

## Experiment VIII.1

### An Evaluation of The Spectrochemical Series: The Preparation and Spectroscopy of Chromium Complexes

The  $d$  orbitals of a metal ion in an octahedral crystal field (surrounded by an octahedral array of ligands) are split into a higher energy  $e_g$  set and a lower energy  $t_{2g}$  set, as shown in Figure 1. The energy difference between the upper and lower energy levels is designated as  $\Delta_o$  (pronounced del-oh) or in the older literature as  $10Dq$ .

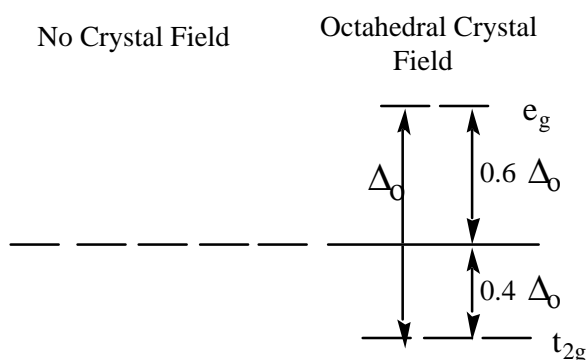
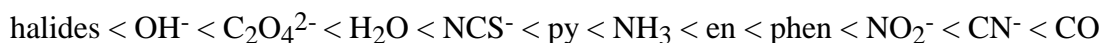


Figure 1.

The degree of splitting of the  $d$  orbitals and hence the magnitude of  $\Delta_o$  depends on several factors including the charge on the metal, the size of the metal, and the nature of the ligand. The situation is simplified considerably by considering a series of complexes with the same metal in a given oxidation state. The only major variable, in this case, is the ligands bonded to the metal. From a large number of studies it is known that ligands can be arranged in a sequence according to their ability to cause  $d$ -orbital splitting. This series is known as the spectrochemical series:



The magnitude of  $\Delta_o$  increases by a factor of about 2 as one moves from halide to  $\text{CN}^-$  in the spectrochemical series. Carbon monoxide has the strongest ligand field of all the common ligands.

The objective of this experiment is to quantify  $\Delta_o$  for a series of  $\text{Cr(III)}$  complexes by electronic absorption spectroscopy.  $\text{Cr(III)}$  compounds are  $d^3$  and their electronic spectral characteristics are reasonably easy to interpret. This is normally done through a Tanabe-Sugano diagram where energy is plotted against the magnitude of the crystal field

splitting parameter for a  $d^3$  ion, Figure 2. The lowest energy state is designated  $^4A_2$  and is the ground state. Optical excitation to other quartet excited states is allowed by

Figure 2.

selection rules. The states in order of ascending energy are labeled  $^4T_2$  (two electrons in the  $t_{2g}$  and one in the  $e_g$ ),  $^4T_1$ , and another  $^4T_1$  (one electron in the  $t_{2g}$  and two in the  $e_g$ ). The energy separation between the two lowest energy levels,  $^4A_2$  and  $^4T_2$  is  $\Delta_0$ . This absorption band will be the one at the longest wavelength (lowest energy) in the spectrum.

## Hazards

**Chromium (III) nitrate nonahydrate** (CAS No. 10060-12-5): Chromium compounds are considered mildly toxic. ORL-RAT LD50: 3250 mg/kg. Chromium (II) compounds in general, have little toxicity. Certain compounds are harmful if inhaled or swallowed.

**Methanol** (CAS No. 67-56-1): This liquid can be fatal if swallowed and is harmful if inhaled or absorbed through the skin. ORL-HMN LDLo: 143 mg/kg, ORL-RAT LF50: 5628 mg/kg. The compound is flammable and highly volatile.

**Zinc** (CAS No. 7440-66-6): Zinc is not generally considered to be a dangerous material, however the usual safety precautions should be taken.

**Ethylenediamine** (CAS No. 107-15-3): This compound is harmful if swallowed, inhaled, or absorbed through the skin. ORL-RAT LD50: 500 mg/kg. It should be used only in the hood.

**2,4-Pentanedione** (CAS No. 123-54-6): Also known as acetylacetonate. This compound is a mild irritant to the skin and mucous membranes. It is a flammable liquid. ORL-RAT LD50: 590 mg/kg.

**Urea** (CAS No. 57-13-6): Urea is not generally considered dangerous and is classified as a diuretic. ORL-RAT LD50: 8471 mg/kg.

## **Experimental Procedure.**

### A. Preparation of Tris(2,4-pentanedionate)chromium(III)

Dissolve 130 mg of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in 2.0 mL of distilled water with stirring. Add 500 mg of urea and 400  $\mu\text{L}$  of acetylacetonate. Heat the mixture to just below boiling with stirring for one hour. As the urea releases ammonia and the solution becomes basic, deep maroon crystals will begin to form.

After one hour, cool the flask to room temperature. Collect the crystals by suction filtration. Wash the crystals with three 200- $\mu\text{L}$  portions of distilled water. Dry the product, determine the percentage yield, and transfer to a labeled vial.

### B. Preparation of Tris(ethylenediamine)chromium(III)

Reflux 100 mg of mossy, granular zinc, 266 mg of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , 1 mL of ethylene diamine, and 1 mL of methanol with stirring for one hour.

Cool the solution to room temperature. Collect the yellow crystalline product by suction filtration using a Hirsch funnel. Remove any unreacted zinc with tweezers. Wash the filtered product with 0.5 mL portions of 10% ethylene diamine in methanol until the washings are colorless. Follow this with a 1 mL rinse with ether. Allow the product to dry, determine the percentage yield, and transfer to a labeled vial.

### C. Spectroscopy of the Cr(III) Complexes.

Prepare aqueous solutions of tris(ethylenediamine)chromium(III), hexaaquochromium(III) nitrate, and chromium(III) chloride and a toluene solution of tris(2,4-pentanedionate)chromium(III). The concentration of all solutions should be such that the low energy absorbance maxima is between 0.2 and 1.5 absorbance units. The chromium(III) chloride solution will slowly convert to the hexaaquo species so it should be analyzed immediately after preparation.

Obtain the absorbance spectrum for each complex. Determine the longest wavelength maximum in units of nanometers. Convert the wavelengths (which correspond to  $\Delta_o$ ) into wavenumbers ( $\text{cm}^{-1}$ ) using the following relationship:

$$\Delta_o = \nu = [1/\lambda \text{ (nm)}] (1 \times 10^7) \text{ cm}^{-1}$$

Other energy units for the absorption may be obtained using the following conversion factors:

$$1 \text{ cm}^{-1} = 1.24 \times 10^{-4} \text{ eV} = 0.01196 \text{ kJ/mol}$$

Arrange the ligands in order of increasing  $\Delta_o$ . Compare this series with the spectrochemical series. Tabulate your data.

### References

1. This experiment is taken from: Szafran, Z.; Pike, R.M.; Singh, M.M. "Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience", **1991**, John Wiley & Sons, New York, NY, pg 248.
2. Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753.