EXPERIMENT 8

The Widely Varying Colors of *d*-Block Metal Complexes

This experiment is assigned on page 402 of the textbook.

FOR THE INSTRUCTOR

This experiment involves groups of three students: one is assigned to make complexes of the Ni^{2+} ion, one is assigned to make complexes of the Co^{2+} ion, and one is assigned the Cu^{2+} ion. If the course does not have a laboratory component, step IB can be done as a demonstration by the instructor, and steps IC–IF can be discussed by the class.

The following solutions are required; to make 100 mL of each solution use the amount of the solids indicated.

0.1 M $Ni(NO_3)_2$	2.91 g of the 6-hydrate
0.1M $CoCl_2$	2.38 g of the 6-hydrate
0.1M $CuSO_4$	2.50 g of the 6-hydrate
1.0M Na glycinate	4.0 g NaOH plus 7.5 g glycine
1.0 M $K_2C_2O_4$	18.4 g of the 1-hydrate. (Product with Cu^{2+} tends to crystallize out.)
1.0 M NH_3, buffered	5.3 g NH_4Cl in 100 mL 1M NH_3 solution. (Store in air-tight bottles.)
1.0 M Pyridine	0.0 mL of C_5H_5N
1.0 M EDTA	38.0 g of tetrasodium salt
1.0 M $H_2NCH_2CH_2NH_2$, buffered	6.7 mL anhydrous ethylenediamine in 100 mL 1M HCl)

Since the "answers" to Part I of this lab experiment are in the book, we prefer to minimize the grading aspects of this experiment.

Part II can be omitted, since it requires that the students or instructor have access to a spectrophotometer that covers the visible and near-infrared region.

FOR THE STUDENTS

Not only are the *d*-block hydrated metal ions of widely different colors, but the colors of the metal ions can be changed by replacing the coordinated water with other ligands. As you do this experiment you will be looking for regularities in the color changes induced by the ligands. But also enjoy the beautiful colors produced!

Part I. Preparation of Complexes and Their Ordering by Visual Inspection

A. Different students will be assigned different metal ions, and will prepare separate complexes of that ion with seven different ligands. Some students will be assigned the Ni^{2+} ion, some the Co^{2+} ion, and some will be assigned the Cu^{2+} ion.

B. Take a series of seven test tubes in a rack. To each test tube add 2 mL of an 0.1 M solution of your metal ion. In turn, add 2 mL of one of the following solutions to each of the test tubes: (1) H_2O (pure); (2) 1.0 M sodium glycinate $Na^+NH_2CH_2CO_2^-$ (Figure 5.5 p. 220 of text); (3) $K_2C_2O_4$ (saturated) (Fig. 5.5); (4) 1.0 M NH_3, buffered; (5) 1.0 M pyridine (Fig. 5.4); (6) 1.0 M sodium ethylenediaminetetraacetate, $(Na^+)_4[(^-O_2CCH_2)_2\,NCH_2CH_2N(CH_2CO_2^-)_2]$ or just EDTA for short (Fig. 5.5); and (7) 1.0 M buffered ethylenediamine, $H_2NCH_2CH_2NH_2$ (Fig. 5.5). Stopper each test tube and mix its contents. Note: The Co^{2+} complexes should be examined as soon as possible after they are prepared, since many of them undergo air oxidation.

C. Does the color of a transition metal complex depend on the ligand present?

D. Arrange your seven test tubes in "rainbow" order, such that the colors lead naturally from one test tube to the next. List the ligands in order, starting from the end that is closest to the color of the pure water test tube.

E. Is the ligand ordering for Ni^{2+} complexes reasonably consistent with the ordering of the ligands for complexes of the Co^{2+} ion, and of the Cu^{2+} ion? As a group, check the possibility that making slight rearrangements would make a more nearly metal-independent listing of ligands in order. Your final group list is a qualitative spectrochemical series of ligands.

F. Analyze the periodicity of your group list: can you note any grouping of nitrogen- and oxygen-donor ligands in this spectrochemical series?

Part II. Analysis of the Spectra and Contents of the Lab Report

Your qualitative spectrochemical series of ligands has uncertainties due to the limited ability of our eyes to discriminate similar colors. Hence, we can check our ordering by measuring the spectra of these complexes. The spectra should be measured in the visible and near-IR region on spectrophotometers available to you. The detailed procedure depends on the type of instrument, so will be provided by your instructor.

A. Attach all spectra, with arrows drawn to indicate any peaks. Tabulate the wavelengths of those peaks.

B. Convert your wavelength measurements to energy units of reciprocal centimeters using the equation:

Wavenumber in $cm^{-1} = 10^7$/wavelength in nanometers (Equation 7.5)

C. In the Cu^{2+} complexes, you will observe only one (possibly asymmetrical) $d \rightarrow d$ transition. The energy of this transition in reciprocal centimeters is the octahedral ligand field splitting, Δ_o. In the other octahedral complexes you will observe more than one $d \rightarrow d$ transition; the longest wavelength (lowest energy) absorbance in these complexes equals Δ_o. Record Δ_o for each of your complexes. Compare the Δ_o you obtain for your hydrated metal ion with the value tabulated in Table 7.4 on page 399 of your text. (You may also compare the spectrum of your hydrated metal ion with that shown in Figure 7.8 on page 398.)

D. The energy of Δ_o for an octahedral complex of a given metal ion can be approximately analyzed as due to a ligand factor f_{ligand} multiplying the Δ_o for the hydrated metal ion (Table 7.4 p. 399).

$\Delta_o = f_{ligand}$ times Δ_o for the hydrated ion.

The ligand factor for water, of course, should then be 1.000. Calculate the ligand factors for each of the six other ligands in your complexes.

E. List your ligands in increasing order of their ligand factors, indicating small and large differences between corresponding ligands with “<” and “<<”, respectively. Compare this spectrochemical series with the qualitative spectrochemical series you obtained in Part I.

F. Re-analyze the periodicity of your spectrochemical series: can you note any grouping of nitrogen- and oxygen-donor ligands in the spectrochemical series?