TWO SPECTROCHEMICAL SERIES: DETERMINATION OF Δ_o

ABSTRACT
Several highly coloured transition metal complexes are prepared. In some cases they are isolated as solids, in others they are prepared in situ. Visible spectroscopy is used to determine the values of Δ_O of the species, and from that, the relative donor strengths of a variety of ligands.

Equipment
No special equipment required.

Safety Hazards
No particular hazards. Metal compounds should be disposed of properly. Ethanol is flammable. Ethylenediamine should be used in a fumehood.

Year Level:	2nd year introductory inorganic
Student time required:	6 hours
Instructor time required:	~4 hour??
Technician notes?	Available upon request
Study question solutions?	Available upon request
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Chemistry 2351: Inorganic Chemistry I
Laboratory Manual

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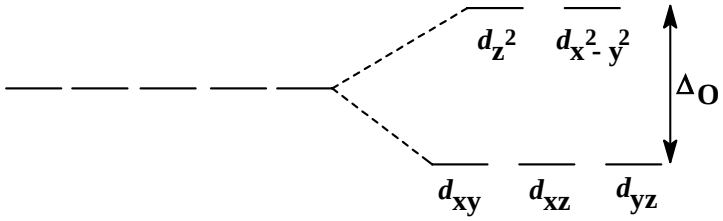
Experiment Five:
Two Spectrochemical Series: Determination of Δ_O

Purpose of the Experiment

Both ligands and metals have an effect on the Crystal Field splitting parameter, Δ_O. In this experiment, you will generate two spectrochemical series. The first will be a ligand series, using octahedral (or pseudo-octahedral) copper(II) complexes. UV/Vis spectroscopy will be the method of determining Δ_O in these complexes. The second series will be a metal series using tetrahedral tetrachloro complexes.

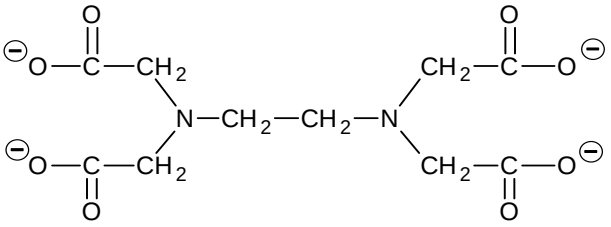
Introduction

Recall that the *d*-orbitals of a transition metal ion in an octahedral field are not degenerate. That is to say, they are split into two sets (shown at right). Tetrahedral coordination of a metal also causes the *d*-orbitals to split, but in a pattern that is essentially the opposite (d_{xy}, d_{xz}, and d_{yz} are equal and higher in energy than the doubly degenerate d_{z^2} and $d_{x^2-y^2}$).



The energy difference between the sets of orbitals is designated Δ_O (Δ_t for tetrahedral), and represents the octahedral (tetrahedral) Crystal Field splitting parameter. The extent to which this splitting occurs (*i.e.* the magnitude of Δ_O) depends on a number of factors, in particular the identity of the ligands coordinated to the metal. Based on many spectral studies performed in the past, the order of common ligands can be ranked according to the extent to which they cause *d*-orbital splitting; this series is known as the "spectrochemical series" (note: this series is empirically derived from experimental data).

In this experiment, the student will record the UV/Vis spectra of $[Cu(H_2O)_6]^{2+}$, $[Cu(EDTA)]^{2-}$ (EDTA = ethylenediaminetetraacetate) and $[Cu(en)_2(H_2O)_2]^{2+}$ (en = ethylenediamine or 1,2-diaminoethane). Each complex contains d^9 copper(II), but the ligands vary from an O_6 donor set, to an N_2O_4 donor set, to finally an N_4O_2 donor set. In each case Δ_O will be determined and compared.



EDTA: hexadentate ligand

$H_2N—CH_2—CH_2—NH_2$

en: bidentate ligand

Metals also have an impact (albeit smaller) on the magnitude of Δ_O and Δt. The second part of this experiment concentrates on generating a metal spectrochemical series.

Experimental Procedure

Special Notes and Safety Precautions

Most of the materials used in this experiment can be handled quite readily with no extra precautions. Ethylenediamine (1,2-diaminoethane, "en") and ethanol are flammable, en is also corrosive liquid with a

strong odour. Despite the small volume used in the synthesis, it still must be handled with care and it must not leave the fumehood.

PART I: A LIGAND SPECTROCHEMICAL SERIES

1. Synthesis of Diaquabis(ethylenediamine)copper(II) Iodide, $[Cu(en)_2(H_2O)_2]I_2$

Prior to beginning, please note that this particular compound is very soluble in water, thus it is crucial that water volumes be kept at a minimum in order to obtain reasonable yields.

In a 250 mL Erlenmeyer flask containing a stir-bar, add $[Cu(CH_3COO)_2]\bullet H_2O$ (1.90 g) followed by distilled water (5 mL). *In the fumehood*, slowly add a volume of ethylenediamine (2.0 mL) to the stirred blue slurry (an intense violet solution should be obtained upon complete addition of the ethylenediamine). Next, dissolve KI (4.2 g) in a minimum amount of water (about 10-15 mL) and add this solution to the stirred violet solution; allow the mixture to stir for about 10 minutes. Add excess ethanol (75 mL) to the solution and cool the mixture in an ice bath for about 30-60 minutes. During this time, a violet crystalline material should deposit. Filter the product (Buchner) and allow it to air dry. Do not attempt to wash the crystals as they are quite soluble in water and ethanol (ice-cold ethanol may be used in very small portions, but in general the product does not require washing). Record the yield.

2. Preparation of Solutions for UV/Vis Spectroscopy

Solutions (of known molarity) of $[Cu(H_2O)_6]^{2+}$, $[Cu(EDTA)]^{2-}$ and $[Cu(en)_2(H_2O)_2]^{2+}$ must be prepared prior to recording their UV/Vis spectra. Be sure to record all masses to the nearest 0.1 mg, and prepare the solutions in 100 mL volumetric flasks using water.

(a) $[Cu(H_2O)_6]^{2+}$ solution: dissolve an accurately known mass of $[CuSO_4]\bullet 5H_2O$ (about 1 g) in water, and fill to the 100 mL mark of the flask.

(b) $[Cu(EDTA)]^{2-}$ solution: dissolve an accurately known mass of $[Cu(CH_3COO)_2]\bullet H_2O$ (about 0.15 g) and Na_2EDTA (about 0.4 g) in water, and fill to the 100 mL mark of the flask.

(c) $[Cu(en)_2(H_2O)_2]^{2+}$ solution: dissolve an accurately known mass of $[Cu(en)_2(H_2O)_2]I_2$ (about 0.5 g) in water, and fill to the 100 mL mark of the flask.

Record and plot the UV/Vis spectra of each solution in the range 400-900 nm. Be sure to record λ_{max} and the absorbance at λ_{max} for each solution.

PART II: PREPARATION OF A METAL SPECTROCHEMICAL SERIES

1. Preparation of Bis(tetraethylammonium) tetrachlorocobaltate(II)

Dissolve 0.55 g of $CoCl_2\bullet 6H_2O$ in 4 mL of absolute ethanol and heat to boiling on a hot plate (use a fumehood if possible). To this solution, with stirring, add a hot solution of 0.92 g of Et_4NCl, also dissolved in absolute ethanol (you may have to filter this solution first). Boil the resultant mixture for 1 min., then cool until crystallisation is complete. Filter and wash with 2-3 mL ethanol. Dry

on filter paper for 15-20 min. until crystals are free-flowing. If you must store the crystals, put them in a dessicator as they are hygroscopic.

You can recover more crystals by allowing the filtrate to evaporate (in a dessicator).

2. *Preparation of Bis(tetraethylammonium) tetrachloromanganate(II)*
Repeat as for #1. Use 0.50 g of $MnCl_2 \bullet 4H_2O$.

3. *Preparation of Bis(tetraethylammonium) tetrachlorocuprate(II)*
Repeat as for #1. Use 0.42 g of $CuCl_2 \bullet 2H_2O$.

Final Report

You will need to include a proper experimental section with masses, yields, and colours of the four complexes you isolated as solids. For the solutions in Part I, include details such as colour, concentration, and molar absorptivity (ε). Be sure to attach your spectra (you can print all three of these on one set of axes) and to give a determination of Δ_O based on the λ_{max} of the spectrum of each species.

Include the following discussion points in your report:

(1) Clearly Δ_O is different for each copper compound. What correlation can be made between ligand type [ie. donor atom(s)] and Δ_o?

(2) Provide an explanation that accounts for the broadness of the absorption signals for each compound.

(3) Based on the complimentary colour of the above three complexes (*i.e.*, the colour that is absorbed), arrange these three metals into a spectrochemical series. (This is not strictly correct because Mn^{2+} and Co^{2+} are not d^1 or d^9 metals, but it's close enough for this course). Figure 11-1 in your text (Miessler and Tarr) may be helpful here.

(4) Using the colour of $CuCl_4^{2-}$, estimate a value of Δ_t. From this value, determine Δ_O for the hypothetical complex $CuCl_6^{4-}$. Arrange the three donor atoms (O, N, Cl^-) in a spectrochemical series.

Reference

1. A.T. Baker *J. Chem. Educ.* **1998**, *75*, 98.