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 \( \Delta_o \) or \( 10D_q \). 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 approximate sequence according to their ability to cause \( d \)-orbital splitting. This series is known as the spectrochemical series:

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

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\(^2\) 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 \( ^4\text{A}_2 \) and is the ground state. Optical excitation to other quartet excited states is allowed by
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

Ethynediamine: 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. tris(2,4-pentanedionato)chromium(III)

In a 10-mL round-bottom flask, dissolve 0.13 g of CrCl$_3$$\cdot$6H$_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$$\cdot$6H$_2$O, 10 mL of ethylenediamine, and 10 mL of methanol are refluxed on a heating block for one hour. Cooled the mixture to room temperature and the product collected on a sintered glass filter and washed with acetone/methanol mixture until the washings are colorless. Unreacted zinc is separated by dissolving the product in a minimal amount of water and filtering. The yellow solid is precipitated from the filtrate with acetone. Filter and allow the product to dry. Save for UV-vis analysis. The formula is [Cr(C$_3$H$_{10}$N$_2$)$_3$]Cl$_3$$\cdot$3H$_2$O.
C. **tris(oxalato)chromate(III)**

In a 100-mL beaker, add 0.46 g of K₂C₂O₄·H₂O and 1.10 g of H₂C₂O₄·2H₂O to 20.0 mL of distilled water and stir vigorously. Add 0.38 g of K₂Cr₂O₇ 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 K₃[Cr(C₂O₄)₃]·3H₂O.

D. **hexakis(urea)chromium(III)**

In a 100-mL beaker, dissolve 2.7 g CrCl₃·6H₂O 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(CH₄N₂O)₆]Cl₃.

E. **hexakis(isothiocyanato)chromate(III)**

Make a solution of 2.5 g KSCN and 3.0 g potassium chromium sulfate dodecahydrate, KCr(SO₄)₂·12H₂O in 10 mL distilled water. Pour the solution into an evaporating dish and place on top of a beaker of boiling water. Evaporate to dryness. Add enough ethanol to dissolve the dark colored solid while K₂SO₄ 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 K₃[Cr(NCS)₆].

F. **hexaamminechromium(III)**³

Assembled the apparatus below (with 24/40 glassware (distillation head)).

Add 50 mL concentrated aqueous ammonia to the 125-mL distilling system. A 250-mL filter flask is placed in a 1-L beaker containing a sodium chloride–ice-
water bath that traps water and prevents it from entering the reaction vessel. A 25-mL round-bottom flask containing a small magnetic stirring bar is placed in a Dewar containing a dry ice–2-propanol bath. The Dewar is placed on a stir plate.

The concentrated aqueous ammonia is heated until ca. 5 to 10 mL of liquid ammonia has been collected in the 25-mL round-bottom flask. The 25-mL round bottom flask is disconnected from the rest of the apparatus, but still cooled in the dry ice–2-propanol bath for the remaining steps, which should be performed relatively quickly.

To the liquid ammonia in the 25-mL round-bottom flask is added ca. 0.015 g (0.65 mmol) of freshly cut sodium metal. Stirring is continued until the sodium has completely reacted. At this point, the liquid ammonia solution will be blue. The blue solution is decolorized with a very small amount of Fe(NO$_3$)$_3$·9H$_2$O if it does not decolorize on its own. Removing the flask from the dry-ice bath momentarily might work as well. Stirred the solution until the blue color disappears.

The dark solution, which contains finely divided iron, is now treated with 0.320 g (2.03 mmol) of CrCl$_3$. The flask is stoppered and stirring is continued for about 20 min until the suspension becomes brown.

In the hood, the mixture is transferred to a small evaporating dish. The liquid ammonia is allowed to completely evaporate to produce a dry solid. In a 10-mL beaker, this solid is quickly dissolved, with stirring, in 3 mL of a 0.75 M HCl solution that has previously been heated to about 40 °C. Filter through a Hirsch funnel and transfer to a 10-mL beaker. Immediately add 1 mL of concentrated HNO$_3$. After stirring, the mixture is cooled in an ice bath.

Collect the yellow solid using a Hirsch funnel and wash with 3.5 M HNO$_3$ solution, then 95% ethanol and then ether. The solid yellow product is allowed to air-dry. Yields of 0.350 to 0.425 g of product (51 to 62%) are typical. Since the compound slowly decomposes in light, it should be stored in your bench. The formula is [Cr(NH$_3$)$_6$](NO$_3$)$_3$.

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, hexaaamminechromium(III) ion and hexaaquachromium(III) ion (Cr(NO$_3$)$_3$·9H$_2$O) and a toluene solution of tris(2,4-pentanedionato)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 $\Delta_\alpha$) into wavenumbers ($\text{cm}^{-1}$) using the following relationship:

$$\Delta_\alpha = \left[\frac{1}{\lambda \, (\text{nm})}\right] (1 \times 10^7) \, \text{cm}^{-1}$$

Calculate the B parameter using the Tanabe-Sugano diagram and the ratio of the second to first transition energy. Calculate the molar absorptivity of each complex. Tabulate all the data with the ligands arranged in order of increasing $\Delta_\alpha$. 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 $\varepsilon$ to the symmetries of the complexes.

**References**

