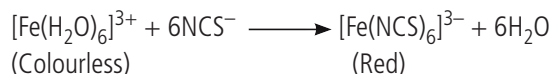
As  $\text{CO}$  is a strong field ligand, the two electrons from  $4s$ -orbital shift to  $3d$ -orbitals and in  $\text{Fe}(\text{CO})_5$ , all the  $3d$ -electrons get paired up leaving one empty  $3d$ -orbital.



Thus, it has trigonal bipyramidal geometry with  $dsp^3$  hybridisation. This is diamagnetic in nature having no unpaired electrons.

14. (i) Since  $\text{H}_2\text{O}$  is a weak field ligand, the value of  $\Delta_0$  for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion is small and this value lies in the visible region. Thus,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion has green colour. On the other hand, since  $\text{CN}^-$  is a strong field ligand, the value of  $\Delta_0$  for  $[\text{Ni}(\text{CN})_4]^{2-}$  ion is large and hence lies in the ultraviolet region. Thus,  $[\text{Ni}(\text{CN})_4]^{2-}$  ion has no colour.

(ii) When  $\text{NCS}^-$  ions are added to  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion,  $[\text{Fe}(\text{NCS})_6]^{3-}$  ion is obtained.

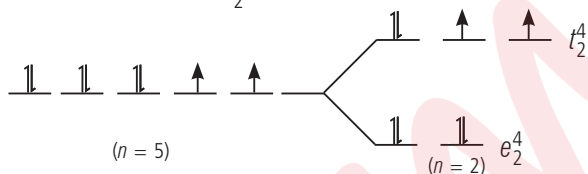


Since  $\text{H}_2\text{O}$  is a weak field ligand,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  ion has so small value of  $\Delta_0$  that the wavelength of the absorption peak of this ion lies in the infrared region and this ion appears colourless. Now since  $\text{NCS}^-$  ions are strong field ligands, the presence of these ligands in  $[\text{Fe}(\text{NCS})_6]^{3-}$  ion makes the value of  $\Delta_0$  high so that the wavelength of the absorption peak lies in the visible region (actually in the blue-green region).

15. (i) Since  $\text{CN}^-$  ions are strong field ligands, all the eight  $3d$ -electrons of  $\text{Ni}^{2+}$  ion get paired up in the splitted  $d$ -orbitals in square planar field of  $[\text{Ni}(\text{CN})_4]^{2-}$  ion.

Thus, no. of unpaired electrons is zero and hence  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic.

Whereas  $[\text{NiCl}_4]^{2-}$  ion has tetrahedral geometry as  $\text{Cl}^-$  ions are weak field ligands. The distribution of eight  $3d$  electrons of  $\text{Ni}^{2+}$  ion in tetrahedral field is as  $e^4 t_2^4$ .



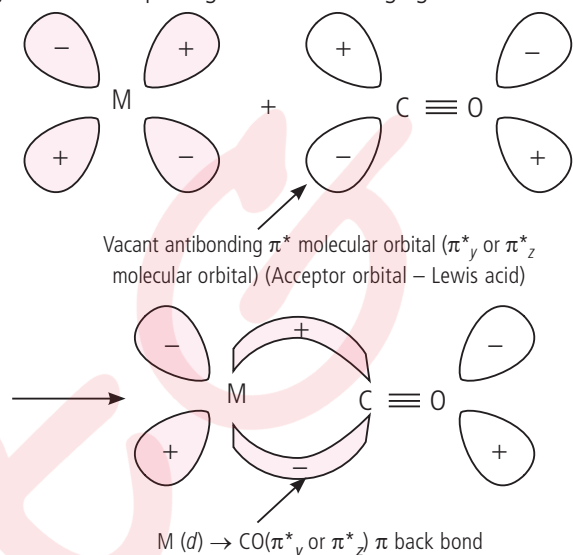
Thus, it has two unpaired electrons and hence  $[\text{NiCl}_4]^{2-}$  is paramagnetic.

(ii) In case of tetrahedral complexes, since  $\Delta_t$  (energy difference between  $t_2$  and  $e$  sets of orbitals) is generally less than pairing energy,  $P$ . Thus, a very high amount of energy is required to pair up the electrons, consequently the electrons tend to remain unpaired. So, tetrahedral complexes are high spin complexes even when strong field ligands are involved.

16. The metal atom in metal carbonyls is low oxidation state or in zero oxidation state. This is because of the fact that there is a higher electron density on the metal atom in its lower or zero oxidation state than in its higher oxidation state. Thus, since the metal is electropositive in nature, it would feel more comfortable if some of the excess electronic charge present on the metal atom

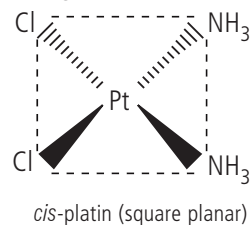
gets transferred to the vacant  $\pi$ -orbitals of  $\text{CO}$  ligand by forming  $\text{M}-\text{CO}$   $\pi$ -bond.

17. In the formation of  $\text{M} \rightarrow \text{CO}$   $\pi$ -bond in metal carbonyls, metal (M) acts as a donor (Lewis base) and  $\text{CO}$  molecule (ligand) acts as an acceptor (Lewis acid). Filled  $d$ -orbital of metal atom back donates its electrons into vacant antibonding  $\pi$ -molecular orbital ( $\pi_y^*$  or  $\pi_z^*$ ) and forms  $\text{M} \rightarrow \text{CO}$   $\pi$ -bond, hence,  $\text{CO}$  is called  $\pi$ -acid ligand or  $\pi$ -acceptor ligand or  $\pi$ -bonding ligand.



18. Coordination compounds generally have a variety of distinctive physical and chemical properties, such as colour, magnetic susceptibility, solubility, volatility, an ability to undergo oxidation reduction reactions and catalytic activity. Due to these properties, coordination complexes have a wide range of applications.

19. *cis*-platin,  $[\text{Pt}(\text{NH}_3)_2, \text{Cl}_2]$ , diamminedichloridoplatinum(II) is used as an anti-tumour agent to treat cancer.



It has square planar geometry.

20. Ziegler-Natta catalyst which is a solution of  $\text{TiCl}_4$  and trialkyl aluminium, acts as a heterogeneous catalyst for polymerization of olefins.

