CHEMISTRY 413

Final, Friday, May 8, 1998, 10:00 am - 11:50 am

(1.) (a) Please draw the *d*-orbital boxes and valence bond description of the hybrid orbitals used in $[FeCl_4]^-$. Is this complex inner or outer valence? Please supply an example of an inner valence complex, again drawing the *d*-orbital boxes and valence bond description of the hybrid orbitals used.

(b) For $[FeCl_4]^{2-}$, please draw the *d*-orbital splitting diagram. What is the point group of this complex? Are the *d*-electrons symmetrically distributed? What is the theoretical magnetic moment? Please draw the *d*-orbital splitting diagram for the corresponding $[RuCl_4]^{2-}$ complex

(c) Please draw all the isomers of the complex $[Co(en)(NH_3)_2BrCl]^+$.

(d) Please write the coordination isomers of the complex $[Cr(en)_2BrCl][Co(ox)_2(H_2O)_2]$. How many unpaired electrons are in each of these isomers?

(e) Imagine that you have a *fcc* array of sulfide ions in a lattice. The center of the cube is occupied by a molybdenum ion; at two other sites *within* the lattice cage are Hg^{2+} ions. Please draw the unit cell. What is the empirical formula? What are the coordination numbers of the metal ions? Please specify the kinds of holes which are occupied by the metal ions? What percentage of the available tetrahedral holes are occupied? Is the complex paramagnetic? Please rationalize your answers.

(2.) (a) What is the spin-state of $[Fe(CN)_6]^{4-}$, given that the pairing energy for Fe^{2+} is 17,600 cm^{-1} and Δ_o is 33,000 cm^{-1} for the complex. Please rationalize.

(b) Please give a complete ligand-field description, including sketches of the symmetry adapted orbitals, of the σ bonding in $[Fe(CN)_6]^{4-}$.

(c) Now please show the π bonding on a separate diagram.

(3.) (a) Please draw all isomers of $[Pt(H_2O)_2BrCl]$

(b) Why does [Pt(en)BrCl] have only one isomer?

(c) Please draw the ligand diethylenetriamine, dien.

(d) Please draw the complex *mer*-$Co(dien)Cl_3$.

(e) The reaction $[Pt(dien)Cl]^+ + X^- \text{------} > [Pt(dien)X]^+ + Cl^-$ proceeds by an associative (A) or dissociative (D) mechanism? Please decide which one, write out the reaction above and please clearly draw the intermediate. Please predict the order of reaction rate for X = I, Br, and Cl. Now, please rationalize your answer.

(f) In part (e), which X forms the most stable complex with Pt? Please rationalize in terms of hardness or softness.

(4.) (a) Please draw the *d*-orbital splitting diagram for the trigonal-bipyramidal high-spin complex $[Fe(CH_3)_5]^{3-}$

(b) What is the point group of $[Fe(CH_3)_5]^{3-}$?

(c) What is the anticipated magnetic moment of $[Fe(CH_3)_5]^{3-}$?

(d) Please draw the *d*-orbital splitting diagram for $[Fe(CH_3)_5]^{2-}$

(e) Please draw the shape of the oxidized high-spin species $[Fe(CH_3)_5]^{2-}$

(f) Do you anticipate π bonding in either complex? Please explain your answer.

(5.) (a) Please thoroughly explain the lanthanide contraction.

(b) Please draw the molecular orbital diagrams for O_2^{2-} and O_2^{+}. What are the bond orders of these species?

(c) Please rationalize, through diagrams of excited and ground states, how oxymyoglobin is diamagnetic (S = 0), although it is a complex of low-spin Fe(III) and superoxide.

(d) Which decisive piece of data supports the assignment of the superoxide in oxymyoglobin?

(e) Please draw, and name, a model ligand that you would use to prepare a synthetic model of oxymyoglobin.

(6.) (a) Please consider the standard reduction potentials below:

$$Fe^{2+}\ (aq) + 2e^- \text{ ---------} > Fe\ (s) \qquad E^0 = -0.44V$$

$$Fe^{3+}\ (aq) + e^- \text{ ---------} > Fe^{2+}\ (aq) \qquad E^0 = +0.77V$$

Please calculate the redox potential for the disproportionation reaction. Is this reaction spontaneous? What is ΔG^0?

(b) Please draw the molecule $Re_2(CO)_{10}$. Is this species coordinatively saturated? Please explain.

(c) For $[Ti(CO)_6]^{2-}$ and $Cr(CO)_6$, which has the larger ν(CO) value, and why?

(d) Please use concepts of Δ and ligand field stabilization energy to explain why $NiCl_4^{2-}$ is tetrahedral and $[Ni(CN)_4]^{2-}$ is square-planar.

(e) Please utilize Lewis structures and VSEPR Theory to predict the shapes of the following molecules: $POCl_3$, ClF_3, SF_2, SF_4, BrF_5

(f) For each of the molecules above, please assign the point group.

(g) Please rationalize: $N(CH_3)_3$ is pyramidal, but $N(SiH_3)_3$ is planar

(h) Please draw a homo-lumo diagram to explain the stability of adducts formed from a Lewis acid, A, and a Lewis base, B.