Experiment 7

The Preparation and Spectroscopy of Octahedral Chromium(III) Complexes

Introduction

A. Theoretical Concepts

Coordination compounds of transition metals are often highly colored. The color results from absorption of light at certain wavelengths of visible light. These absorptions are associated with electronic transitions within the d-orbitals. Thus, these d-d transitions give many transition metal ions their characteristic color (e.g., cobalt blue).

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 (Figure 1). This is due to electron clouds around each ligand (L) destabilizing those d-orbitals that lie along the X, Y, and Z axes. The energy difference between the upper and lower energy levels is designated as $\Delta_0$ (pronounced del-oh) or 10Dq.

![Figure 1. d-orbitals split by an octahedral crystal field.](image)

The degree of splitting of the d orbitals and hence the magnitude of $\Delta_0$ depends on several factors including the charge on the metal, the size of the metal, and the identity of the ligand. Understanding the trends in ligand-field splitting 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 ligand identity. 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:

halides $< OH^- < C_2O_4^{2-} < H_2O < NCS^- < py < NH_3 < en < phen < NO_2^- < CN^- < CO$
The magnitude of $\Delta_o$ increases by a factor of about 2 as one moves from halide to 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 2).

![Tanabe-Sugano Diagram](image)

**Figure 2.** Tanabe-Sugano Diagram appropriate for Cr(III). The vertical arrow denotes the relevant $d$-$d$ transition for determining $\Delta_o$. After Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753
The lowest energy state is designated \(^4\!A_{2g}\) (“quartet A-two-g”) and is the ground state. The \(^4\) tells you the spin multiplicity (# unpaired electrons + 1), while the \(A_{2g}\) indicates the symmetry of the electronic state. Optical excitation to other quartet excited states is allowed by selection rules, as this does not require any change in the total electron spin (spin-flip). The quartet states, in order of ascending energy, are labeled \(^4\!T_{2g}\) (two electrons in the \(t_{2g}\) and one in the \(e_g\)), \(^4\!T_{1g}\), and another \(^4\!T_{1g}\) (one electron in the \(t_{2g}\) and two in the \(e_g\)).

A detailed interpretation of all of the electronic states and transitions is beyond the scope of this course, however we will rely upon the simple guideline that promoting a single electron will require less energy than any of the multi-electron excitations, or the spin-flips. And such a transition will be more ‘allowed’ and therefore more intense, than any transition involving states of differing spin-multiplicity.

The energy separation between the two energy levels, \(^4\!A_{2g}\) and \(^4\!T_{2g}\) is \(\Delta_o\), and this transition is the only single electron excitation. Thus, this absorption band will be the one at the longest wavelength (lowest energy) in the spectrum, and it will be more intense than any other nearby transition. Ordering the octahedral \(\text{Cr}^{III}\!L_6\) compounds from longest to shortest wavelength will place the ligands “L” in order of increasing crystal field strength, as \(\lambda \propto 1/\Delta_o\).

Mixed-ligand complexes:  The “Rule of Average Environment” states that the observed value of \(\Delta_o\) in mixed-ligand complexes is the weighted average of \(\Delta_o\) for each of the homoleptic complexes. The first equation is general, the second equation below is for the specific example of \([\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+\). By rearranging the second equation, you can solve for \(\Delta_o\) for \(\text{Cl}^-\) in \([\text{CrCl}_6]^{3+}\).

\[
\Delta_o M_{mB_{n}} = (1/6) \{ n\Delta_o M_{6} + m\Delta_o M_{6} \}
\]

\[
\Delta_o [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+ = (1/6) \{ 4\Delta_o [\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 2\Delta_o [\text{CrCl}_6]^{3+} \}
\]

B. Synthetic Concepts

In this experiment, the bidentate ligand acetylacetonate (acac-) will be generated via the deprotonation of acetylacetone (acacH) by ammonia. The ammonia is generated by hydrolysis of urea (figure 3); subsequently, ammonia acts as a base to deprotonate acacH.

\[
\text{H}_2\text{NNH}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2
\]

\[
\text{H}_2\text{C} = \text{C} = \text{C} = \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C}
\]

\[
\text{H}_2\text{N}^+\text{C} = \text{C} = \text{C} = \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C}
\]

\[
\begin{align*}
\text{H}_2\text{N}^+\text{C} = \text{C} &= \text{C} = \text{C} = \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
&\xrightarrow{\text{H}^+} \text{H}_2\text{N}^-\text{C} = \text{C} = \text{C} = \text{H}_3\text{C} \\
&\quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\end{align*}
\]

**Figure 3.** Top: Hydrolysis of urea. Bottom: Deprotonation of acetylacetone forms the bidentate ligand acetylacetonate (acac-). Systematic name is 2,4-pentanedione. Note resonance form!
Object
The object of this experiment is to verify the spectrochemical series for homoleptic octahedral Cr(III) complexes of the ligands Cl\(^-\), H\(_2\)O, NH\(_3\), en, and acac\(^-\).

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.

**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
You will prepare two compounds: Cr(acac)\(_3\), and [Cr(en)\(_3\)]Cl\(_3\)•2H\(_2\)O. [Cr(H\(_2\)O)\(_6\)](NO\(_3\))\(_3\)•3H\(_2\)O and [Cr(NH\(_3\))\(_3\)]Cl\(_2\) are provided.

*A. Cr(acac)\(_3\)*

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

Dissolve 260 mg of CrCl\(_3\)•6H\(_2\)O in 4.0 mL of distilled water within a small Erlenmeyer flask. Add 1 g of urea and 800 µL of acetylacetone. 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 300-µL portions of distilled water. Dry the product, determine the percentage yield, and transfer to a labeled vial. You will need this product in a later lab.
B. \([Cr(en)_3]Cl_3\cdot2H_2O\)

*Preparation of Tris(ethylenediamine)chromium(III)*

Add 100 mg of mossy zinc, 266 mg of \(\text{CrCl}_3\cdot6\text{H}_2\text{O}\), and 1 mL of methanol to a 10 mL round bottom flask. In the hood, add 1 mL of ethylenediamine. Next place a reflux condenser on the flask, then reflux your reaction, with stirring, for one hour.

**NOTE:** methanol refluxes at a lower temperature than water!

Cool the solution to room temperature. Collect the yellow crystalline product by suction filtration using a Hirsch funnel. Remove any un-reacted zinc with tweezers.

Wash the filtered product with 0.5 mL portions of 10% ethylenediamine in methanol until the washings are colorless. Follow this with a 0.5 mL rinse with ether. Allow the product to dry, determine the percentage yield, and transfer to a labeled vial. You will need this product for a later lab.

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

Prepare aqueous solutions of tris(ethylenediamine)chromium(III), hexaaquochromium(III) nitrate, chromium(III) tri-chloride penta-amine, and chromium(III) chloride hexahydrate. Prepare an ethanol solution of tris(2,4-pentanedionato)chromium(III). As the analysis of \(\Delta_0\) only requires that \(\lambda_{\text{max}}\) be identified, you can use approximately 10 mg of each complex in about 5 mL of solvent. The concentration of all solutions should be such that the low energy absorbance maxima is between 0.2 and 1.5 absorbance units.

**NOTE:** The chromium(III) chloride hexahydrate solution, consisting of \([\text{CrCl}_2(\text{H}_2\text{O})_4]^+\) ions, will slowly convert to the hexaaquo species, \([\text{Cr}(\text{H}_2\text{O})_6]^{3+}\), 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 \(\Delta_0\)) into wavenumbers (cm\(^{-1}\)) using the following relationship:

\[
\Delta_0 = \nu = \left[\frac{1}{\lambda} \text{ (nm)}\right] \times 10^7 \text{ cm}^{-1}
\]

Recall that \(\Delta E = h\nu\), and \(\nu = 1/\lambda\), and that this electronic transition occurs between the \(^4\text{A}_{2g}\) and \(^4\text{T}_{2g}\) states (ie: \(\Delta E = \Delta_0\)).

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 \(\Delta_0\). Compare this series with the spectrochemical series. Tabulate your data.

**Questions**

1. Why is the visible spectrum of \(\text{Cr(acac)}_3\) significantly different from the other
complexes? There are two possible reasons.

2. Does the order of ligands obtained by this experiment correspond to the established order of the spectrochemical series? Explain any deviations.

3. Mn(II) and Fe(III) are examples of transition metals that form complexes which are much less colored than those of Cr(III). Why are they so weakly colored?

References

1. This experiment is taken from: Szafran, Z.; Pike, R.M.; Singh, M.M.