An Evaluation of The Spectrochemical Series:
The Preparation and Spectroscopy of Chromium(III) 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}. The energy difference between the upper and lower energy levels is designated as Δ_o or, in the older literature, as **10Dq**. The degree of splitting of the ***d*** orbitals and hence the magnitude of Δ_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**:

$$\text{halides} < OH^- < C_2O_4^{2-} < H_2O < NCS^- < \text{py} < NH_3 < \text{en} < \text{phen} < NO_2^- < CN^- < CO$$

The magnitude of Δ_o increases by a factor of about 2 as one moves from halide to 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 Δ_o for a series of Cr(III) complexes by electronic absorption spectroscopy. 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 1. The lowest energy state is designated $^4A_2$ and is the ground state. Optical excitation to other **quartet** excited states is allowed by

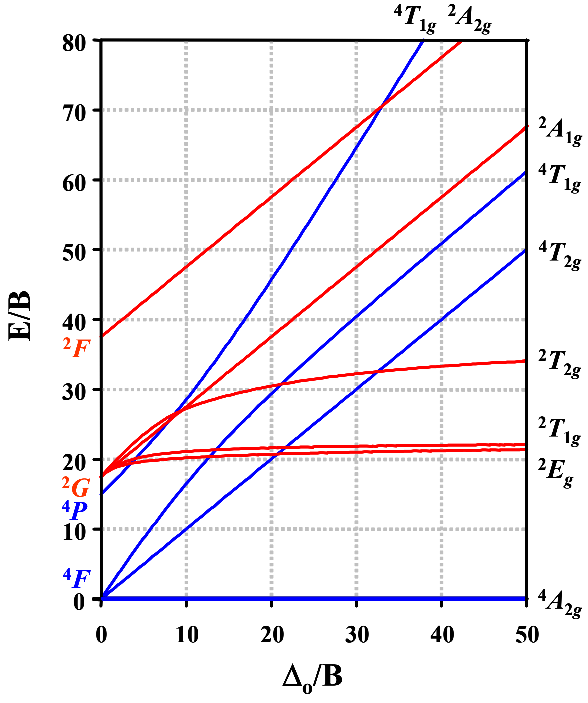

Figure 1

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 $\boldsymbol{\Delta_o}$. This absorption band will be the one at the longest wavelength (lowest energy) in the spectrum.

Hazards

Chromium(III) chloride hexahydrate (CAS No. 10060-12-5): Chromium compounds are considered mildly toxic. ORL-RAT LD50: 1790 mg/kg. Chromium(II) compounds in general, have little toxicity. Certain compounds are harmful if inhaled or swallowed.

Chromium(III) nitrate nonahydrate (CAS No. 7789-02-8): ORL-RAT LD50: 3250 mg/kg.

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, ORLRAT 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 acetylacetone. 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.

Potassium dichromate (CAS No. 7778-50-9): Chromium(VI) compounds are generally more toxic than chromium(III) compounds. May be fatal if absorbed through the skin, if swallowed or inhaled. Contains chromium(VI), a known cancer hazard. Allergen. Skin eye and respiratory irritant. ORL-RAT LD50 177 mg/kg.

Potassium oxalate monohydrate (CAS No: 6487-48-5): Corrosive - causes burns. Very destructive of mucous membranes. Toxicology not fully investigated.

Oxalic acid dihydrate (CAS No: 6153-56-6): Harmful if swallowed, inhaled or absorbed through skin. Corrosive - causes burns. Very destructive of mucous membranes. ORL-RAT LD50 7500 mg/kg.

Experimental Procedure.

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

Dissolve 130 mg of $CrCl_3•6H_2O$ in 2.0 mL of distilled water with stirring. Add 500 mg of urea and 400 μL of 2,4-pentanedione. 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 20-mL portions of distilled water. Dry the product, determine the percentage yield, and transfer to a labeled vial.

B. Preparation of Tris(ethylenediamine)chromium(III) Chloride Trihydrate

Reflux 100 mg of mossy, granular zinc, 266 mg of $CrCl_3•6H_2O$, 1 mL of ethylenediamine, and 1 mL of methanol with stirring for one hour. Cool the solution to room temperature.

The solution is then cooled to room temperature and the yellow product collected on a sintered glass. The filtered product is then washed with acetone/methanol mixture until the washings are colorless. Unreacted zinc is separated by dissolving the product using a minimal amount of distilled water. The yellow solid is precipitated from the filtrate with acetone. Filter, rinse with acetone and ether and allow the product to dry. Determine the percentage yield and transfer to a labeled vial.

C. Preparation of Potassium Tris(oxalato)chromate(III) Trihydrate

In a 50-mL beaker, add 0.46 g of $K_2C_2O_4•H_2O$ and 1.10 g of $H_2C_2O_4•2H_2O$ to 20.0 mL of distilled water and stir vigorously. Add 0.38 g of $K_2Cr_2O_7$ in one portion. Stir the mixture (white suspension in yellow-orange solution) for about 45 min or until it becomes a dark olive **solution** with no undissolved solids. Continue stirring and add an equal volume (~20 mL) of ethanol. When the complex has oiled out, decant off the mostly colorless solution and discard. **Triturate** the oily solid with ether to isolate a powdery dark blue-green solid. Collect the complex by suction filtration and wash with three 10-mL portions of ether. Allow the solid to dry under vacuo. Determine the percentage yield, and transfer to a labeled vial.

D. Preparation of Hexakis(urea)chromium(III) Chloride

$CrCl_3•6H_2O$ (2.7 g) and urea (3.6 g) are dissolved in 10 mL of distilled water and a few drops of 3 M HCl is added. The solution is heated on a steam bath until a crystalline crust forms. The slurry obtained is dissolved in the minimum of water at 50-60 ^oC and rapidly filtered. The salt crystallizes as light green needles. Allow the solid to dry under vacuo. Determine the percentage yield, and transfer to a labeled vial.

E. **Preparation of Potassium Hexa(thiocyanato)chromate(III)**

Make an aqueous solution of potassium thiocyanate, KSCN (2.5 g), chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$ (3.0 g) using distilled water (10 mL). Pour the solution into an evaporating dish and place on a steam bath. Evaporate to dryness, to obtain a mass of red crystals. Extract the solid, via suction filtration, using alcohol. The desired $K_3[Cr(NCS)_6]$, should dissolve very readily while K_2SO_4 remains as a residue. After evaporation of the filtered alcohol extract, collect the dark red-violet crystals. Allow the solid to dry under vacuo. Determine the percentage yield, and transfer to a labeled vial.

F. **Spectroscopy of the Cr(III) Complexes**.

Prepare **aqueous** solutions of tris(ethylenediamine)chromium(III) chloride, hexakis(urea) chromium(III) chloride, potassium tris(oxalato)chromate(III), ion), potassium hexa(thiocyanato)chromate(III), and $Cr(NO_3)_3 \cdot 9H_2O$ (hexaaquochromium(III) nitrate) 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.

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

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

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

References

1. This experiment is adapted 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 and Bailer, J. C.; Jones, E. M. *Inorg. Synth.*, **1939**, ***1***, 37.

2. Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753.