

5.14: Problems

1. Predict the shape of the following complexes, and determine whether each will be diamagnetic or paramagnetic:

- (a) $[\text{Fe}(\text{CN})_6]^{4-}$
- (b) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$
- (c) $[\text{Zn}(\text{NH}_3)_4]^{2+}$
- (d) $[\text{Mo}(\text{CO})_6]$
- (e) $[\text{Rh}(\text{NH}_3)_4]^+$

2. For each of the following transition metal complexes, give (i) the d-electron count), (ii) the approximate shape of the complex, and (iii) an energy level diagram showing the splitting and filling of the d-orbitals.

- (a) $[\text{Os}(\text{CN})_6]^{3-}$
- (b) *cis*- $\text{PtCl}_2(\text{NH}_3)_2$
- (c) $[\text{Cu}(\text{NH}_3)_4]^+$

3. Tetrahedral complexes are almost always high spin, whereas octahedral complexes can be either high or low spin. Explain.

4. For each of the Mn complexes in the table below, give electronic configurations (within the t_{2g} and e_g sets of 3d orbitals) that are consistent with the observed magnetic moments.

Compound	μ (BM)
$[\text{Mn}(\text{CN})_6]^{4-}$	1.8
$[\text{Mn}(\text{CN})_6]^{3-}$	3.2
$[\text{Mn}(\text{NCS})_6]^{4-}$	6.1
$[\text{Mn}(\text{acac})_3]$	5.0

5. For each of the following pairs, identify the complex with the higher crystal field stabilization energy (and show your work).

- (a) $[\text{Fe}(\text{CN})_6]^{3-}$ vs. $[\text{Fe}(\text{CN})_6]^{4-}$
- (b) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ vs. $[\text{Cd}(\text{en})_2]^{2+}$, where $\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
- (c) $\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ vs. $[\text{PdCl}_4]^{2-}$

6. In a solution made by combining FeCl_3 with excess ethylenediaminetetraacetic acid (EDTA) at neutral pH, the concentration of $\text{Fe}^{3+}(\text{aq})$ ions is on the order of 10^{-17} M. However, in a solution of ethylenediamine and acetic acid at comparable concentration, the $\text{Fe}^{3+}(\text{aq})$ concentration is about 10^{-7} , i.e., 10^{10} times higher. Explain.

7. The complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is violet, while the analogous complex with another monodentate neutral ligand L, $[\text{Ti}(\text{L})_6]^{3+}$ is orange. How many of the following statements are true? Explain briefly.

- (a) L is a stronger field ligand than H_2O .
- (b) $[\text{Ti}(\text{L})_6]^{3+}$ is a high-spin complex.
- (c) $[\text{Ti}(\text{L})_6]^{3+}$ absorbs yellow and red light.
- (d) Both complexes have two 3d electrons associated with the metal.

8. OH^- and CN^- are both Brønsted bases, and both can form complexes with metal ions. Explain how OH^- can be a much stronger Brønsted base than CN^- , and at the same time much lower in the spectrochemical series.

9. A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is faint green and paramagnetic ($\mu = 2.90$ BM), whereas a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is yellow and diamagnetic.

(a) Draw the molecular geometry and the d-orbital energy level diagrams for each complex, showing the electronic occupancy of the d-orbitals.

(b) Explain the differences in magnetism and color.

10. W. Deng and K. W. Hipps (J. Phys. Chem. B 2003, 107, 10736-10740) reported an STM study of the electronic properties of Ni(II)tetraphenyl porphyrin (NiTPP), a red-purple, neutral diamagnetic complex that is made by reacting Ni(II) perchlorate with tetraphenylporphine. When NiTPP is reacted with sodium thiocyanate it forms another complex that is paramagnetic. Draw the structures of NiTPP and the product complex, and the crystal field energy level diagram that explains each. What value of the magnetic moment (in units of μ_B) would you expect for the paramagnetic complex?

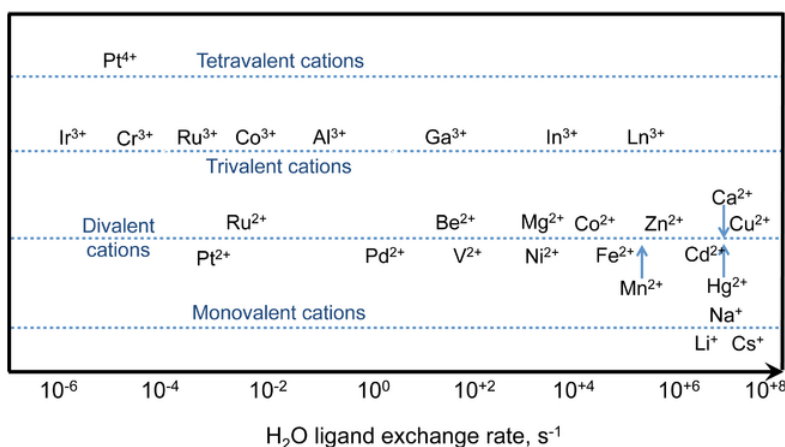
11. One of the simplest reactions a coordination complex can do is **ligand exchange**. For example, metal aquo complexes can exchange a coordinated water molecule with a free (solvent) water molecule, and the rate of the reaction can be measured by isotope labeling, NMR, and other techniques. Interestingly, these rates vary widely for water exchange with different metal ions - over a range of *14 orders of magnitude* - as shown in the figure below. For some metal ions, the rate is so slow that it takes weeks for one water molecule to exchange for another. In other cases, the timescale of the exchange is nanoseconds.

(a) There is an overall trend in which the rate of exchange decreases as the oxidation state of the metal increases. Explain this trend in terms of crystal field stabilization energy (CFSE). How is the CFSE related to the activation energy of the water exchange reaction?

(b) Explain any trends you observe for the rate of water exchange among divalent metal ions.

(c) Cu^{2+} has an anomalously fast ligand exchange rate. Why?

(d) What are the geometries and d-electron counts of the aquo complexes of the slowest divalent, trivalent, and tetravalent metal ions in the figure? Do they have particularly high or low CFSE's? Explain.



12. Ligand exchange rates for main group ions increase going down a group, e.g., $\text{Al}^{3+} < \text{Ga}^{3+} < \text{In}^{3+}$. For transition metal ions, we see the opposite trend, e.g., $\text{Fe}^{2+} > \text{Ru}^{2+} > \text{Os}^{2+}$. Explain why these trends are different.

13. Seppelt and coworkers reported the very unusual ion $[\text{AuXe}_4]^{2+}$ in the salt $[\text{AuXe}_4]^{2+}(\text{Sb}_2\text{F}_{11})_2$ (Science 2000, 290, 117-118). This was the first report of a compound containing a bond between a metal and a noble gas atom. Draw a d-orbital energy diagram for this ion and predict whether it should be diamagnetic or paramagnetic. Would you expect to be able to form a similar complex using Cu in place of Au, or Kr in place of Xe? Why or why not?

14. For the reaction $\text{cis-Mo(CO)}_4\text{L}_2 + \text{CO} \rightarrow \text{Mo(CO)}_5\text{L} + \text{L}$, the reaction rate is found to vary by a factor of 500 for two different ligands L, but it is relatively insensitive to the pressure of CO gas. (a) What kind of mechanism does this reaction have? (b) What are the signs of the activation volume and the activation entropy?

15. In Rosenberg's initial discovery of the biological effects of $\text{cis-Pt(NH}_3)_2\text{Cl}_2$, the compound was made accidentally by partial dissolution of a Pt anode in an electrolyte solution that contained glucose and magnesium chloride.^[24] The electrolysis reaction also produced small amounts of ammonium ions. Explain mechanistically why the *cis*-isomer is formed selectively under these conditions.

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