

1. Predict whether following complexes will show any Jahn-Teller distortion:

Ans: (i) $[\text{Co}(\text{NH}_3)_6]^{2+}$ is a low-spin Co^{II} d^7 complex (electronic config. $t_{2g}^6 e_g^1$). Thus, unsymmetrical population of electrons in e_g level and will show significant J-T distortion along Z-axis.

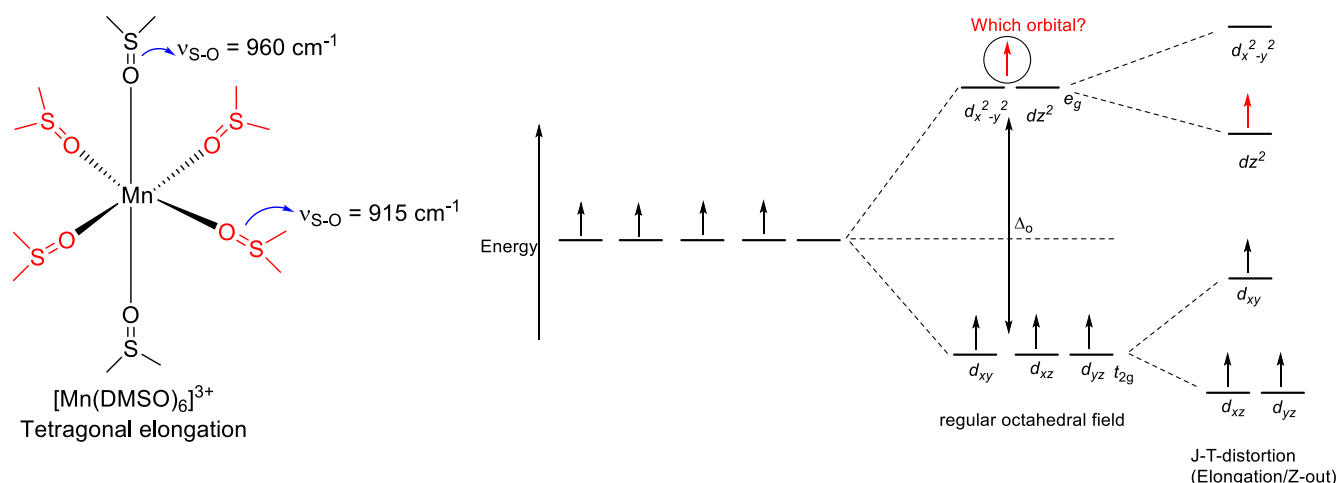
(ii) $[\text{CoF}_6]^{3-}$ is a high-spin Co^{III} d^6 complex (electronic config. $t_{2g}^4 e_g^2$). Thus, unsymmetrical electron distribution in t_{2g} level. It will show weak J-T distortion with preferably compression along Z-axis (tetragonal compression or Z-in, stabilization energy = $-2/3\delta_2$).

(iii) $[\text{MnF}_6]^{3-}$ is a high-spin Mn^{III} d^4 complex (electronic config. $t_{2g}^3 e_g^1$), have unsymmetrical electron distribution in e_g level. Thus, there will have strong J-T distortion along Z-axis.

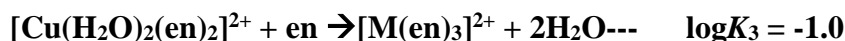
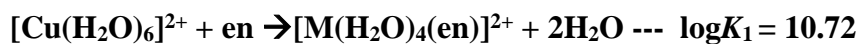
(iv) $[\text{FeCl}_4]^{2-}$ is a high-spin tetrahedral Fe^{II} complex with electronic config. $e^3 t_2^3$, so having unsymmetrical population at e level and it will be J-T sensitive.

2. Infrared spectrum of $[\text{Mn}(\text{DMSO})_6](\text{ClO}_4)_3$ (DMSO = dimethyl sulfoxide) shows two S-O stretching frequencies at 915 cm^{-1} and 960 cm^{-1} . The intensity of the 915 cm^{-1} band double than that of 960 cm^{-1} band. From these observation, find out the position (orbital) of 4th electron.

Ans: High-spin octahedral $[\text{Mn}(\text{DMSO})_6]^{3+}$ having Mn^{3+} (d^4) with unsymmetrical distribution of electrons in e_g level and Jahn-Teller distortion sensitive. Two $\nu_{\text{S=O}}$ indicate different types of DMSO ligands with varying S-O bond strengths. Since the intensity of 915 cm^{-1} band is double (four DMSO ligands) than 960 cm^{-1} (two DMSO ligands), the nuclear screening is less effective in the equatorial plane giving four strongly bound DMSO ligands and two weakly bound axial DMSO ligand. Thus this is a case of tetragonal elongation (Z-out) and electronic configuration is $d_{xz}^1, d_{yz}^1 < d_{xy}^1 < d_{z^2}^1 < d_{x^2-y^2}^0$

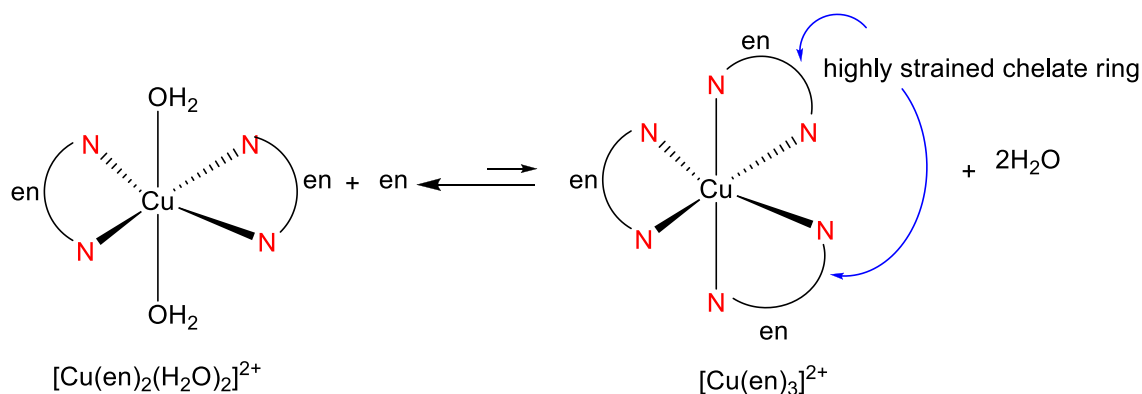


3. The stepwise stability constants in aqueous solution at 25 °C, K_1 , K_2 , and K_3 , for successive reactions of ethylenediamine with Cu^{2+} are follows:



Explain why there is striking difference in K_3 .

Ans: $[Cu(en)_3]^{2+}$ is remarkably unstable due to strong Jahn-Teller distortion for octahedral d^9 $Cu(II)$ system. The first two en ligands add in equatorial plane, with water molecules in the axial positions, and the coordination of these two monodentate ligands allows for the Jahn-Teller distortion without any strain by letting two H_2O ligands away from Cu^{2+} . $[Cu(en)_3]^{2+}$ can not distort tetragonally without straining at least two of the chelate rings. Thus, adding a third en ligand requires a geometry change and with a preference for uniform M—N bond distances towards the six nitrogen atoms. This is counter to the Jahn-Teller distortion, and the third addition is much less favorable than the first two and consistent with extremely low stability constant.



4. Determine the nature of following spinel structures from CFSE? Show your calculation. (i) Fe_3O_4 (ii) ZnFe_2O_4

Ans: (i) Fe_3O_4 : Fe^{2+} (d^6) in tetrahedral hole: config. $e^3t_2^3$, $\text{CFSE} = -0.6\Delta_t = -0.26\Delta_o$

Fe^{2+} (d^6) in octahedral hole: config. $t_{2g}^4e_g^2$, $\text{CFSE} = -0.4\Delta_o$

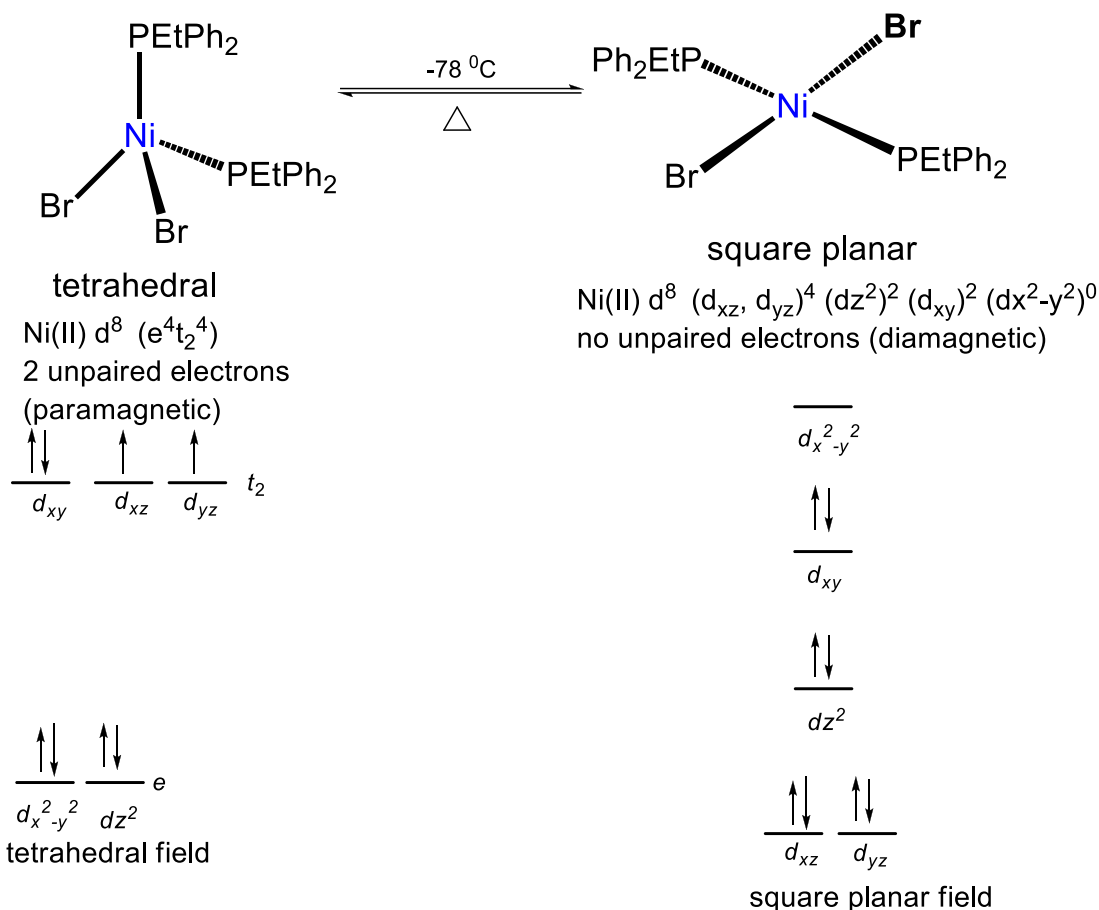
For Fe^{3+} (d^5), $\text{CFSE} = 0$ in both tetrahedral or octahedral holes.

Thus, it's energetically favourable for Fe^{2+} to be in octahedral holes. This results in inverse spinel structure, $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}]\text{O}_4$.

(ii) ZnFe_2O_4 : normal spinel. Here Nature of spinel structure for ZnFe_2O_4 you won't be able to predict from just CFSE calculation as here for Zn^{2+} or Fe^{3+} (h.s.), $\text{CFSE} = 0$ in both Oh./Td. holes. Though from experimental structure determination it's observed, all Zn^{2+} occupy Td holes and Fe^{3+} occupy Oh. holes. Td. is preferred geometry compared to Oh. for Zn^{2+} , and thus forces Fe^{3+} to occupy Oh. holes. Lattice energy play important role here and is favourable for normal spinel.

5. Dark green colored and paramagnetic $[\text{NiBr}_2(\text{PEtPh}_2)_2]$ complex on cooling to -78°C becomes brown colored and diamagnetic in nature. Explain this unique observation.

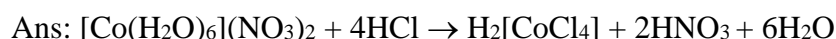
Ans: This is a case of conformational isomerism which are interconvertible between tetrahedral and square planar geometry. These isomers also termed as alloisomers.



More details: B. T. Kilbourn and H. M. Powell *J. Chem. Soc. A*, 1970, 1688-1693,
 DOI: 10.1039/J19700001688

6. (a) When dil HCl is added to a pale pink coloured aqueous solution of cobaltous nitrate, the color changed to dark blue.

(i) Write down the equilibrium reaction. Identify the complex species in solution and explain this observation.



$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$: centrosymmetric octahedral, Laporte-forbidden, spin-forbidden, very low molar extinction coefficient so pale pink color.

$[\text{CoCl}_4]^{2-}$: $\text{Co(II)} d^7$ in tetrahedral geometry, non-centrosymmetric, Laporte rule is relaxed, having higher molar extinction coefficient so dark blue color. Change from pink to blue color due to lowering crystal field splitting parameter (Δ) from octahedral to tetrahedral geometry.

(ii) Check whether there will be any difference in observed magnetic moments in the starting material and products formed in the above reaction.

[Co(H₂O)₆](NO₃)₂ : Co(II) d⁷ in octahedral geometry, H₂O weak field ligand, so high-spin, electronic config. t_{2g}⁵e_g², no. of unpaired electrons = 3, μ_{s.o.} = 3.87 μ_B. Due to presence of orbital contribution from t_{2g} level, μ_{eff} will be higher (~5 μ_B).

H₂[CoCl₄]: Co(II) d⁷ in tetrahedral geometry, electronic config. e⁴t₂³, no. of unpaired electrons = 3, μ_{s.o.} = 3.87 μ_B. No orbital contribution. Expected μ_{eff} closer to μ_{s.o.}

But due to possible orbital contribution from low-lying excited state (e³t₂⁴) through spin-orbit coupling, μ_{eff} (4.4 μ_B) higher than μ_{s.o.}

7. Account for the following observation in electronic spectra of listed transition metal complexes:

Ans: Solve yourself. Hint: electronic configuration, geometry, selection rules.

Compound	ε _{max} (M ⁻¹ cm ⁻¹)	Reason
[Mn(H ₂ O) ₆] ²⁺	0.1	Mn ²⁺ high-spin d ⁵ , spin-forbidden d-d transition
[Ti(H ₂ O) ₆] ³⁺	10	Centrosymmetric compound, Laporte forbidden, spin-allowed transition
[CoCl ₄] ²⁻	500	Tetrahedral structure, non-centrosymmetric molecule, Laporte selection rule not applicable
[TiCl ₆] ²⁻	10,000	octahedral Ti ⁴⁺ (d ⁰) system, ligand (Cl ⁻) to metal (Ti ⁴⁺) charge-transfer transition (LMCT), Laporte and spin-allowed.

8. Potassium dichromate is having bright orange colour whereas [Cu(MeCN)₄](BF₄) is colourless. Give a proper reason.

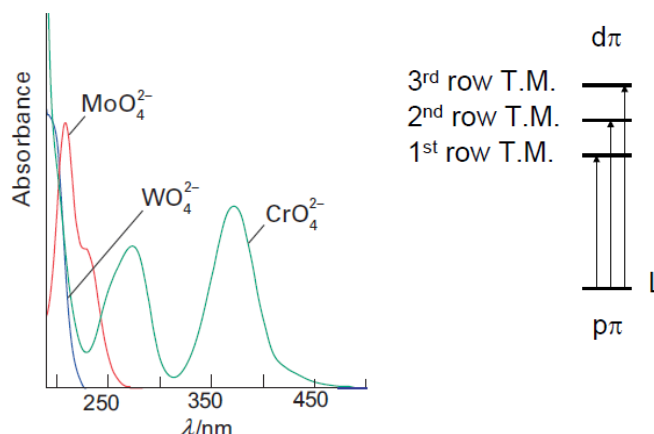
Ans: K₂Cr₂O₇ : Cr(VI) is d⁰ system with high oxidation state, so no d-d transition possible.

Bright orange color originates due to ligand-to-metal charge transfer (LMCT) transition.

Here oxygen lone pair electron is promoted to an empty orbital of Cr(VI).

[Cu(MeCN)₄](BF₄): Cu(I) is d¹⁰ system with tetrahedral geometry and all five d-orbitals are completely filled so, no d-d transition possible. Moreover, no LMCT transitions possible due to absence of lone pair over N and lower oxidation-state (no vacant d-orbitals in Cu(I)). Thus it's colorless.

9. Absorption spectra for CrO₄²⁻, WO₄²⁻ and MoO₄²⁻ are shown below. Identify the species corresponding to respective spectra. Mention the origin of the spectra.



Ans: On descending the group, the absorption maximum moves to shorter wavelengths, indicating an increase in the energy of the LMCT band originating from $d\pi(M) \leftarrow p\pi(O)$ transitions. $d\pi(M)$ energy level increases down the group so need higher energy for electronic transition.

10. $[\text{Et}_4\text{N}]_2[\text{NiBr}_4]$ paramagnetic, but $\text{K}_2[\text{PdBr}_4]$ is diamagnetic. Rationalize these observations.

Ans: $[\text{NiBr}_4]^{2-}$: Ni(II) is $3d^8$ ion and geometry is tetrahedral and high-spin state. Electronic config. $e^4 t_2^4$ having 2 unpaired electrons, so paramagnetic ($\mu_{\text{S.O.}} = 2.84 \text{ B.M.}$)

$[\text{PdBr}_4]^{2-}$: Pd(II) is $4d^8$ ion, higher CF splitting, square planar geometry low spin electronic configuration ($d_{xz}^2, d_{yz}^2, d_{z^2}^2, d_{xy}^2$). All electrons are paired, diamagnetic ($\mu_{\text{S.O.}} = 0.0 \text{ B.M.}$)

11. Calculate the spin only ($\mu_{\text{S.O.}}$) and total magnetic moment ($\mu_{\text{L+S}}$) for Cr(III)

Ans: Cr(III) is $3d^3$ system. Hence, $S = 3/2$, $L = 3$.

$$\mu_{\text{S.O.}} = [4S(S+1)]^{1/2} \text{ B.M.} = [4 \times 3/2 \times 5/2]^{1/2} = 3.87 \text{ B.M.}$$

$$\mu_{\text{L+S}} = [L(L+1) + 4S(S+1)]^{1/2} = [(3 \times 4) + (4 \times 3/2 \times 5/2)]^{1/2} \text{ B.M.} = 5.20 \text{ B.M.}$$