

Experiment 5

Studying the Spectrochemical Series: Crystal Fields of Cr(III)

Introduction

A. Theoretical Concepts

Coordination compounds of transition metals are often highly colored. The color results from absorption of light at specific wavelengths of visible light associated with electronic transitions within the d -orbitals. Thus, these $d-d$ transitions give many transition metal ions their characteristic color (eg: 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 Δ_o (pronounced del-oh) or $10Dq$.

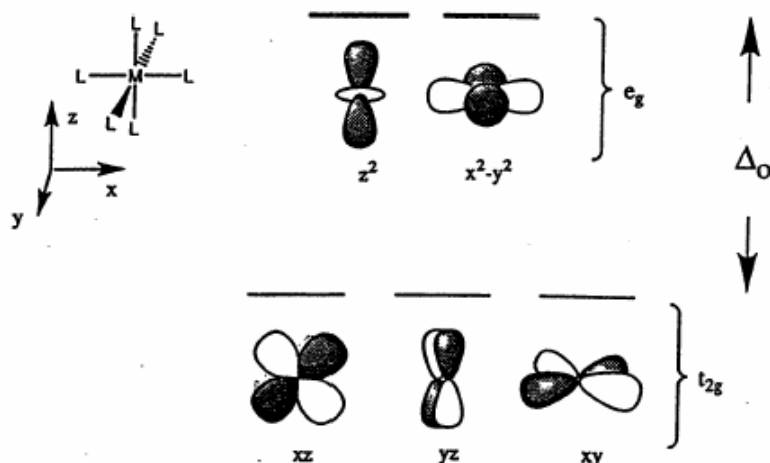


Figure 1. d -orbitals split by an octahedral crystal field.

The degree of splitting of the d orbitals and hence the magnitude of Δ_o depends on several factors, but the most important are the charge on 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:



The magnitude of Δ_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 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 2).

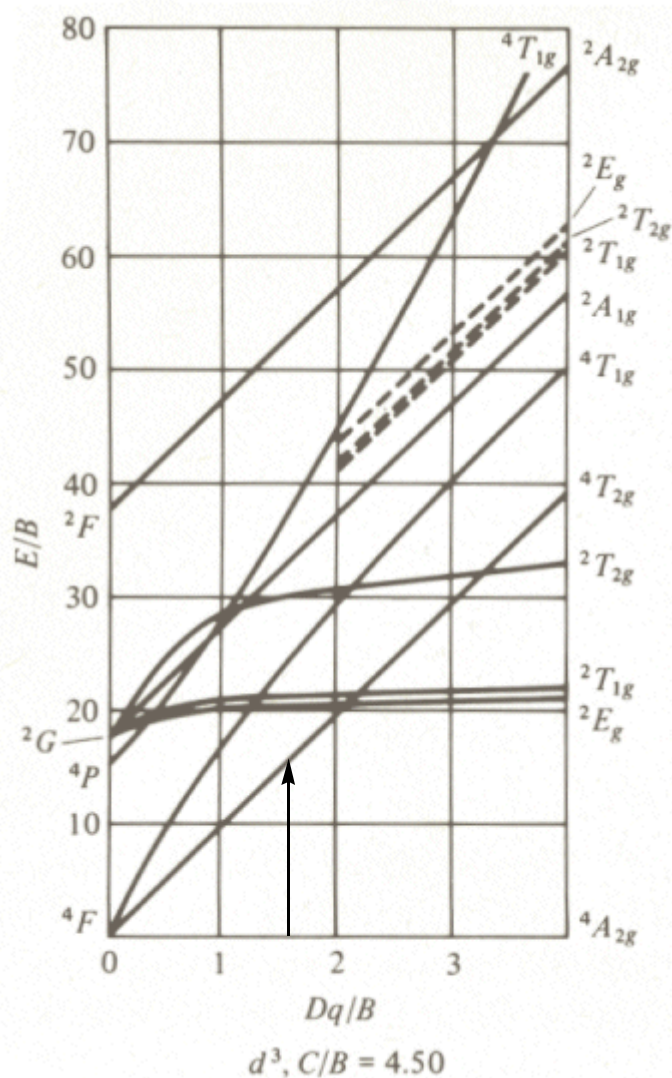


Figure 2. Tanabe-Sugano Diagram appropriate for Cr(III). The vertical arrow denotes the relevant $d-d$ transition for determining Δ_o . After Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753

The lowest energy state is designated $^4A_{2g}$ (“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 $^4T_{2g}$ (two electrons in the t_{2g} and one in the e_g), $^4T_{1g}$, and another $^4T_{1g}$ (one electron in the t_{2g} and two in the e_g).

A detailed understanding 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-flip transitions (quartet→non-quartet state). Quartet-quartet transitions are more ‘allowed’, and therefore more intense, than transitions involving states of differing spin-multiplicity.

The energy separation between the two energy levels, $^4A_{2g}$ and $^4T_{2g}$ is Δ_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 $Cr^{III}L_6$ compounds from longest to shortest wavelength will place the ligands “L” in order of increasing crystal field strength, as $\lambda \propto 1/\Delta_o$, and will allow you to build your own spectrochemical series.

In mixed-ligand complexes, the “Rule of Average Environment” states that the observed value of Δ_o in mixed-ligand complexes is the weighted average of Δ_o for each of the homoleptic (single type of ligand) complexes. The first equation is general, the second equation below is for the specific example of $[Cr(H_2O)_4Cl_2]^+$. By rearranging the second equation, you can solve for Δ_o for Cl⁻ in $[CrCl_6]^{3+}$.

$$\Delta_o MA_n B_m = (1/6) \{ n\Delta_o MA_6 + m\Delta_o MB_6 \} \quad (1)$$

$$\Delta_o [Cr(H_2O)_4Cl_2]^+ = (1/6) \{ 4\Delta_o [Cr(H_2O)_6]^{3+} + 2\Delta_o [CrCl_6]^{3+} \} \quad (2)$$

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 $acacH$.

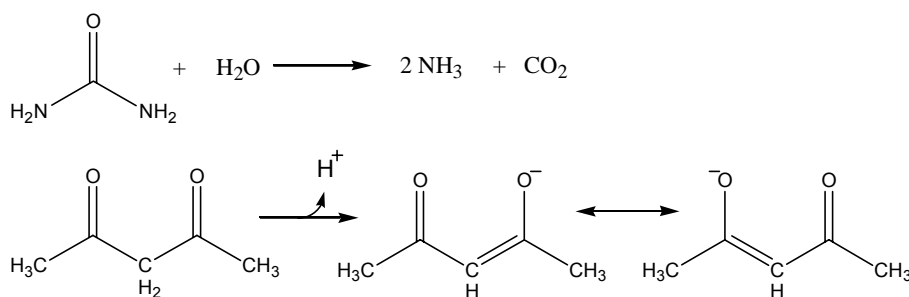


Figure 3. Top: Hydrolysis of urea. Bottom: Deprotonation of acetylacetone forms the bidentate ligand acetylacetonate ($acac^-$). Systematic name is 2,4-pentanedione. Note the resonance forms of this compound.

Experimental Procedure

You will prepare two compounds: $\text{Cr}(\text{acac})_3$, and $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. Two other compounds, $[\text{Cr}(\text{H}_2\text{O})_6](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, will be provided to you.

A. $\text{Cr}(\text{acac})_3$ – the preparation of *Tris(2,4-pentanedionate)chromium(III)*

Dissolve 260 mg of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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. $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ – the preparation of *Tris(ethylenediamine)chromium(III)*

Add 100 mg of mossy zinc (wash it with 6M HCl immediately prior to use), 266 mg of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 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 over a sand bath.

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), hexaquo chromium(III) nitrate, chromium(III) trichloride pentaamine, and chromium(III) chloride hexahydrate. Prepare an ethanol solution of tris(2,4-pentanedionate)chromium(III). As the analysis of Δ_o only requires that λ_{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 hexaquo 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 Δ_o) into wavenumbers (cm^{-1}) using the following relationship:

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

Recall that $\Delta E = h\nu$, and $\nu = 1/\lambda$, and that this electronic transition occurs between the ${}^4A_{2g}$ and ${}^4T_{2g}$ states (ie: $\Delta E = \Delta_o$)

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 five ligands in order of increasing Δ_o . Compare this series with the spectrochemical series given in the introduction.

Questions

1. The ligand acac^- is not included in the spectrochemical series given earlier in this lab report. Using your chemical intuition, explain where you would expect to find this ligand.
2. Draw the crystal field energies levels and electron occupancies for octahedral Cr^{3+} ions. Indicate the energy gap that corresponds to the transition that is being investigated.
3. Prepare a table of your data, including columns for λ_{max} in nm and Δ_o in cm^{-1} , eV, and kJ/mol. Arrange the entries in order of increasing gap energy.
4. Does the order of ligands obtained by this experiment correspond to the established order of the spectrochemical series? Explain any deviations.
5. Why is the visible spectrum of $\text{Cr}(\text{acac})_3$ significantly different from the other complexes?
6. High-spin Mn(II) and Fe(III) complexes 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. "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.