

Crystal Field Theory and the Spectrochemical Series for Cobalt (III) Complexes

Introduction

The chemistry of transition metal ions (elements in the middle of the periodic table whose atoms and ions contain partially filled *d*-orbitals) is interesting, extensive, and complex. A **coordination complex** consists of a central (often transition) metal atom or ion that is surrounded by chemically bound molecules or ions. These bound molecules or ions are called **ligands**. The partial filling of electrons in *d*-orbitals of transition metals leads to a variety of interesting properties that are observed only for elements in this region of the periodic table. In this experiment, we will explore the *photophysical* properties of a variety of cobalt (III) complexes, *i.e.*, how they interact with light. To understand the interaction of a transition metal ion with light, we must first explore how *d*-orbitals and their electrons are affected by bound ligands.

In a free transition metal ion with no bound ligands, the 5 *d*-orbitals all have the same energy and are said to be *degenerate*. Ligand binding leads to a “lifting” of the degeneracy and the *d*-orbitals are said to *split*, so that some orbitals are higher in energy than others. The manner in which some *d*-orbitals shift in energy depends on how many ligands are bound and the symmetry of the ligand arrangement around the central metal ion. A common example is an *octahedral complex* (as in the figure below), in which six ligands bind to a metal ion in an octahedral arrangement. This splits the *d*-orbitals into two sets--one set of two orbitals that is higher in energy, and a set of three orbitals that is lower in energy (as seen in the figure above). This “two above three” energy diagram is characteristic of any octahedral complex, but the extent of the energy splitting between the two sets of orbitals depends on the identity of the bound ligands. The energy difference between the two sets of orbitals is referred to as Δ_o (“delta octahedral”). Ligands that result in a large value of Δ_o are called *strong field* ligands, while those that result in a small Δ_o are called *weak field* ligands. Chemists have ranked a variety of ligands by their ability to split *d*-orbital energies and have compiled a list called the *spectrochemical series*, ranging from the weakest field ligands (small Δ_o) to the strongest field ligands (large Δ_o).

How might one test the degree of *d*-orbital splitting, or in other words, the magnitude of Δ_o ? The interaction of metal complexes with light is useful in this regard. When exposed to light equal in energy to Δ_o , the electrons in lower energy *d*-orbitals can absorb this light and be excited to higher energy orbitals, as depicted in the figure below. Because of the typical range of magnitudes of Δ_o , many coordination complexes absorb light in the visible region of the electromagnetic spectrum. When visible light passes through a solution containing these coordinated metal ions, only light of the appropriate wavelength (energy, $E = h\nu = hc/\lambda$) is absorbed, which results in solutions of metal complexes taking on a characteristic color. (See your text for further discussion of this matter.)

In this experiment we will use the UV-VISIBLE absorption spectra of a variety of cobalt complexes to rank Δ_o and compile a spectrochemical series of our own and then compare these results to the accepted spectrochemical series.

Experimental

Nine complexes of Co^{3+} will be synthesized during two consecutive lab periods, and their UV-Visible spectra will be obtained.

Instructions for UV-VIS spectrophotometer use:

- 1.) To calibrate the instrument, place a blank cuvette containing distilled water into the cuvette slot of the spectrophotometer and select Calibrate ► Spectrometer from the Experiment menu in *Logger Pro 3*. The calibration dialog box will display the message: "Waiting 90 seconds for lamp to warm up." After 90 seconds, the message will change to "Warmup complete."
- 2.) Remove the blank cuvette, and place the Co^{3+} solution cuvette into the cuvette slot. Click **Collect**. The absorbance vs. wavelength spectrum will be displayed. Click **Stop**.
- 3.) To analyze your absorption spectrum graph, click the **Examine** icon on the toolbar in *Logger Pro 3*. Record the wavelengths of the two maxima that occur in each spectrum. Export the data points of the spectrum and save as a CSV file (can be opened with Excel)

Lab Period 1

Stock solutions of 0.00422 M hexaaquacobalt (II) chloride, 0.24 M HCl, 4 M HNO_3 , 0.85 M KCN, and 30% H_2O_2 will be provided for you.

For each of the synthesized complexes, record its color in your lab notebook.

Tricarbonatocobaltate(III) $[\text{Co}(\text{CO}_3)_3]^{3-}$ solution

Add 1.45 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.2 mL of water, and 2.0 mL of 30% H_2O_2 to a 25 mL beaker. To a 50 mL beaker, add 3.5 g KHCO_3 and 3.5 mL of water. Place both beakers in an ice bath to cool. Add a stir bar in the beaker containing KHCO_3 and place the ice bath containing the reaction flask on a stir plate to stir the potassium bicarbonate mixture.

[While the above reactants are cooling, complete the of the hexanitrocobaltate(III) $[\text{Co}(\text{NO}_2)_6]^{3-}$ solution described in the next paragraph. After the nitrite complex has been prepared and characterized, return to this synthesis.]

Using a Pasteur pipette, add the solution containing cobalt nitrate dropwise, but not too slowly, to the stirred mixture of KHCO_3 . After the addition is complete, vacuum filter the excess KHCO_3 using a Büchner funnel. As soon as the filtration is complete, pour the filtrate into a 30 mL beaker and place the beaker in an ice bath. Using a Pasteur pipette, add two drops of the cobalt carbonate solution to a quartz cuvette and fill the cuvette $\frac{3}{4}$ full with distilled water. Cap the cuvette and invert it a few times to ensure proper mixing. Obtain a UV-Visible spectrum. Keep the beaker containing the remaining $[\text{Co}(\text{CO}_3)_3]^{3-}$ filtrate in the ice bath until you use it for making the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ solution below.

Hexanitrocobaltate(III) [Co(NO₂)₆]³⁻ solution

To a 50 mL beaker, add 0.38 g Co(NO₃)₂·6 H₂O (1.31 mmol) and dissolve it in 8 mL of water. Add 3.07 g NaNO₂ (44.5 mmol). Add 1.5 mL of glacial acetic acid. The solution will bubble vigorously. Add the entire solution to a 50 mL volumetric flask and dilute to the mark with water. Stopper the flask and shake vigorously for 2 to 3 min. Add 1 mL of the solution to a separate 50 mL volumetric flask, dilute to the mark with water, and mix thoroughly. Add 15 drops of this solution to a cuvette and dilute with distilled water, cap, and mix the solution. Obtain a UV-VIS spectrum of this dilute solution.

Triglycinatocobalt(III) [Co(gly)₃] solution

Add 10 mL of Co²⁺ stock solution and 0.75 g of sodium glycinate to a 50 mL beaker. Swirl until the sodium glycinate is dissolved. Add 0.5 mL of 30% H₂O₂ to the solution. Swirl the resulting solution periodically for about 5 minutes to ensure that oxidation is complete. Obtain the UV-VIS spectrum of the solution.

Trioxalatocobaltate(III) [Co(ox)₃]³⁻ solution

Add 5 mL of the Co²⁺ stock solution and 0.775 g of potassium oxalate to a 30 mL beaker. Swirl until the potassium oxalate is dissolved. Add 0.5 mL of 30% H₂O₂. Heat gently (30°C – 40°C) until a blue-green color is obtained. Obtain the UV-VIS spectrum.

Hexaaquacobalt (III) [Co(H₂O)₆]³⁺ solution

Slowly add 1 mL of the chilled, dark green tricarbonatocobalt (III) solution to 20 mL of 4 M HNO₃ in a 125 mL beaker. Swirl to ensure homogeneity. Obtain a UV-VIS spectrum of this solution.

Tris(1,10-phenanthroline)cobalt (III) [Co(phen)₃]³⁺ solution

With stirring, dissolve 0.30 g of cobalt chloride hexahydrate and 0.57 g of 1,10-phenanthroline in 7 mL of water. Add 1.25 mL of 30% H₂O₂ and 1.25 mL of concentrated hydrochloric acid. Heat and stir for 5 minutes. Add 5 drops of this solution to a cuvette and dilute with distilled water, cap, and mix the solution. Obtain a UV-VIS spectrum of the solution.

Lab Period 2**Hexaamminecobalt (III) [Co(NH₃)₆]³⁺ solution**

To a 50 mL beaker, add 0.80 g of cobalt chloride hexahydrate (CoCl₂·6H₂O) and 1.0 g of ammonium chloride (NH₄Cl). Weigh out 0.080 g of activated carbon on weighing paper. Add this to the 50 mL beaker. Add 4 mL of water, swirl to dissolve, then add 4 mL of aqueous ammonia (“ammonium hydroxide”). Add a stir bar. Slowly add 1.75 mL of 30% H₂O₂ to the beaker. After bubbling has mostly subsided, stir and heat the mixture at 60 °C for 30 minutes (a hot plate setting of just under 3 should be adequate).

[While heating the above reaction mixture, perform the synthesis of hexacyanocobaltate(III) [Co(CN)₆]³⁻ described below.]

After heating for 30 minutes, place the reaction beaker in an ice bath and cool for 10 minutes. Vacuum filter the mixture using a fritted glass funnel. The precipitate will be the desired product, $[\text{Co}(\text{NH}_3)_6]^{3+}$, together with the activated carbon. Scrape the carbon-contaminated product off of the frit into a 50 mL beaker. With heating, dissolve your product in 15 mL of 0.24 M HCl. Vacuum filter the solution using a fritted funnel to remove the active carbon. Using a Pasteur pipette, place 10 drops of the filtrate in a cuvette, add water, mix, and obtain a UV-VIS spectrum.

Hexacyanocobaltate(III) $[\text{Co}(\text{CN})_6]^{3-}$ solution

In a 150 mL beaker, dissolve 1.125 g of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ in 37 mL of water, add a stir bar, and bring to a boil. Using a Pasteur pipette, add 15 mL of the 0.85 M KCN solution to the cobalt chloride solution. Vacuum filter the purple $\text{Co}(\text{CN})_2$ precipitate and wash with cold water. Allow the suction to pull air through the product for 5-10 minutes so that the product is at least partly dry. Add the still moist purple $\text{Co}(\text{CN})_2$ to 25 mL of the 0.85 M KCN solution in a 150 mL flask. Transfer as much product as you can to the KCN solution, but don't worry about getting every bit of it. Add a stir bar and heat the solution to boiling. After a yellow color is formed, boil for 5 additional minutes. Add 4 drops of the solution to a cuvette, add water, mix, and obtain a UV-VIS spectrum.

Tris(ethylenediamine)cobalt (III) $[\text{Co}(\text{en})_3]^{3+}$ synthesis and solution

In a 30 mL beaker, add 0.60 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 2.5 mL of water, 1.33 g of ethylenediamine hydrochloride and swirl until dissolved. Add 0.8 g of sodium hydroxide and stir until all solids have dissolved. Add 2.0 mL of 30% hydrogen peroxide, dropwise with swirling. Gently boil the solution for around 10-15 minutes, until there is a layer of precipitate on the surface of the liquid. Cool the mixture in an ice bath for 10 minutes, and then vacuum filter the mixture. Dry the crystals, record the yield and transfer to a labelled vial. Add a few crystals of the $[\text{Co}(\text{en})_3]\text{Cl}_3$ to a quartz cuvette, dilute with distilled water, mix well, and acquire a UV-VIS spectrum of the solution.

Included the following in the report:

- 1.) A table that includes the following information for each of the nine complexes:
 - 1.) Visually observed color of the metal complex
 - 2.) Measured maximum absorption wavelengths (usually two)
 - 3.) Energy (in kJ/mol) corresponding to the absorption wavelength(s), according to Planck's equation, $E = h\nu = hc/\lambda$.
- 2.) Based on the maximum absorption wavelengths that you measured for each of the complexes, arrange the ligands in order of ligand field strength, from largest to smallest (*i.e.*, a spectrochemical series). Include a spectrum overlapping the spectra of all nine complex solutions.
- 3.) Compare your measured spectrochemical series with the literature series.
- 4.) Many of the complexes have two absorption peaks in their spectra. Do absorption peaks in the region much less 400 nm affect the color of the complexes?
- 5.) Which two complexes did not require the oxidizing agent? Something must have oxidized the initial Co^{2+} species to Co^{3+} . Make an educated guess as to what that might have been for each of these two complexes.