

CML 100 Inorganic Part
Home assignment and Solved problems for self study- Part 1
Crystal Field Theory and its applications to metal complexes

(lectures 1-4)

Solved problems for self study- Part 1

Points to remember;

- Arrive at your metal *d* electron count of a complex carefully by considering anionic ligands and overall charge. For example Fe^{3+} is $3d^5$, Mn^{2+} $3d^5$ etc
- While determining pairing energy *P* in CFSE always compare with the situation before the splitting
- Significant Jahn Teller distortion means degeneracy in the e_g orbital

1. Calculate crystal field stabilization energy (CFSE) for the following complexes
(a) $[Co(CN)_6]^{3-}$ (b) $[Fe(CN)_6]^{3-}$ (c) $[CoCl_6]^{4-}$

Soln.

- (a) $[Co(CN)_6]^{3-}$ Co^{3+} , d^6 , CN^- strong ligand; low spin CFSE = $-2.4 \Delta_o + 2P$
(b) $[Fe(CN)_6]^{3-}$ Fe^{3+} , d^5 low spin CFSE = $-2.0 \Delta_o + 2P$
(c) $[CoCl_6]^{4-}$ Co^{2+} , d^7 , Cl^- weak ligand high spin CFSE = $-0.8 \Delta_o$

2. Magnetic moments of some complexes are as follows. Predict on the basis of this data whether they are high spin or low spin complexes

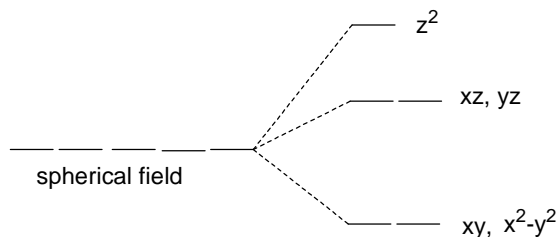
- (a) $K_3[Mn(NO_2)_6]$ 2.87 BM
(b) $[Co(NH_3)_6]Cl_2$ 1.73 BM
(c) $K_4[Fe(CN)_6]$ 0 BM

Soln.

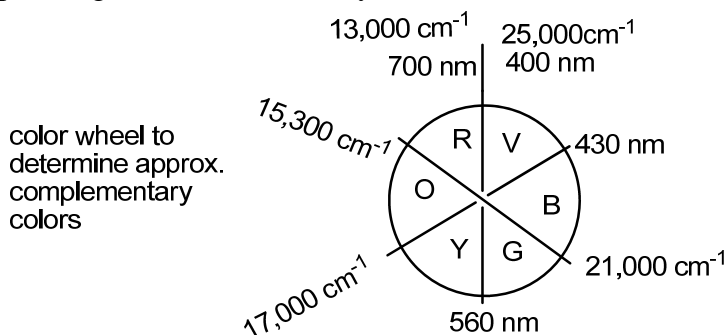
- (a) $K_3[Mn(NO_2)_6]$ 2.87 BM = 2 Unpaired electrons, Mn^{3+} , d^4 low spin
(b) $[Co(NH_3)_6]Cl_2$ 1.73 BM = 1 Unpaired electron, Co^{2+} , d^7 low spin
(c) $K_4[Fe(CN)_6]$ 0 BM = 0 Unpaired electron, Fe^{2+} , d^6 low spin

3. Draw the crystal field splitting diagram of *d* orbitals in a linear complex MX_2 , assuming the ligands (X) to be along the *z* axis.

Soln. Electron-electron repulsion between M and X will be there only for *d* orbitals having an *z* component. Out of these maximum repulsion will be for d_z^2 since lobes are along the *z* axis. Next will be d_{xz} and d_{yz} having lobes in between *z* and another axis and both will be degenerate. The other two orbitals have no *z* component and will be stabilized to maintain barycentre.



4. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic and orange yellow. $[\text{CoF}_6]^{3-}$ on the other hand is paramagnetic and blue. Why?



$[\text{Co}(\text{NH}_3)_6]^{3+}$: t_{2g}^6 diamagnetic = no unpaired electrons

Orange yellow means absorption in the Violet-blue region (higher frequency, larger Δ_o) d^6 LS

$[\text{CoF}_6]^{3-}$ paramagnetic $t_{2g}^4 e_g^2$

Blue means absorption in the orange region (lower frequency, smaller Δ_o) therefore d^6 HS

5. $\text{K}_3[\text{Co}(\text{CN})_6]$ is colorless while $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)]$ is colored. Why?

Soln.

$\text{K}_3[\text{Co}(\text{CN})_6]$ $\text{Co}^{3+} d^6$ LS $t_{2g}^6 e_g^0$: $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)]$ $\text{Co}^{3+} d^6$ HS $t_{2g}^4 e_g^2$

d-d transitions are spin allowed in both cases. However CN^- being a very strong ligand the magnitude of Δ_o will be high and absorption can occur in the UV region for the cyano complex. Therefore it is colorless.

6. Calculate the magnetic moments of only those complexes which have significant tetragonal distortion: $\text{K}_2[\text{PdCl}_6]$, $[\text{Co}(\text{Phen})_3]^{2+}$, $[\text{MnBr}_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

Soln. Significant JT distortion means degeneracy in the e_g orbitals.

$[\text{Co}(\text{Phen})_3]^{2+}$ LS d^7 One unpaired e

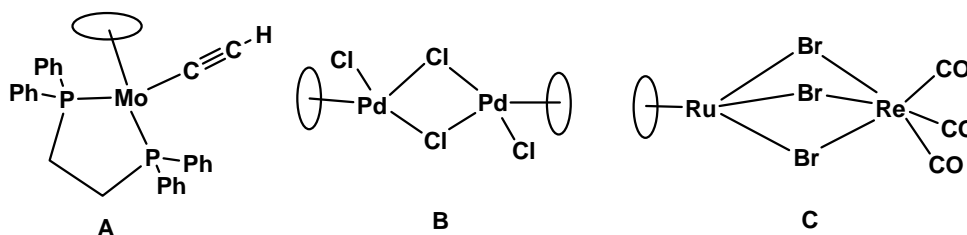
$[\text{Cu}(\text{NH}_3)_6]^{2+}$ HS/LS d^9 One unpaired e

$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ HS d^4 Four unpaired e's

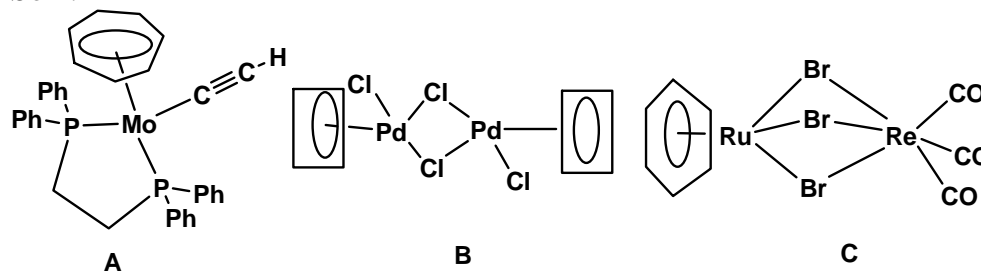
6. In the crystal structure of CuF_2 , the Cu^{2+} ion is six coordinate with four F^- ions at a distance of 1.93 \AA and two F^- ions at a distance of 2.27 \AA . Explain.

Soln. Cu^{2+} d^9 significant JT distortion. Leading to 'z out' resulting in tetragonal distortion.

7. Given that it shows the highest hapticity possible, find out the missing planar, unsaturated and conjugated carbocyclic haptic ligands in the following organometallic compounds, all of which obey the 18 electron rule.



Soln.



Home Assignment 11 problems Inorganic Part Part 1 (submit on 17 march Tuesday. please submit separate sheet for inorganic assignment)

- Explain the following by crystal field theory
Magnetic moment of $[\text{Fe}(\text{CN})_6]^{3-}$ is nearly one third of that of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- Arrange the following complexes in the ascending order of Δ_o
 $[\text{Co}(\text{CN})_6]^{3-}$ $[\text{FeCl}_6]^{4-}$ $[\text{Fe}(\text{NH}_3)_6]^{2+}$ $[\text{Fe}(\text{ox})_3]^{4-}$ $[\text{Fe}(\text{en})_3]^{2+}$ $[\text{Fe}(\text{EDTA})]^{2-}$
- On the basis of CFT, predict with justification which of the following two complex ions would be more stable $[\text{Mn}(\text{CN})_6]^{4-}$ or $[\text{Fe}(\text{CN})_6]^{4-}$.
- The magnetic moment of an octahedral complex of cobalt $[\text{CoL}_6]\text{SO}_4$ is 3.8 BM. Draw the CFT diagram of the complex and choose the correct ligand L from the list provided. [CN^- , NH_3 , H_2O , Cl^-]
- Determine if NiFe_2O_4 is a normal or inverse Spinel ?

6. Arrange $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ in decreasing order of metal ion radii with justification.
7. $\text{K}_3[\text{Co}(\text{CN})_6]$ is colorless while $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)]$ is colored. Why ?
8. $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ is dark pink whereas $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is pale pink. Explain
9. Which of the following ligands F^- , CN^- , H_2O and NO_2 will form significantly distorted octahedral complexes with cobalt (II) ? Explain.
10. Which of the following octahedral complexes are expected to show very weak tetragonal distortion and why?
- (a) $[\text{Cr}(\text{CN})_6]^{4+}$ (b) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
11. Four chlorine ligands are missing in each of the given skeletons of dimeric organometallic compounds A, B and C. Given that all of them obey the 18 electron rule and no additional metal-metal bonds are present, attach the missing Cl ligands on the complexes in the most appropriate manner.

