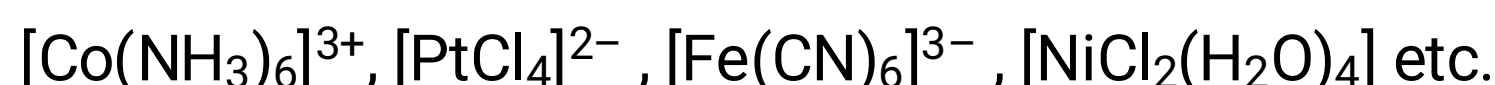


Co-ordination Compound and Organometallics

(Some Important Problem of NCERT)

Q. 1. Define the terms: coordination entity, central metal, ligand, donor atom, coordination number and oxidation number.

Ans. (i) Coordination entity. It constitutes a central metal atom / ion, generally of a metal, to which are attached a fixed number of other atoms or groups each of which is called a *ligand*. It may be a neutral or a charged species. e.g.



(ii) Central metal. It is the atom or ion in a complex to which a fixed number of ligands are bonded in a definite geometrical arrangement around it e.g. in $[\text{Fe}(\text{CN})_6]^{4-}$, the central metal ion is Fe^{2+} .

(iii) Ligands. It is an ion or a molecule that is bound to the central metal atom or ion of the complex. It generally has a lone pair of electrons e.g. Br^- , Cl^- , CN^- , OH^- , O^{2-} , NH_3 , H_2O etc.

(iv) Donor atom. The atom which donates the pair of electrons to the central metal atom is called donor atom e.g. In NH_3 , N is the donor atom. In H_2O , O is the donor atom.

(v) Coordination Number. The number of ligands directly bonded to the central metal ion in definite geometric arrangement is the coordination number of the metal atom e.g. In $[\text{Co}(\text{NH}_3)_6]^{3+}$ the 6 NH_3 molecules are bonded to Co^{3+} atom so coordination number of Co^{3+} is six.

(vi) Oxidation Number. It is the charge on the central atom that it would carry when all the ligands are removed. e.g. in $[\text{Co}(\text{NH}_3)_6]^{3+}$ the oxidation number of cobalt (Co) is + 3.

Q. 2 What is meant by the denticity of a ligand? Give examples of a unidentate and a didentate ligand.

Ans. Denticity of a Ligand. It is the number of sigma () electron pair donor groups. It may be 1, 2, 3, 4, 6 etc.

Denticity	Nomenclature	Example
1	uni dentate	Cl^- , Br^- , $\ddot{\text{N}}\text{H}_3$, $\text{H}_2\ddot{\text{O}}$ etc.
2	bi dentate	COO^- , $\text{CH}_2\ddot{\text{N}}\text{H}_2$ etc.
3	tridentate	COO^- , $\text{CH}_2\ddot{\text{N}}\text{H}_2$
4	tridentate	

5	tetradentate
6	hexadentate.

Q. 3 Which postulates did Werner use to explain the bonding in coordination compounds? What is the main weakness of Werner's theory?

Ans. *Main postulates of Werner's Theory.*

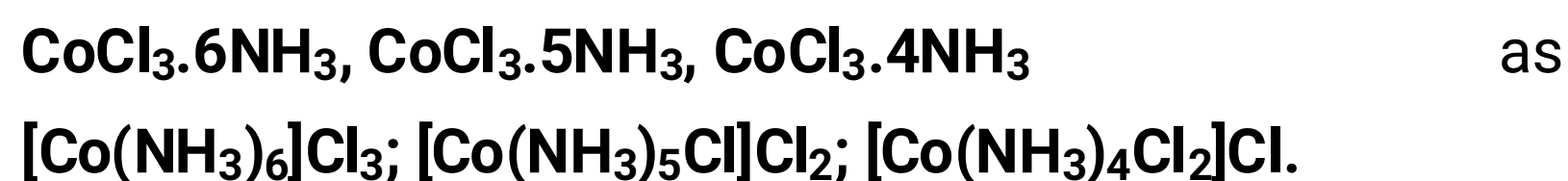
(i) Metals possess two types of valencies i.e. primary (ionisable) and secondary (non – ionisable).

(ii) Primary valencies are satisfied by negative ions and it is equal to the oxidation state of the metal ion.

(iii) The secondary valencies can be satisfied by neutral or negative ions / groups. It is equal to the coordination number of the metal and is a fixed number.

(iv) The ions / groups bound by secondary linkage have characteristic spatial arrangement corresponding to different oxidation numbers. Such arrangements are called *coordination polyhedra*.

On the basis of these postulates, Werner formulated the coordination compounds



Main Weaknesses of Werner's Theory

(i) It failed to explain as to why certain elements possess the property of forming coordination complexes.

(ii) It failed to explain the directional properties of bonds in coordination compounds.

(iii) It failed to explain the characteristic magnetic and optical property of the coordination compounds.

Q. 4 What is understood by:

(a) a chelating ligand,

(b) an ambidentate ligand?

Answer using specific examples.

Ans. (a) **Chelating Ligand.** When the coordination of more than one sigma – electron pair donor group (i.e. bidentate or polydentate) from the ligand to the same metal ion occur, it is called *chelation* and such a ligand is called as **chelating ligand** e.g. $\text{C}_2\text{O}_4^{2-}$ (oxalato).

(b) **Ambident Ligands.** The monodentate ligand which can coordinate with the central metal atom through more than one site are called *ambident ligands* e.g. CN^- , NO_2^- etc.

Q. 5 Complete the following statements for the coordination entity (complex ion) $[\text{CrCl}_2(\text{OX})_2]^{3-}$:

- (a) OX is abbreviation for _____
 (b) The oxidation number of chromium is _____
 (c) The coordination number of chromium is _____
 (d) _____ is a didentate ligand.

Ans. 5. (a) Oxalate ion  or $\text{C}_2\text{O}_4^{2-}$

- (b) + 3 (c) 6
 (d) oxalate ion or $\text{C}_2\text{O}_4^{2-}$ ion.

Q. 6 Specify the oxidation numbers of the metals in the following coordination entities:

- (a) $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{en})_2]^{2+}$ (b) $[\text{PtCl}_4]^{2-}$ (c) $[\text{CrCl}_3(\text{NH}_3)_3]$
 (d) $[\text{CoBr}_2(\text{en})_2]^+$ (e) $\text{K}_3[\text{Fe}(\text{CN})_6]$.

Ans. (a) $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{en})_2]^{3+}$ – O. N. of Co is +3 (b) $[\text{PtCl}_4]^{2-}$ – The O. N. of Pt is +2
 (c) $[\text{CrCl}_3(\text{NH}_3)_3]$ – The O. N. of Cr is +3 (d) $[\text{CoBr}_2(\text{en})_2]^+$ – The O. N. of Co is +3
 (e) $\text{K}_3[\text{Fe}(\text{CN})_6]$ – The O. N. of Fe is +3.

Q. 7 Using IUPAC norms write the formulae for the following:

- (a) Tetrahydroxozincate (III) (b) Hexaamine cobalt (III) sulphate
 (c) Potassiumtetrachloropalladate (II) (d) Potassium tri (oxalato) chromate (III)
 (e) Diamminedichloroplatinum (II) (f) Hexaammineplatinum (IV)
 (g) Potassium tetracyanonickelate (II) (h) Tetrabromocuprate (II)
 (i) Pentaamminenitrito – O – cobalt (III) (j) Penetaamminenitrito – N – cobalt (III)

Ans. (a) $[\text{Zn}(\text{OH})_4]^{2-}$ (b) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ (c) $\text{K}_2[\text{PdCl}_4]$ (d) $\text{K}_2[\text{Cr}(\text{C}_2\text{O}_4)_2]$
 (e) $[\text{PtCl}_2(\text{NH}_3)_2]$ (f) $[\text{Pt}(\text{NH}_3)_6]^{4+}$ (g) $\text{K}_2[\text{Ni}(\text{CN})_4]$ (h) $[\text{CuBr}_4]^{2-}$
 (i) $[\text{Co}(\text{ON})(\text{NH}_3)_5]^{2+}$ (j) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]_2^{2+}$.

Q. 8 Using IUPAC norms write the systematic names of the following:

- (a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (b) $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]\text{Cl}$ (c) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$
 (d) $[\text{PtCl}(\text{NH}_2\text{CH}_3)(\text{NH}_3)_2]\text{Cl}$ (e) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (f) $[\text{Co}(\text{en})_3]^{3+}$
 (g) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (h) $[\text{NiCl}_4]^{2-}$ (i) $[\text{Ni}(\text{CO})_4]$

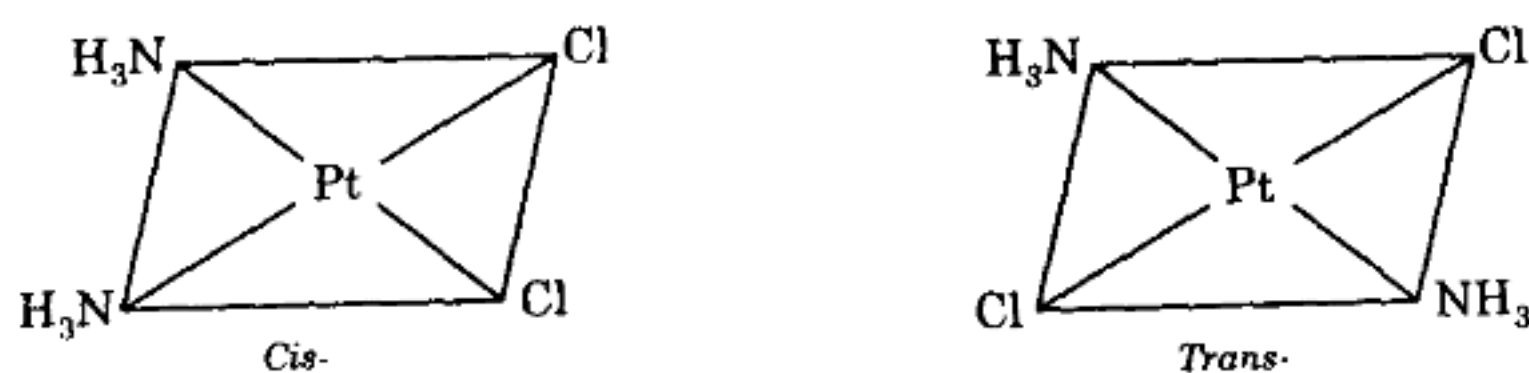
Ans. (a) Hexamine cobalt (III) chloride

- (b) Tetrammine chloro nitro cobalt (III) chloride
- (c) Hexaamine chloro (methylamine) platinum (II) chloride
- (d) Diammine chloro (methylamine) platinum (II) chloride
- (e) Hexaaqua manganese (II)
- (f) Tris (ethylenediamine) cobalt (II)
- (g) Hexaaqua titanium (III)
- (h) Tetrachoro nicklate (II)
- (i) Tetracarbonyl nickel (0).

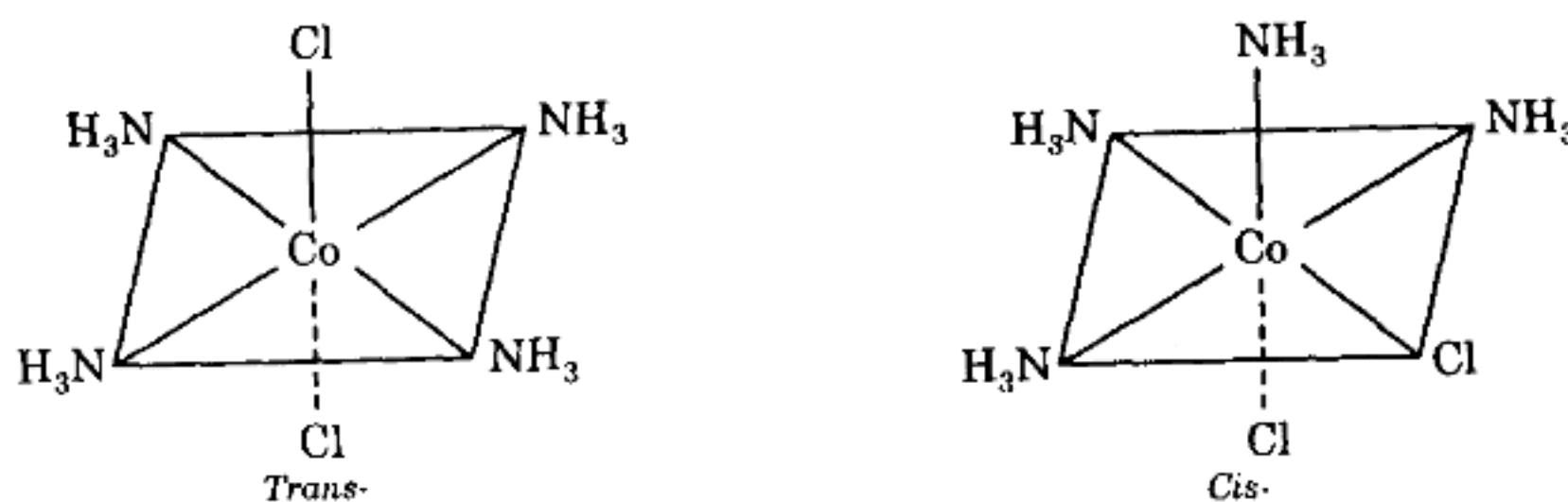
Q. 9 Explain with examples geometric and optical isomerism.

Ans. Geometrical Isomerism. This type of isomerism arises in coordination compounds due to the difference in geometrical arrangement of the ligands around the central metal atom / ion. This is also known as *cis - trans isomerism*.

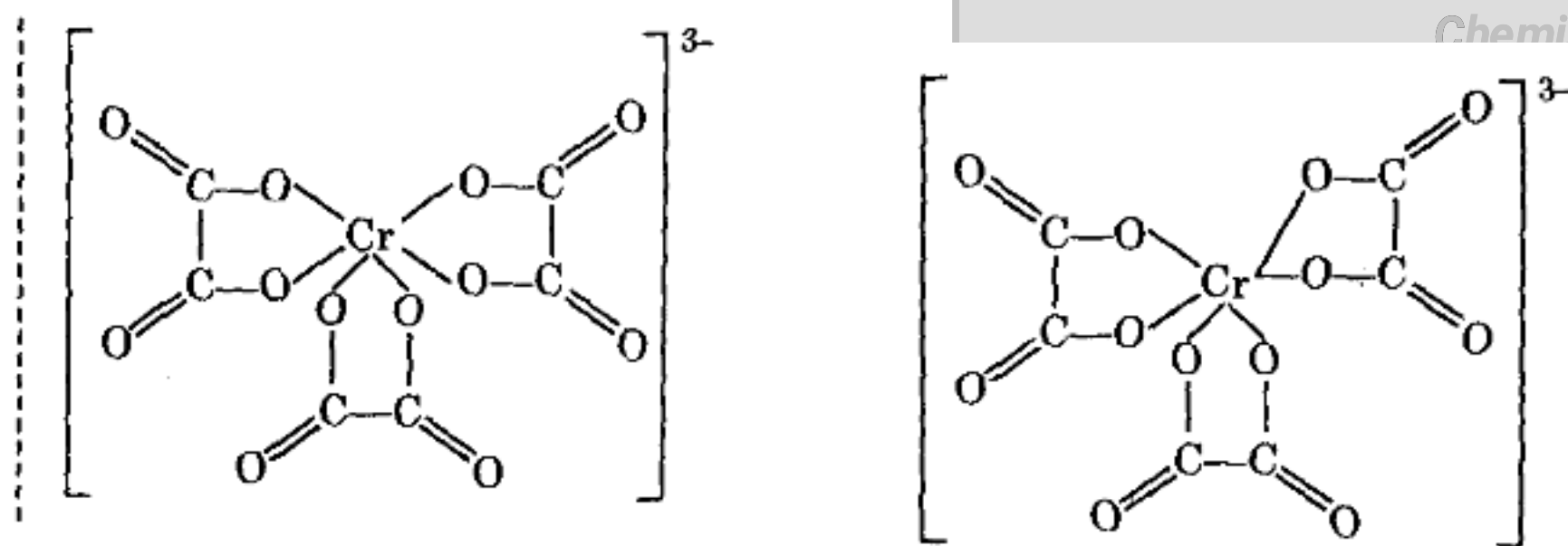
In tetra coordinate square planar complex the *cis - isomer* has the same groups on the same side where as in *trans - isomer* the same groups are on opposite sides. e.g.



This type of isomerism is also shown by octahedral complexes e.g. $\text{Co}(\text{NH}_3)_4\text{Cl}_2$



Optical Isomerism. Optical isomers are non - superimposable mirror images of each other. They possess the property of **chirality**. They have identical physical and chemical properties but differ in **optical rotation**. One of them rotates the plane polarized light toward right and is called *dextro - rotatory* (d - isomer) and the other rotates plane polarized right towards left and is called *laevo rototy* (l - isomer) e.g. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$



Q. 10 Specify which out of the following complex structures exhibit geometric isomerism:

- (a) linear (b) square – planar (c) tetrahedral (d) octahedral

Ans. The following will show geometrical isomerism.

(b) – Square planar

(d) – tetrahedral.

Q. 11 How many geometric isomers are possible in the following coordination entities:

- (a) $[\text{Cr}(\text{OX})_3]^{3-}$ (b) $[\text{CoCl}_3(\text{NH}_3)_3]$

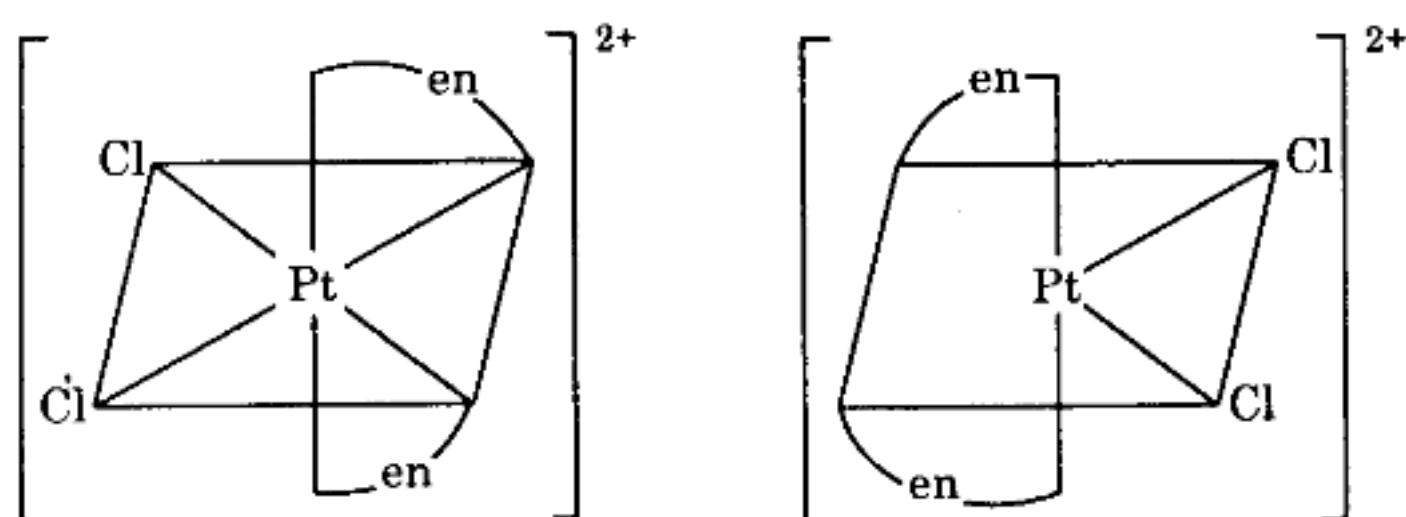
Ans. (a) Two (b) Two.

Q. 12 Draw the structure of optical isomers of:

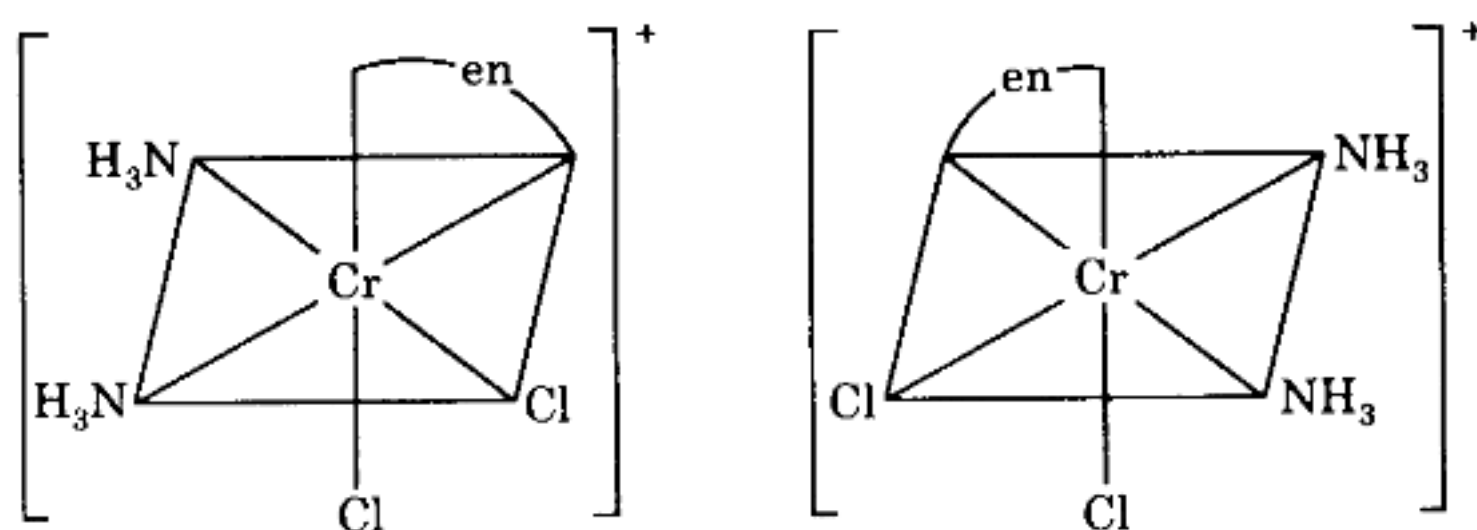
- (a) $[\text{Cr}(\text{OX})_3]^{3-}$ (b) $[\text{PtCl}_2(\text{en})_2]^{2+}$ (c) $[\text{CrCl}_2(\text{en})(\text{NH}_3)_2]^+$

Ans. (a) Refer to Q. 9.

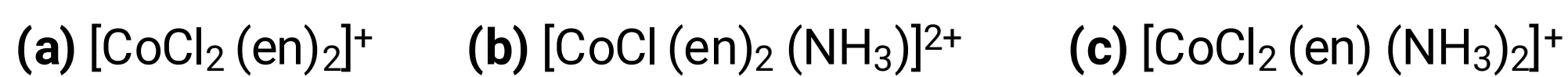
(b)



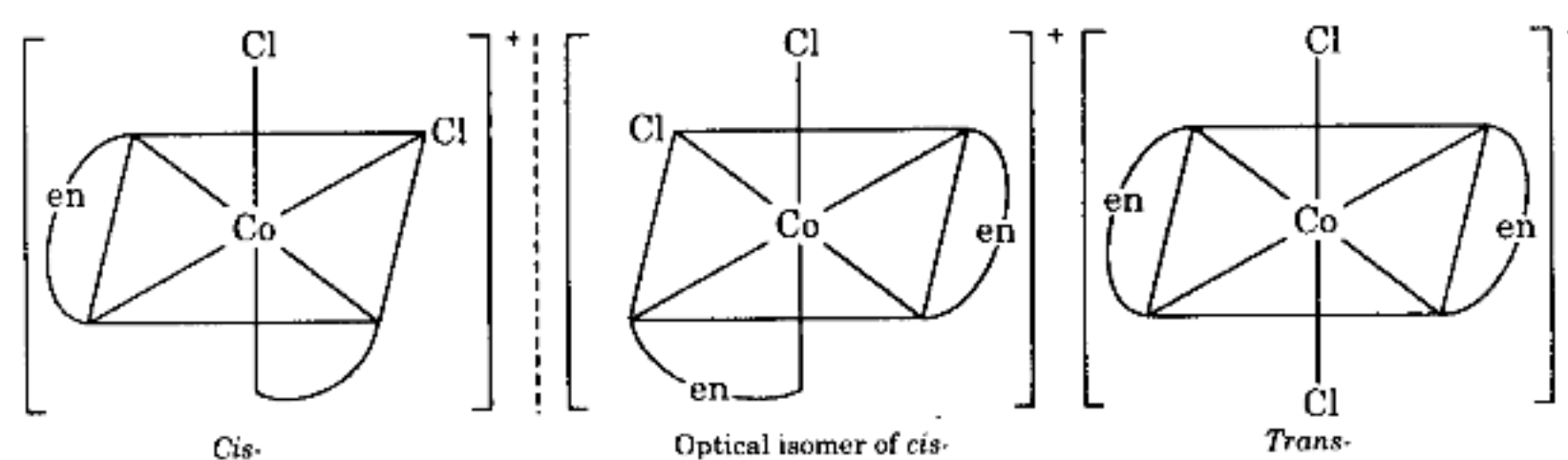
(c)



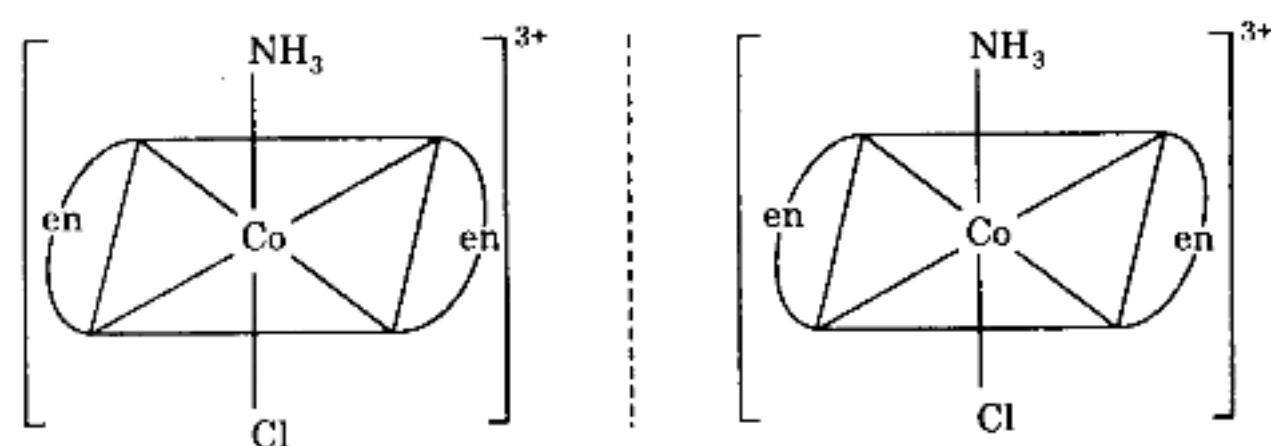
Q. 13 Draw all the isomers (geometric and optical) of:



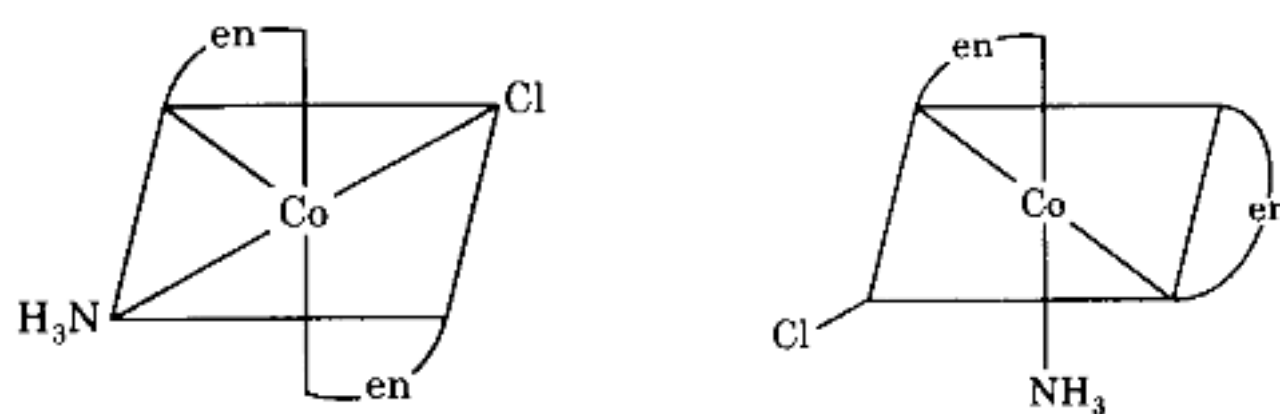
Ans. (a)



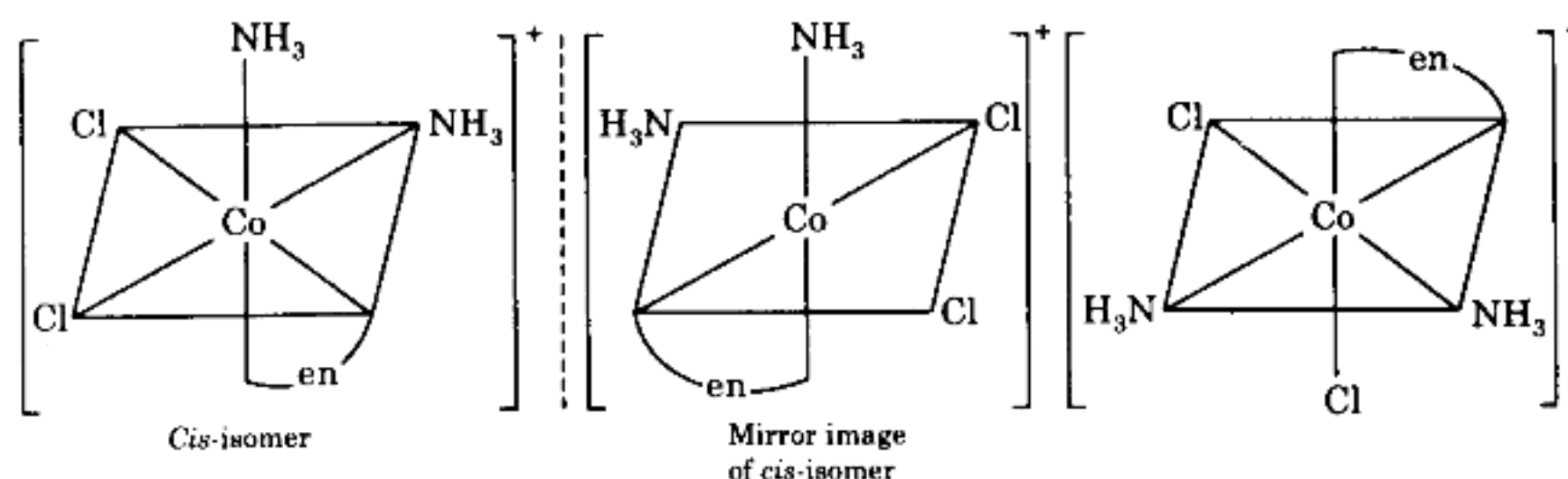
(b) Optical Isomers



Geometrical Isomers



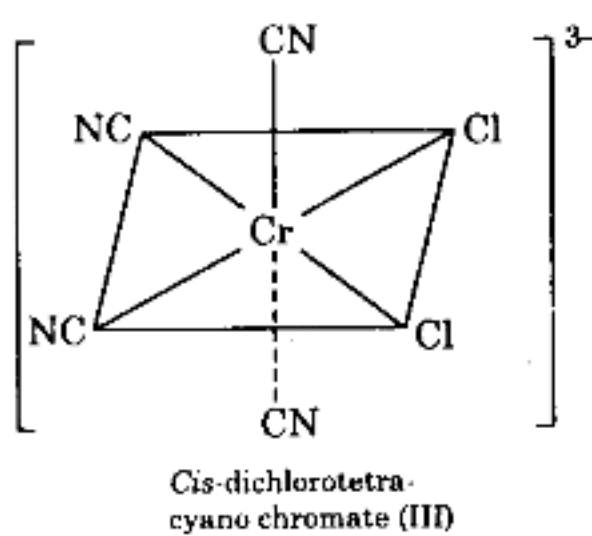
(c)



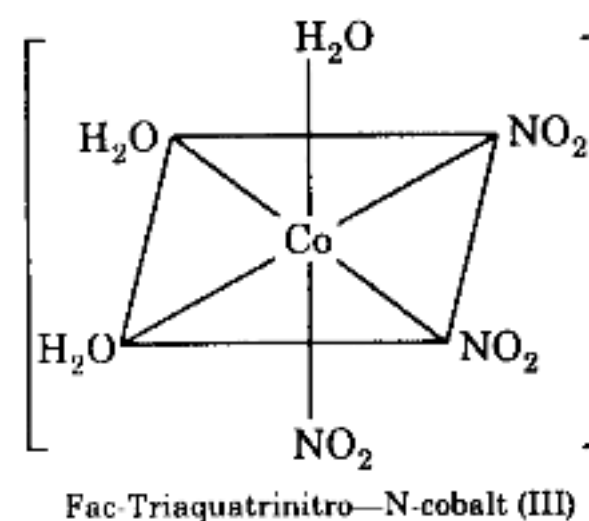
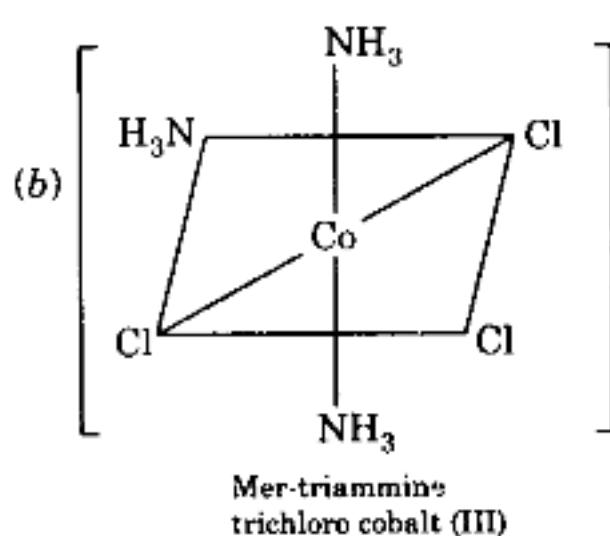
Q. 14 Draw the structures of:

- (a) Cis – dichlorotetracyano – chromate (III)
 (b) Mer – triamminetri chlorocobalt (III)
 (c) Fac – triaquatrinitor – N – cobalt (III).

Ans. (a)



(c)



Q. 15. Illustrate with an example each of the following:

- (a) ionization isomerism
 (b) linkage isomerism
 (c) coordination isomerism.

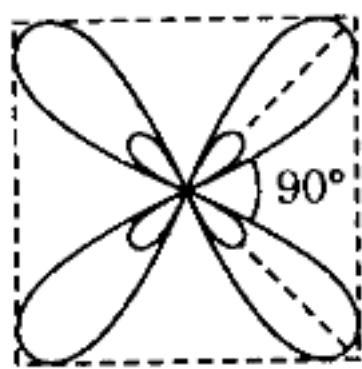
- Ans.** (a) $[\text{Co}(\text{NO}_3)(\text{NH}_3)_5]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$ are *ionization isomers*.
 (b) $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$ linkage isomers.
 (c) $[\text{Cr}(\text{NH}_3)_6]\text{Co}(\text{CN})_6$ and $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ are coordination isomers.

Q. 16 Sketch the geometrical shapes of the following sets of hybrid orbitals:

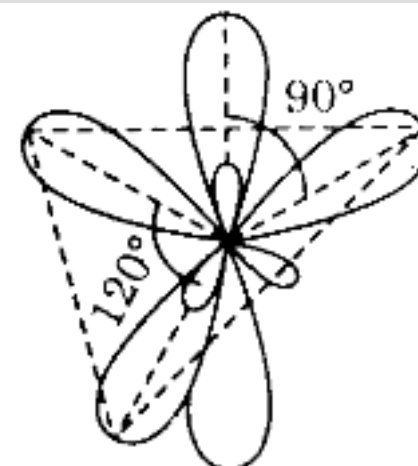
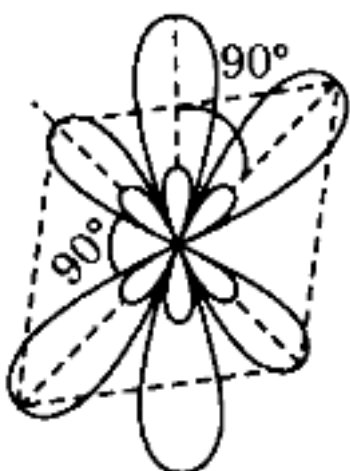
- (a) dsp^2 (b) dsp^3 (c) d^2sp^3 (d) sp^3

Ans. (a) dsp^2

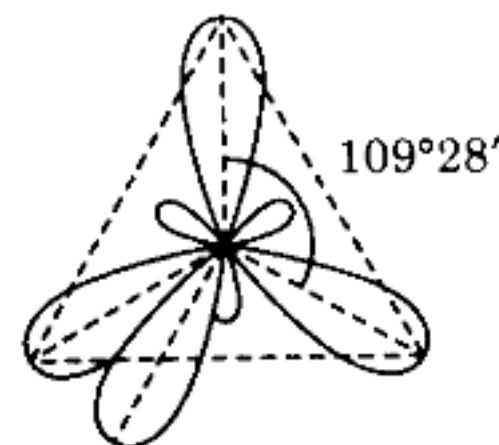
(b) sp^3d or dsp^3



(c) sp^3d^2 or d^2sp^3

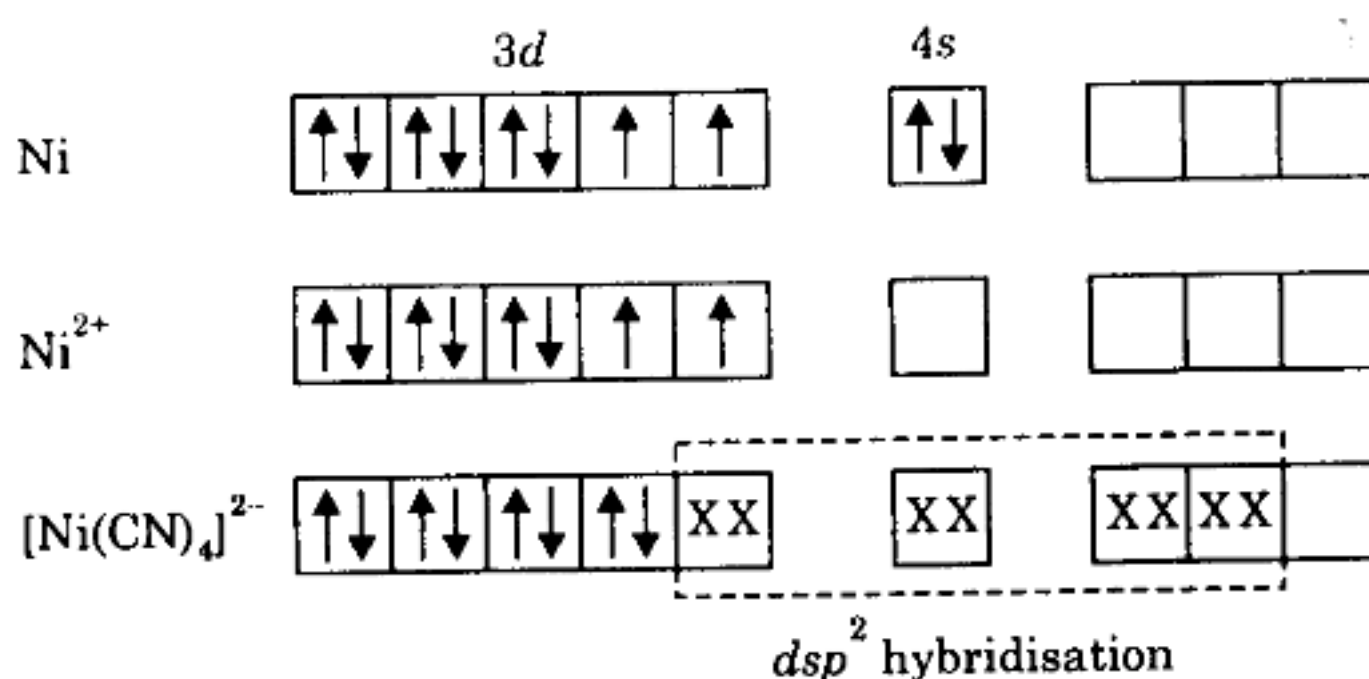


(d) sp^3



Q. 17 Explain on the basis of valence bond theory, the experimental finding that $[Ni(CN)_4]^{2-}$ ion with a square – planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Ans. $[Ni(CN)_4]^{2-}$



Where XX represents the lone pair of electrons from CN^- .

Because of dsp^2 hybridization, it is *square planar complex*.

Since there is no unpaired electron so it is *diamagnetic*.

$[NiCl_4]^{2-}$

XX is electron pair donated by each Cl.

Because of sp^3 hybridization it is *tetrahedral* due to the presence of two unpaired electrons it is *paramagnetic*.

Q. 18 Write the correct formulae for the following coordination compounds:

(a) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (violet, with 3 chloride ions / unit formula)

(b) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (light green colour, with 2 chloride ions / unit formula)

(c) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (dark green colour, with 1 chloride ions / unit formula)

[Hint: Some of these compounds may exist as hydrates].

Ans. (a) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (b) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (c) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

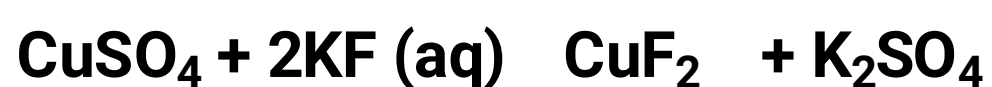
Q. 19 Aqueous copper sulphate solution (blue in colour) gives:

(a) A green precipitate with aqueous potassium fluoride, and

(b) a bright green solution with aqueous potassium chloride.

Explain these experimental results.

Ans. The green precipitate is of CuF_2 .



(green)

The green colour solution is due to $\text{K}_2[\text{CuCl}_4]$



(green solution) (Soluble complex)

Q. 20 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?

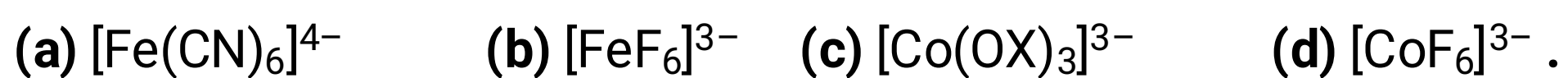
Ans. KCN reacts with CuSO_4 to form $\text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$

Complex

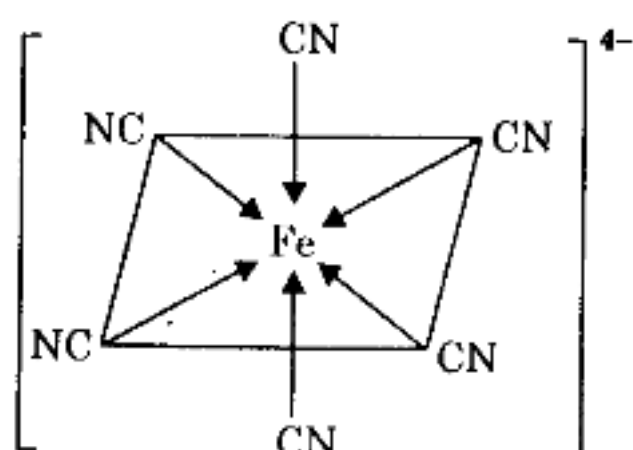
The coordination entity is $[\text{Cu}(\text{CN})_4]^{2-}$

Since the complex ion does not yield Cu^{2+} ions and remains as a single entity so not ppt. of CuS is obtained when H_2S is passed through this solution.

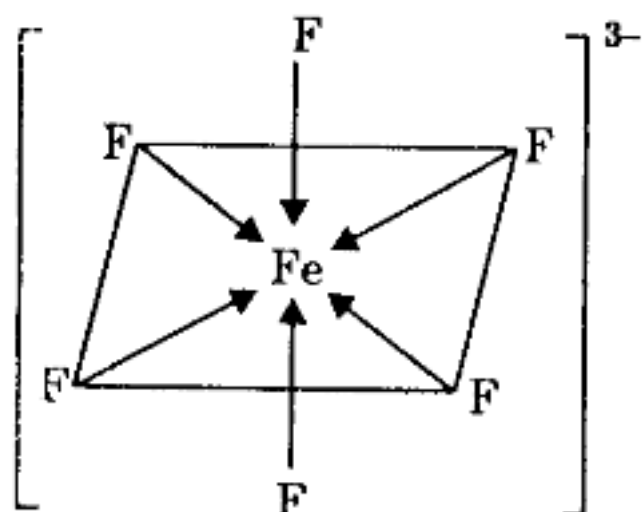
Q. 21 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:



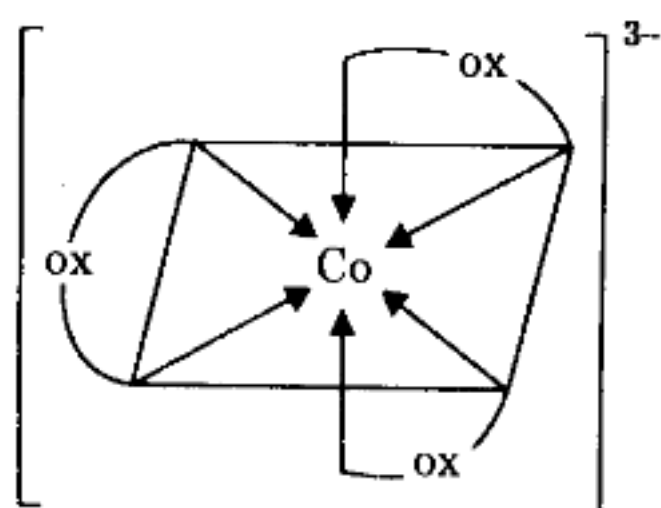
Ans. (a) Since it is a complex compound so it has coordinate bonds between ligands CN^- and central metal Fe^{2+}



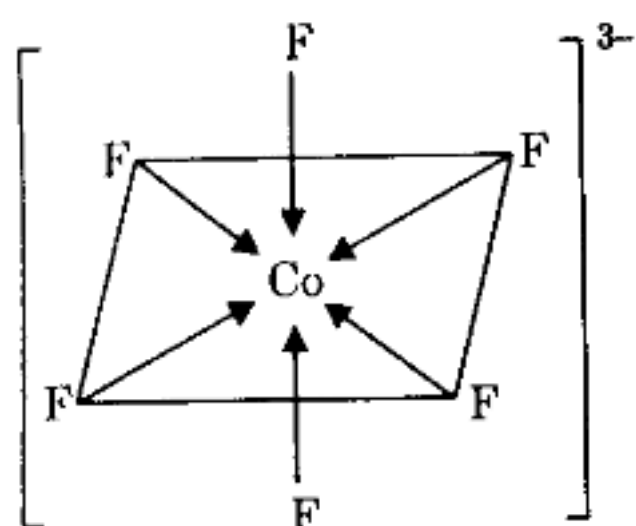
(b) Coordinate bonds between Fe^{3+} and F^-



(c) Coordinate bonds between Co^{3+} and $\text{C}_2\text{O}_4^{2-}$ (ligand)



(d) Coordinate bonds between Co^{3+} and F^- .



Q. 22 Write the valence bond description of:



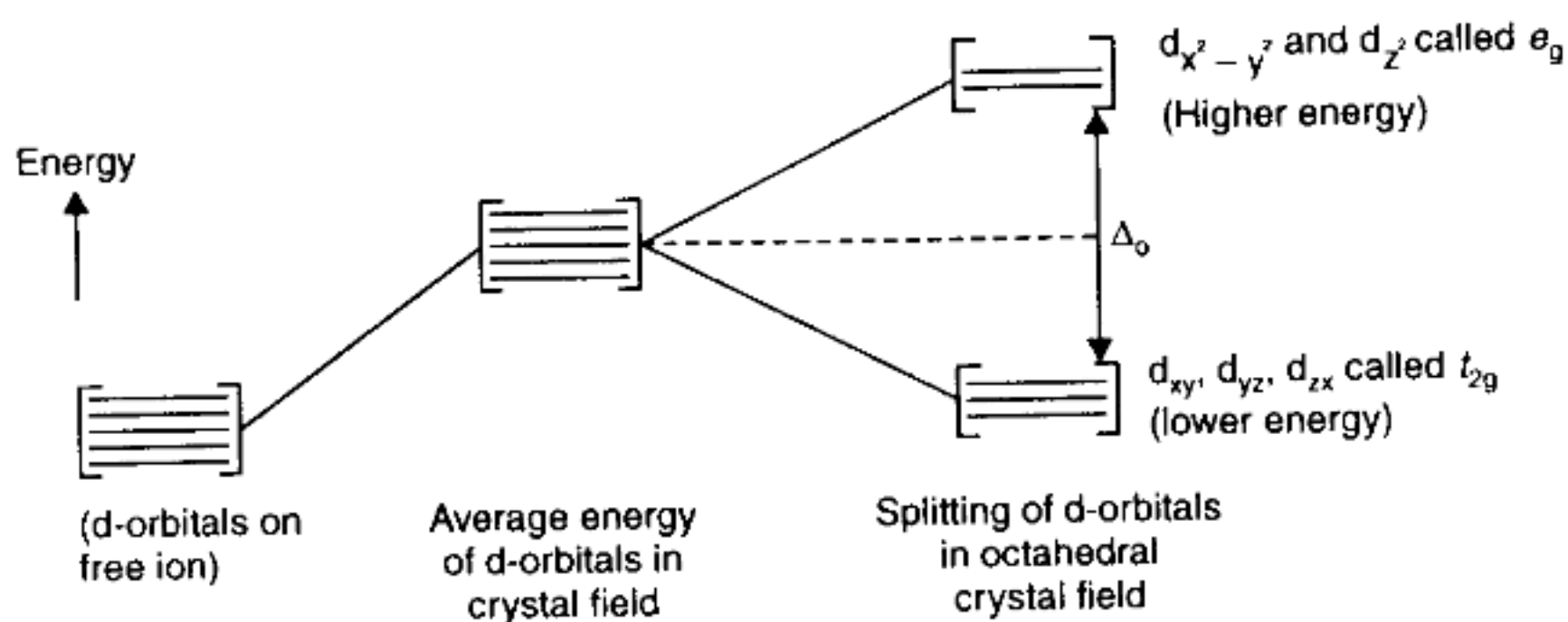
Ans. Refer to Q. 17 of this section.

Q. 23 What is understood by the generalization, 'magnetic criteria of the bond type'? Illustrate your answer with suitable examples.

Ans. By *magnetic criterion of bond type* we mean that it is possible to predict the geometry of the *coordinate entity* if we know its magnetic behaviour. e.g. $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic, so we can predict that it has undergone dsp^2 hybridization and has a square planar geometry but since $[\text{NiCl}_4]^{2-}$ is paramagnetic; so it has sp^3 hybridization and thus tetrahedral shape.

Q. 24 Draw figure to show splitting of degenerate d orbitals in an octahedral crystal field.

Ans. The splitting of d – orbital in an octahedral field is shown below.



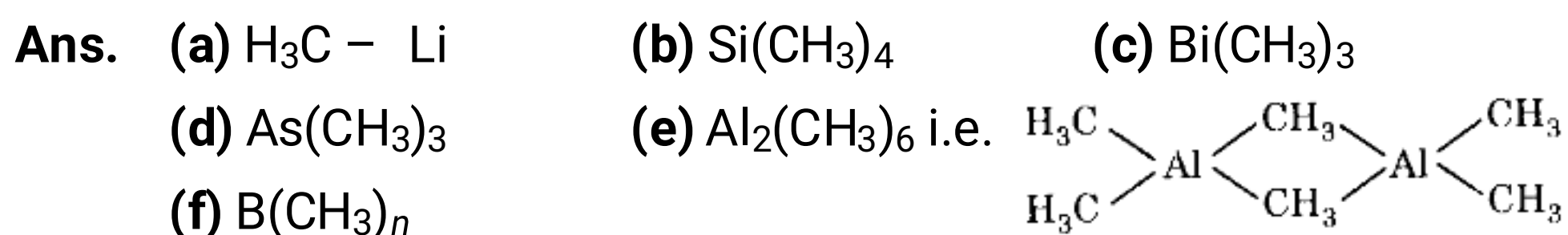
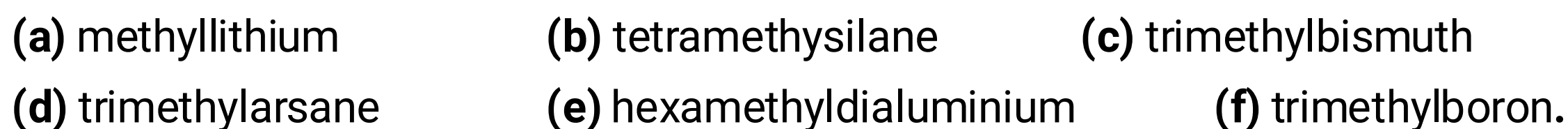
Q. 25 State the essential requirements for regarding a compound as an organometallic. Which amongst the following are organometallic compounds:



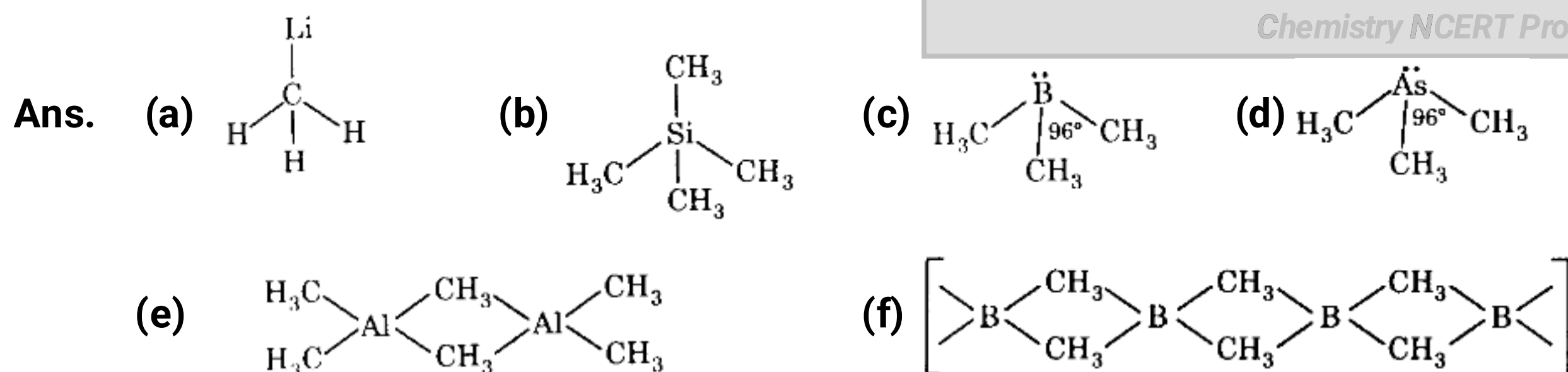
Ans. The essential requirement for regarding a compound as organometallic compound is that it must have a *metal – carbon bond*

Of the given compounds (a) and (c) may be classified as organometallic compounds.

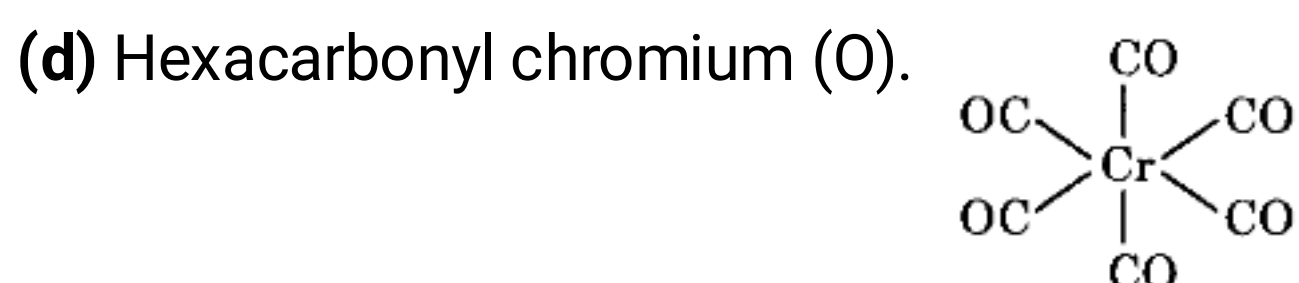
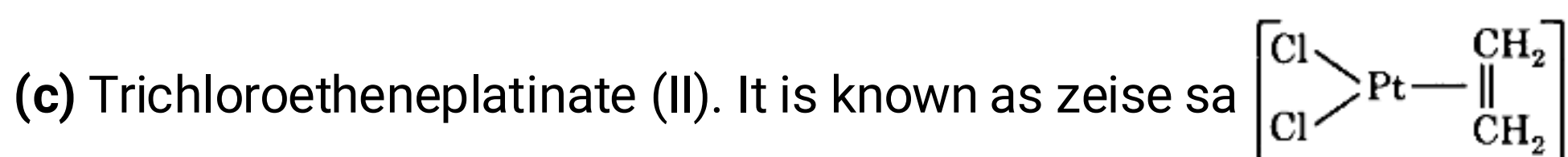
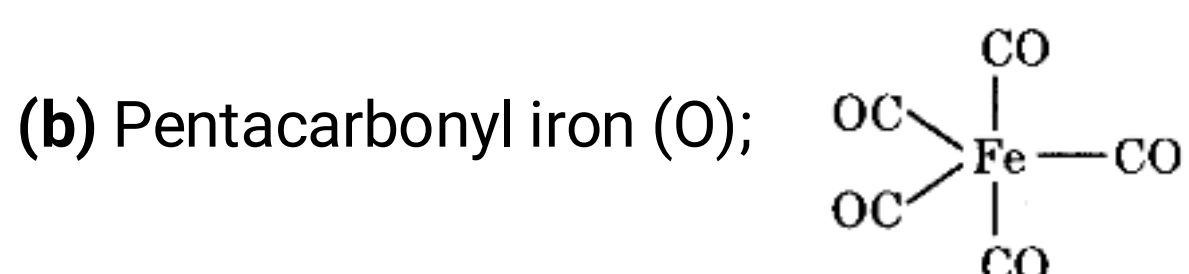
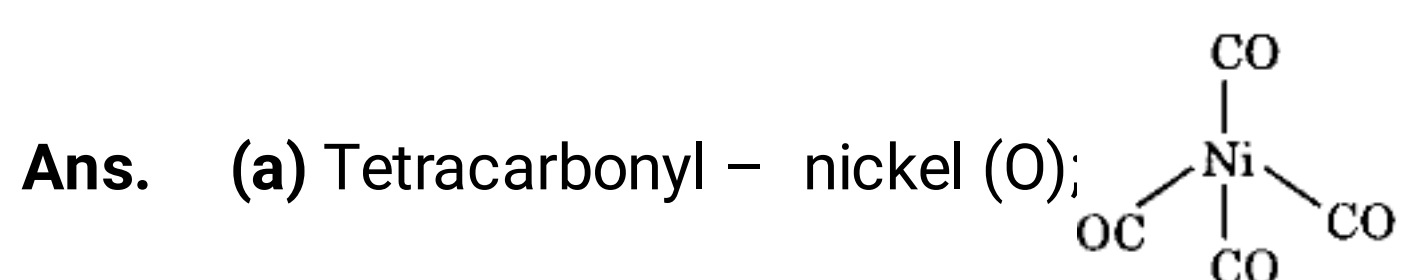
Q. 26 Write the formulae of the following:



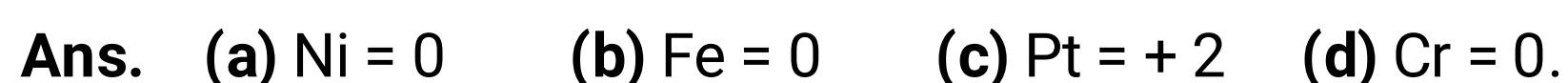
Q. 27. Sketch the structure of the organometallic compounds given in 10.26.



Q. 28 Give IUPAC name and draw the structure of:



Q. 29 Assign oxidation number to the metal atom in the compounds given in 10.28.



Q. 30. Discuss the nature of bonding in $[\text{Ni}(\text{CO})_4]$.

Ans. In $\text{Ni}(\text{CO})_4$, we find that both σ or π bonds are formed. Sigma (σ) bonds is formed by donation of lone pair of electron by CO to vacant d – orbitals of nickel. The pi (π) bonds is formed by back donation of pair of electrons from filled d – orbitals of nickel to vacant antibonding orbital of CO.

Q. 31. Discuss briefly the role of coordination compounds in:

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

Ans. Role of coordination compounds

(a) In biological systems. *Haemoglobin*, a complex of iron acts as carrier of oxygen in animals and human beings. *Chlorophyll*, a complex of Mg is helpful in the process of photosynthesis. It is present in green plants.

(b) In Analytical chemistry. To determine the hardness of water we use EDTA. In laboratory EDTA (a complex compound) is used in the estimation of Ca^{2+} , Mg^{2+} ions. Another complex known as DMG (Dimethyl glyoxime) is used in the estimations of Ni^{2+} .

(c) In Medicines. *Cis – platin* another coordination compound is used as an anti – cancer agent in the treatment of cancer.

(d) In Metallurgy. In the metallurgy of Ag and Au we first prepare their cyanide complexes which are then reduced with zinc metal to get pure Ag or Au.