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 \( eg \) set and a lower energy \( t_{2g} \). The energy difference between the upper and lower energy levels is designated as \( \Delta_o \) or 10Dq. 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 only variable, in this experiment is the ligands bonded to the metal. From a large number of studies it is known that ligands can be arranged in an \textit{approximate} sequence according to their ability to cause d-orbital splitting. This series is known as the \textbf{spectrochemical series}:

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\Gamma^- < \text{Br}^- < \text{OCrO}_2^{2-} \text{chromate} < \text{Cl}^- \approx \text{SCN}^- < \text{N}_3^- < \text{F}^- \approx \text{SSO}_3^{2-} \text{thiosulfate} \approx \text{urea} \ (\text{O}) < \text{OCO}_2^{2-} \text{carbonate} < \text{O}CO_2\text{R}^- \text{carboxylate} < \text{ONO}^- \approx \text{OH}^- < \text{OSO}_3^{2-} \text{sulfate} < \text{ONO}_2^- \text{nitrte} < \text{O}_2\text{CCO}_2^{2-} \text{oxalate} \text{ (bidentate)} < \text{H}_2\text{O} < \text{NCS}^- < \text{glycine} \\
\approx \text{EDTA}^{4-} < \text{pyridine} < \text{NH}_3 < \text{en} < \text{SO}_3^{2-} < \text{bipy} < \text{o-phen} < \text{NO}_2^- < \text{PPh}_3 < \text{Cp} < \text{CN}^- < \text{CO}
\]

The magnitude of \( \Delta_o \) increases by a factor of about 2 as one moves from the halides to \text{CN}^- in the spectrochemical series.

The objective of this experiment is to quantify \( \Delta_o \) 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 \textbf{quartet} excited states is allowed by

\[
\text{Figure 1}
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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 $\Delta_o$. This absorption band will be the one at the longest wavelength (lowest energy) in the spectrum.

Hazards

**Ethylenediamine:** This compound is harmful if swallowed, inhaled, or absorbed through the skin. It should be used only in the hood.

**2,4-Pentanedione:** Also known as acetylacetone. This compound is a mild irritant to the skin and mucous membranes. It is a flammable liquid.

**Potassium dichromate:** Chromium(VI) compounds are generally more toxic than chromium(III) compounds. May be fatal if absorbed through the skin, if swallowed or inhaled. Allergen. Skin eye and respiratory irritant.

**Potassium oxalate monohydrate:** Corrosive - causes burns. Very destructive of mucous membranes. Toxicology not fully investigated.

**Oxalic acid dihydrate:** Harmful if swallowed, inhaled or absorbed through skin. Corrosive - causes burns. Very destructive of mucous membranes.

Experimental Procedure.

I. A. **tris(2,4-pentanedionato)chromium(III)**

In a 10-mL round-bottom flask, dissolve 0.13 g of CrCl$_3$·6H$_2$O in 2.0 mL of distilled water with stirring. Add 0.50 g of urea and 400 µL of 2,4-pentanedione. Add a condensor and heat the mixture to reflux, 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 and save for UV-vis analysis. Note that 2, 4-pentanedionato is also known as acetylacetonato. The formula is [Cr(C$_5$H$_7$O$_2$)$_3$].

B. **tris(ethylenediamine)chromium(III)**

In a 50-mL round-bottom flask, 1 g granular zinc, 2.66 g CrCl$_3$·6H$_2$O, 10 mL of ethylenediamine, and 10 mL of methanol are refluxed on a heating block for one hour. Cooled the mixture to room temperature and the product collected on a sintered glass filter and washed with acetone/methanol mixture until the washings are colorless. Unreacted zinc is separated by dissolving the product in a minimal amount of water and filtering. The yellow solid is precipitated from the filtrate with acetone. Filter and allow the product to dry. Save for UV-vis analysis. The formula is [Cr(C$_3$H$_{10}$N$_2$)$_3$]Cl$_3$·3H$_2$O.
C. tris(oxalato)chromate(III)

In a 100-mL beaker, add 0.46 g of $K_2C_2O_4 \cdot H_2O$ and 1.10 g of $H_2C_2O_4 \cdot 2H_2O$ 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 enough ethanol to oil out the olive-green product. 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. Save for UV-vis analysis. The formula is $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$.

D. hexakis(urea)chromium(III)

In a 100-mL beaker, dissolve 2.7 g $CrCl_3 \cdot 6H_2O$ and 3.6 g urea in 10 mL of distilled water and add a few drops of 3 M $HCl$. Heat the solution, with stirring, until a crystalline crust forms. Add a minimum amount of water to redissolve and vacuum filter while hot. The complex should crystallize out as a green solid. Allow the solid to dry under vacuo. Save for UV-vis analysis. The formula is $[Cr(CH_4N_2O)6]Cl_3$.

E. hexakis(isothiocyanato)chromate(III)

Make a solution of 2.5 g KSCN and 3.0 g potassium chromium sulfate dodecahydrate, $KCr(SO_4)_2 \cdot 12H_2O$ in 10 mL distilled water. Pour the solution into an evaporating dish and place on top of a beaker of boiling water bath. Evaporate to dryness. Add enough ethanol to dissolve the dark colored solid while $K_2SO_4$ remains as a white residue. Vacuum filter. Evaporation the alcohol solution to collect the dark red-violet crystals. Allow the solid to dry under vacuo. Save for UV-vis analysis. The formula is $K_3[Cr(NCS)_6]$.

II. Spectroscopy of the Cr(III) Complexes.

Prepare aqueous solutions of tris(ethylenediamine)chromium(III) ion, hexakis(urea) chromium(III) ion, tris(oxalato)chromate(III) ion, hexa(thiocyanato)chromate(III) ion, and hexaaquachromium(III) ion ($Cr(NO_3)_3 \cdot 9H_2O$) and a toluene solution of tris(2,4-pentanedionate)chromium(III). Know the concentrations of all solutions which should be such that the low energy (long wavelength) absorbance is between 0.5 and 1.0.

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

$$\Delta_o = \left[\frac{1}{\lambda \ (nm)}\right] (1 x 10^7) \ cm^{-1}$$
Calculate the B parameter using the Tanabe-Sugano diagram and the ration of the second to first transition energy. Calculate the molar absorptivity of each complex. Tabulate all the data. Arrange the ligands in order of increasing $\Delta_o$. Compare this series with the spectrochemical series. Acetylacetonato is not on the list. From what you know about the ligand structure and coordinating atom, does its position in the series make sense?

Comment on the **nephelauxetic effect** of the ligand based on B. Finally, relate the magnitude of $\epsilon$ to the symmetries of the complexes.

**References**
