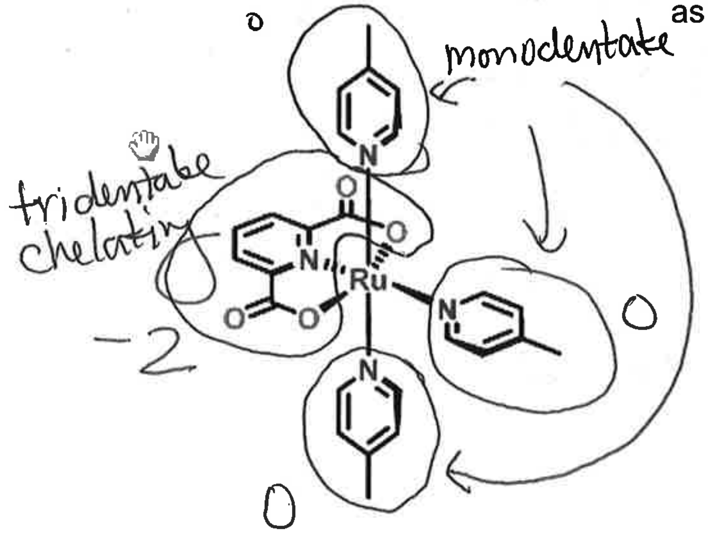
Chem 130, Eppley

KEY

In Class 16: Coordination Chemistry, Crystal Field theory and Colors

1. (10 pt) The following Ru complex was studied by researchers from Sweden and China and published a recent issue of *Inorganic Chemistry*. It was found to serve as a water oxidation catalyst!



   a. For each of the ligands below, circle each individual ligand, indicate the charge on each ligand, and indicate the type of ligand binding mode (note that the C's (the corners in the stick diagrams will not have any formal charges). (4 pt)

   b. If the complex (metal + ligand) is neutral, what is the charge on the metal? (2 pt)

   +2

   c. What is the coordination number of the metal? (2 pt)

   6

   d. If this complex (or a derivative of it) is serving as a "water oxidation catalyst," propose a possible change in oxidation state of the Ru that you expect for the reaction. (2 pt)

   If it is oxidizing the water it would have to be reduced (Ru^{+})

2. The crystal field splittings, Δ_o, are listed below for four complexes of chromium. Explain the differences in values briefly (why are some higher and some lower?). What color would you expect each of them to be? (use chart to figure out color)

	Complex	$\Delta_o(cm^{-1})$		absorbed color
blue	$[CrF_6]^{3-}$	15000	$\frac{1}{15000 cm^{-1}} \Rightarrow 667 nm$	orange
red-violet	$[Cr(OH_2)_6]^{3+}$	17400	$\frac{1}{17400 cm^{-1}} \Rightarrow 574 nm$	yellow-green
red ~~yellow~~ orange	$[CrF_6]^{2-}$	20000	$\frac{1}{20000 cm^{-1}} \Rightarrow 500 nm$	blue green
colorless	$[Cr(CN)_6]^{3-}$	26600	$\frac{1}{26600 cm^{-1}} \Rightarrow 376 nm$	ultraviolet

outside of visible!

They would appear as the complementary colors to the ones absorbed

For the 3 Cr^{3+} complexes the higher Δ_o are due to the different splittings caused by ligands that are higher or lower on the spectrochemical series, CrF_6^{2-} has Cr^{4+}, so its bond is shorter and stronger than in CrF_6^{3-}

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3. a. A coordination complex of Fe^{2+} with H_2O has a Δ_o value of 16,500 cm^{-1}. The pairing energy (P) for 2e- in for this complex is about 18,000 cm^{-1}. How many unpaired electrons should it have? What color should the complex appear? Explain and support your answers carefully. (7 pt)

$\Delta_o < P$ Fe^{2+} d^6

∴ high spin

4 u.e.

Color absorbed

$$\frac{1\ cm}{16500} \times \frac{1\ m}{100\ cm} \times \frac{1\times10^{9}\ nm}{1\ m} =$$

yellow 606 nm

so appear violet

b. Calculate the energy of the d-d transition for the complex above in kJ/mol. (6 pt)

$$E = \frac{6.626\times10^{-34}\ J\cdot s\ (3.00\times10^{8}\ m/s)}{6.06\times10^{-7}\ m}$$

$$= \frac{3.28\times10^{-19}\ J}{photon} \times \frac{6.02\times10^{23}\ photons}{1\ mol\ photons} \times \frac{1\ kJ}{1000\ J}$$

$$= \boxed{197\ kJ/mol}$$