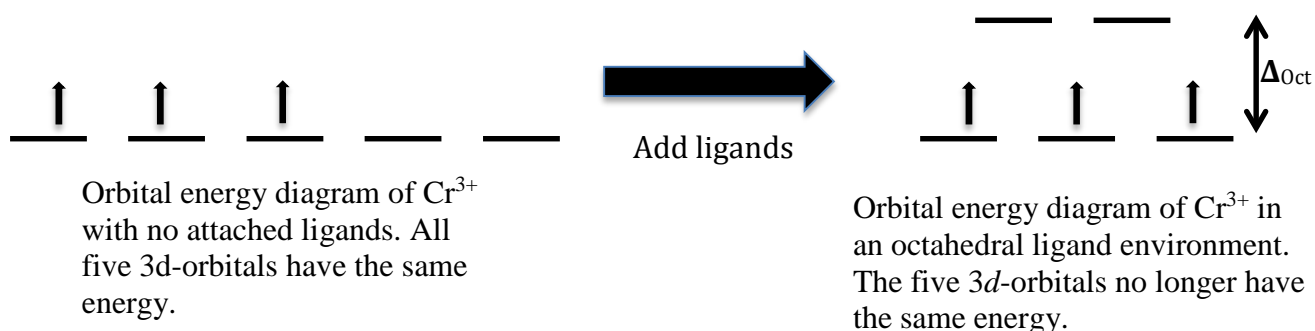


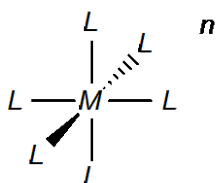
Spectrochemical Series for Cobalt (III)

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.

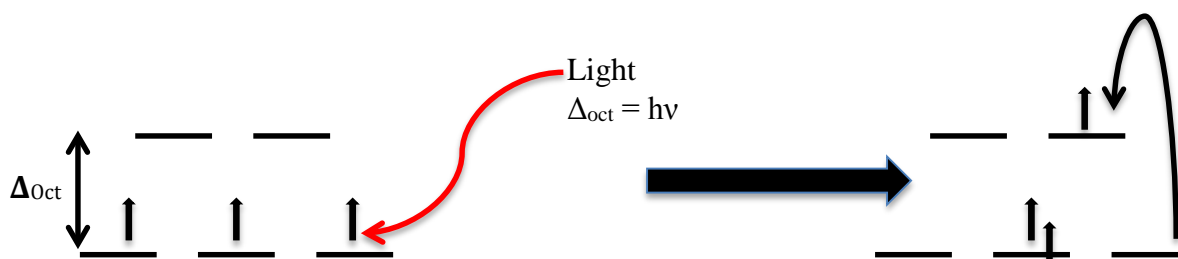


In a free transition metal ion with no bound ligands, the 5 d -orbitals all have the same energy and are said to be *degenerate*. Ligand binding leads to a “lifting” of the degeneracy and the d -orbitals are said to *split*, so that some orbitals are higher in energy than others. The manner in which 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_{Oct} (“delta octahedral”). Ligands that result in a large value of Δ_{Oct} are called *strong field* ligands, while those that result in a small value of Δ_{Oct} 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_{oct}) to the strongest field ligands (large Δ_{oct}).

How might one test the degree of d -orbital splitting, or in other words, the magnitude of Δ_{oct} ? The interaction of metal complexes with light is useful in this regard. When exposed to light equal in energy to Δ_{oct} , 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_{oct} , 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_{oct} and compile a spectrochemical series of our own and then compare these results to the accepted spectrochemical series.

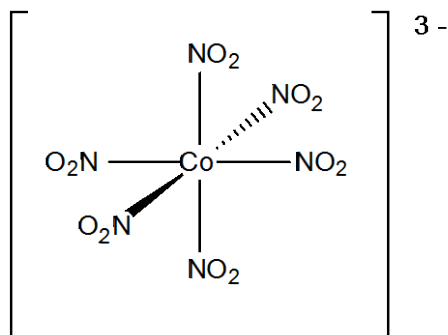
Note: The principal source of information on the theory of metal complexes and coordination compounds that you will need for this experiment is your lecture text. Prior to the first of the two lab periods used for this experiment, study carefully the reference pages from your lecture text that are listed in the lab calendar.

Safety Considerations

Review the material on laboratory safety on pp. 1-12 in your lab manual. In addition to safety goggles, throughout the experiment you must wear the rubber gloves that will be provided. It is standard safety practice to not touch any part of your face with your hands while you are wearing the gloves and handling the various chemicals and solutions that will be used. Immediately report any chemical spill to your T.A.

Pre-Lab Questions

1. The charge on this hexanitrocobalt complex is -3 . The charge of each nitro ligand (NO_2^-) is -1 . What is the oxidation state (*i.e.*, charge) of cobalt in this complex?



2. An easy way to assign the number of d -electrons (the “d count”) in a transition metal ion is to first look at the periodic table and take note of which group the element is in. For example, chromium is in Group 6, so elemental chromium has 6 valence electrons. Therefore, chromium $3+$ has three $3d$ -electrons. What is the number of $3d$ -electrons in cobalt $3+$?
3. Using your answer from Question 2, draw a d -orbital splitting diagram for low-spin Co^{3+} similar to the one given for Cr^{3+} in the introduction to this experiment. Almost all Co^{3+} complexes are low-spin, with a minimum number of unpaired electrons. (Refer to your text for further explanation.)
4. Suppose that light of sufficient energy strikes the cobalt ion and effects the transition of an electron from its ground state (lowest energy) to an excited state, like the diagram in the introduction. Draw a d -orbital splitting diagram for the excited state.

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.

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.

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

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 synthesis of hexanitrocobalt (III) ($[\text{Co}(\text{NO}_2)_6]^{3-}$) 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 the synthesis of $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ below.

Hexanitrocobalt (III) [Co(NO₂)₆]³⁻

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]

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.

Trioxalatocobalt(III) [Co(ox)₃]³⁻

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⁺

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⁺

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

Hexaaminecobalt (III) [Co(NH₃)₆]³⁺

To a 50 mL beaker, add 0.80 g of cobalt chloride hexahydrate (CoCl₂•6 H₂O) and 1.0 g of ammonium chloride (NH₄Cl). Weigh out 0.080 g of activated carbon on weighing paper, fold the paper so that it covers the carbon, and use a spatula to crush the carbon chunks into small pieces. 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 Büchner funnel. The precipitate will be the desired product, [Co(NH₃)₆]³⁺, together with the activated carbon. Scrape the carbon-contaminated product off of the filter paper into a 50 mL beaker. With heating, dissolve your product in 15 mL of 0.24 M HCl. Vacuum filter the solution using a Büchner 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.

Hexacyanocobalt(III) [Co(CN)₆]³⁻

In a 150 mL beaker, dissolve 1.125 g of CoCl₂•6 H₂O 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 Co(CN)₂ precipitate and wash with cold water. Allow the suction to pull air through the product/filter paper for 5-10 minutes so that the product is at least partly dry. Add the still moist purple Co(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) [Co(en)₃]³⁺

In a 30 mL beaker, add 0.60 g of CoCl₂•6 H₂O, 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, from the burette in the hood. 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. Add a few crystals of the [Co(en)₃]Cl₃ to a quartz cuvette, dilute with distilled water, mix well, and acquire a UV-VIS spectrum of the solution.

Discussion

Prepare a table that includes the following information for each of the nine synthesized complexes:

- 1.) Identity and formula of the ligand
- 2.) Visually observed color of the metal complex
- 3.) Measured maximum absorption wavelengths (usually two)
- 4.) Energy (in kJ/mol) corresponding to the absorption wavelength(s), according to Planck's equation, $E = hv = hc/\lambda$.

Which two ligands cause the largest d-orbital energy splitting, and which two the smallest? Consult your lecture text to discuss the structural and/or electronic properties of ligands that cause them to behave as strong-field or weak-field ligands?

Post-Lab Questions

- 1.) 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).
- 2.) Compare your measured spectrochemical series with that given in your lecture text.
- 3.) 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? What region of the electromagnetic spectrum is this?
- 4.) Which two complexes did not require the oxidizing agent you identified in the pre-lab questions? 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.