

Problem Set 5

The following problem set is due Friday, March 28th, by 5PM.

1. Identify the ground-state terms for the following transition metal **(a)** ions, **(b)** high-spin octahedral complexes, and **(c)** tetrahedral complexes: **i)** Cu^{2+} ; **ii)** V^{3+} ; **iii)** Mn^{2+} ; **iv)** Fe^{2+} ; and **v)** Ni^{2+}

2. For $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ absorption bands are observed at 12 300, 18 500, and 27 900 cm^{-1} . Assign the bands and calculate or estimate the values of Δ_o and B . Why would transitions to (${}^1\text{E}_g$, ${}^1\text{T}_{2g}$) and ${}^1\text{A}_{1g}$ not be expected or observed? *Hint: Look at the Tanabe-Sugano diagram for . . .*

3. Interpret the following comparisons of intensities of absorption bands for transition metal complexes.

(a) Two isomers of a Co^{3+} complex believed to be *cis* and *trans* isomers give the following spectral features: Both give two absorptions in the visible region. Complex A has two symmetrical bands with $\epsilon = 60 - 80$. The lower energy band for complex B is broad with a shoulder and has lower intensity. Assign the isomers. Explain.

(b) An octahedral complex of Co^{3+} , with an amine and Cl^- coordinated, gives two bands with $\epsilon = 60 - 80$, one very weak peak with $\epsilon = 2$, and a high-energy band with $\epsilon = 20\ 000$. What are the nature of these transitions? Explain.

4. Two different isomers of $[\text{Co}(\text{NH}_3)_4(\text{SCN})_2]^+$ were separated. How could you determine whether the SCN groups in both were bonded through the sulfur? If both isomers were coordinated through sulfur, how could you determine which is *cis* and which is *trans*? (*Hint: -SCN is near Cl^- in the spectrochemical series, while -NCS creates a stronger field; $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is easily prepared.*)

5. Explain why the *d-d* transitions in a $[\text{CoX}(\text{NH}_3)_5]^{2+}$ ions ($\text{X} = \text{F}^-$, Cl^- , Br^- , and I^-) are shifted only slightly in energy, while the LMCT bands are shifted greatly for the series. *Hint: Think about the ease of oxidation of F_2 compared to Cl_2 compared to Br_2 compared to I_2 .*

6. Vanadium(IV) species that have the V=O group have quite distinct spectra. **(a)** What is the d electron configuration of V(IV)? **(b)** The most symmetrical of such complexes are VO_5 with C_{4v} symmetry with the O atom on the z -axis. What are the symmetry species for the 5 d orbitals under the C_{4v} point group? **(c)** How many $d-d$ bands are expected in the spectra of these complexes? **(d)** A band near $24\,000\text{ cm}^{-1}$ in these complexes shows vibrational progressions of the V=O vibration, implicating an orbital involving V=O bonding. Which $d-d$ transition is a candidate? (See C.J. Ballhausen and H.B. Gray, *Inorg. Chem.*, 1962, **1**, 111).

7. Prove that the intense, purple color of the permanganate ion (MnO_4^- , where Mn is in a tetrahedral coordination environment) cannot be caused by a $d-d$ transition. *Hint: Think about what the MO diagram of MnO_4^- would look like.*

8. Both H^- (hydride) and $\text{P}(\text{C}_6\text{H}_5)_3$ (triphenylphosphine) are ligands of similar field strength, high in the spectrochemical series. Phosphines are known to be good π acceptors. Using this piece of information, is π -acceptor character required for strong-field behavior? What orbital factors account for the strength of each ligand?

9. Using Tanabe-Sugano diagrams, estimate Δ_o and B for **(a)** $[\text{Ni}(\text{OH}_2)_6]^{2+}$ (absorptions at 8500 , $15\,400$, and $26\,000\text{ cm}^{-1}$) and **(b)** $[\text{Ni}(\text{NH}_3)_6]^{2+}$ (absorptions at $10\,750$, $17\,500$, and $28\,200\text{ cm}^{-1}$).

10. If an octahedral Fe^{2+} complex has a large paramagnetic susceptibility, what is the ground-state label according to the Tanabe-Sugano diagram?

11. When visible light travels through an aqueous solution of NiSO_4 , a green color results. What are the spin-allowed transitions responsible for this color? Would you expect a Jahn-Teller distortion for this complex?

12. The complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{MnCl}_4]^{2-}$, and $[\text{FeCl}_4]^-$ all have magnetic moments of nearly 5.92 BM. What does this tell you about the geometric and electronic structures of these complexes? Why is the spin-only formula so precise in these cases?

13. BONUS QUESTION (10 points)

Addition of TiCl_3 to an aqueous solution of urea followed by addition of KI gave deep blue crystals of a complex containing titanium, urea, and iodine. The

visible spectrum of the material showed one absorption at $18\,000\text{ cm}^{-1}$ and its magnetic moment was determined to be 1.76 BM. When 1.000 g of the compound was decomposed at high temperatures in an oxygen atmosphere, all ligands were volatilized and 0.101 g TiO_2 formed. **(a)** Deduce the formula and structure of the complex. **(b)** Do you think urea or water lies higher in the spectrochemical series? **(c)** How might you determine whether urea is bound to titanium or through oxygen or nitrogen?