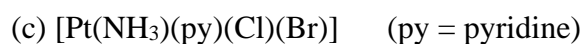
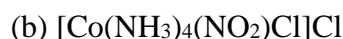


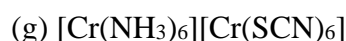
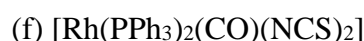
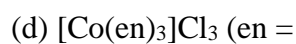
1. Identify the species present in aqueous solution of Potash alum upon dissociation.

**Ans:** Potash alum is  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , it's a double salt and not a complex, so it will dissociate in solution into its component ions:  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$ .

2. Predict the type(s) of isomerism shown by the following complexes. Also draw the structures or formula of the possible isomers.



(ethylenediamine)



**Ans:** (a)  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  show hydrate isomerism; i.e.,  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet),  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (blue-green),  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$  (dark green).

(b) Ionization isomerism:  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{Cl}$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$

(c) Shows geometrical isomers (*cis*-, *trans*-) due to square planar geometry, total three isomers are possible.

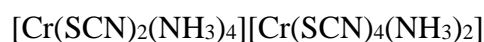
(d) Two optical isomers can exist ( $\Lambda$  and  $\Delta$  forms).

(e) Coordination isomerism where Pt is in two different oxidation states.

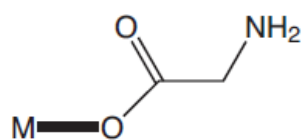


(f) Linkage isomerism:  $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{NCS}-N)_2]$  and  $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{NCS}-S)_2]$

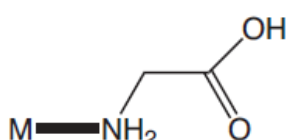
(g) Coordination isomerism:  $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{SCN})_6]$  and



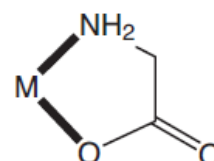
3. Draw the possible coordination modes of glycine to a metal ion?



*O*-monodentate



*N*-monodentate



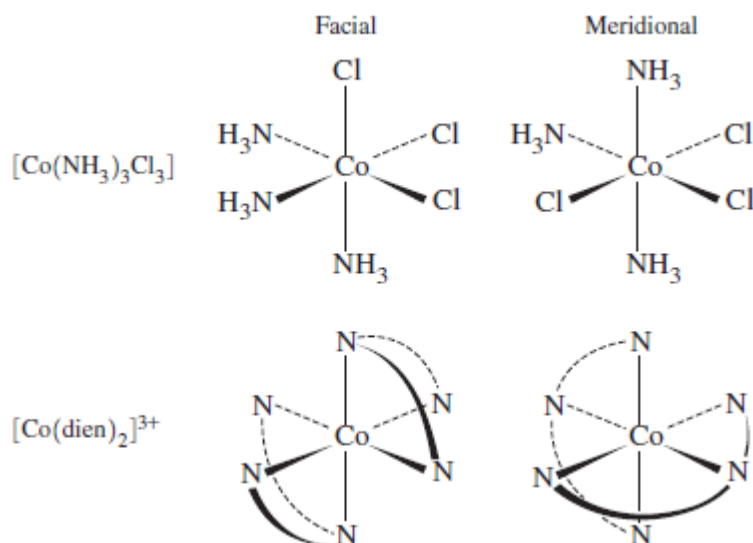
*N,O*-bidentate

4. Suggest a simple analytical test to distinguish between the hydrate isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

Three possible hydrate isomers are  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ ,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ .

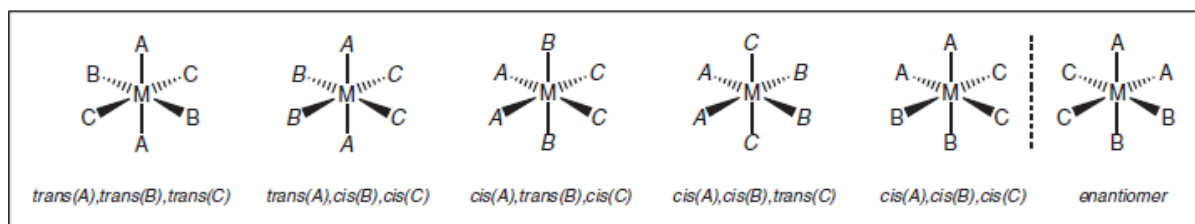
**Ans:** The complexes can be distinguished by precipitation of the free chloride ion as  $\text{AgCl}$  using aqueous silver nitrate (by measuring weight of the  $\text{AgCl}$  precipitate, gravimetry).

5. Draw the geometrical isomers of  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  and  $[\text{Co}(\text{dien})_2]^{3+}$  and appropriately designate them.

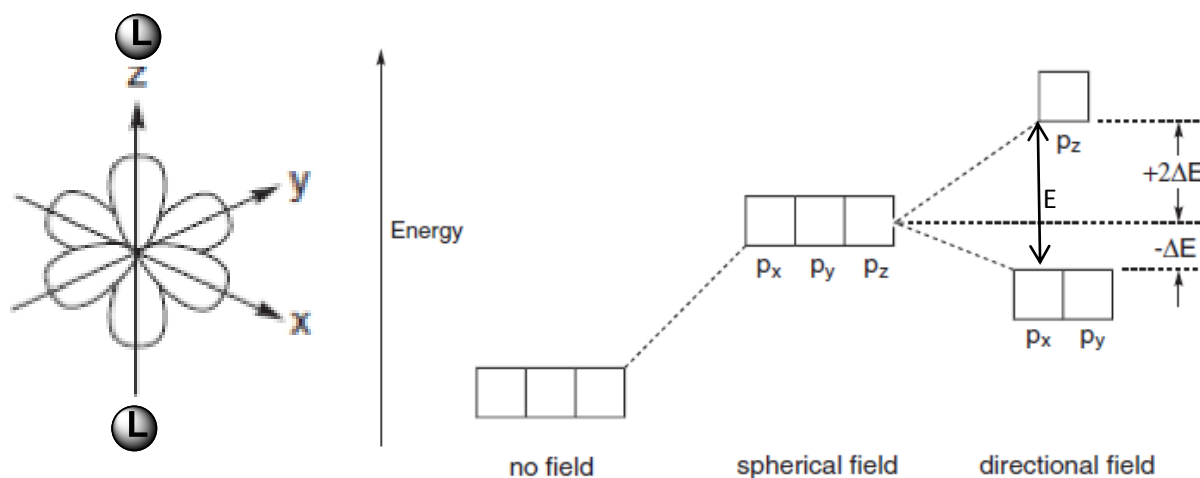


*Note: Fac (facial) isomers have three identical ligands on one triangular face; mer (meridional) isomers have three identical ligands in a plane bisecting the molecule.*

6. Draw the possible stereoisomers for  $\text{MA}_2\text{B}_2\text{C}_2$ . Which one of these have enantiomer.



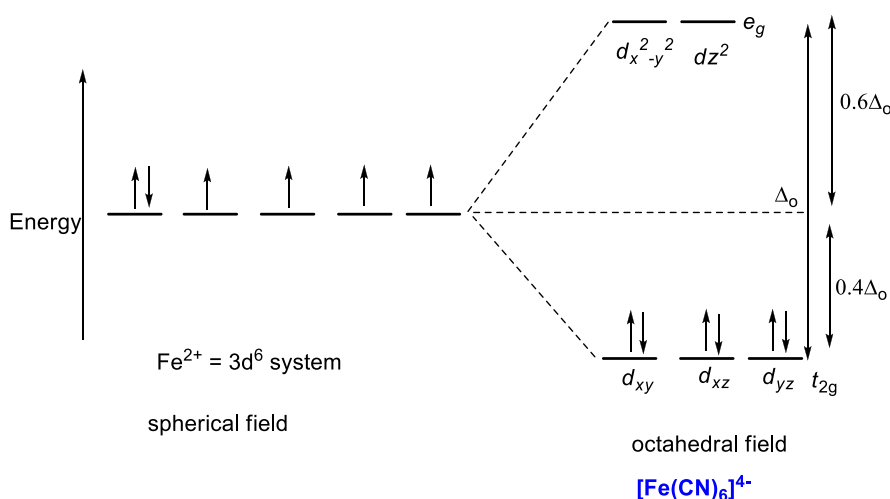
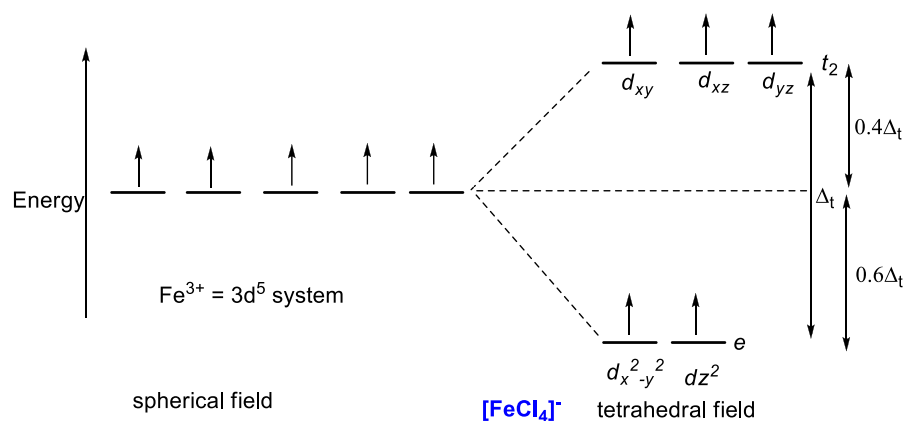
7. Apply the concept of crystal field theory to a set of  $p$ -orbitals for a specific interaction along Z-axis. Draw the splitting diagram with labelling and energy values.



8. Consider the coordination complexes (a)  $\text{NaFeCl}_4$  and (b)  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , and answer the following questions. Atomic number of Fe = 26.
- (a) Show the crystal field splitting diagram with appropriate labelling and filling up of the electrons in these orbitals.
- (b) Calculate the Crystal Field Stabilization Energy (CFSE) for both the compounds (you may ignore the pairing energy).
- (c) Calculate the spin only magnetic moments for both the complexes.

Ans.  $\text{Na}[\text{FeCl}_4]$ : structure of  $[\text{FeCl}_4]^-$  is tetrahedral and  $\text{Fe}^{3+}$  is  $3d^5$  system.  
 $[\text{Fe}(\text{CN})_6]^{4-}$  is octahedral and  $\text{Fe}^{2+}$  is a  $3d^6$  system.

(a)



(b) CFSE for  $[\text{FeCl}_4]^- = (2 \times 0.6) - (3 \times 0.4)\Delta_t = 0$ ;  $[\text{Fe}(\text{CN})_6]^{4-} = (6 \times 0.4)\Delta_o = 2.4\Delta_o$

(c)  $\mu_{s.o.} = [n(n+2)]^{1/2}$  (n = number of unpaired electrons).

So, for  $[\text{FeCl}_4]^-$ , n = 5,  $\mu_{s.o.} = [5(5+2)]^{1/2} = \sqrt{35} = 5.92 \text{ B.M.}$

For  $[\text{Fe}(\text{CN})_6]^{4-}$ , n = 0,  $\mu_{s.o.} = 0 \text{ B.M.}$

9. Which of the following complexes will have larger crystal field splitting ( $\Delta$ ) in the given series? Give exact explanation for your choice.

- (i)  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Ir}(\text{en})_3]^{3+}$ ,  $[\text{Rh}(\text{en})_3]^{3+}$  :  $\text{Ir}^{3+}$  having larger size 5d-orbitals and thus stronger interaction along with being larger metal ion, ligands experience less steric crowding and
- (ii)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$  :  $\text{CN}^-$  is strong-field ligand than  $\text{NH}_3$  or  $\text{H}_2\text{O}$ .
- (iii)  $[\text{CoF}_6]^{3-}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  : order of ligand strength:  $\text{F}^- < \text{H}_2\text{O} < \text{NH}_3$
- (iv)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{FeCl}_4]^{2-}$  :  $\text{CN}^-$  is strong-field ligand than  $\text{NH}_3$  or  $\text{Cl}^-$ .

10. The complexes  $[\text{NiCl}_2(\text{PPh}_3)_2]$  and  $[\text{PdCl}_2(\text{PPh}_3)_2]$  are paramagnetic and diamagnetic respectively. Predict their structures from this observation.

$\text{Ni}^{2+}$  is  $3d^8$  system. Here, C.N. = 4, either tetrahedral or square planar geometry possible.

In tetrahedral geometry: Configuration =  $e^4 t_2^4$ , 2 unpaired electrons and paramagnetic ( $\mu_{s.o.} = 2.84 \mu_B$ ). Thus  $[\text{NiCl}_2(\text{PPh}_3)_2]$  is tetrahedral.

$[\text{PdCl}_2(\text{PPh}_3)_2]$ :  $\text{Pd}^{2+}$  is  $4d^8$ , prefer square planar geometry, electron configuration:  $(d_{xz}, d_{yz})^4 (d_z^2)^2 (d_{xy})^2$ , no unpaired electrons and diamagnetic ( $\mu_{s.o.} = 0.0 \mu_B$ ) and having square planar structure.