The Ligand Field Spectra of Copper(II) Complexes

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In introducing students to ligand field spectra and the spectrochemical series, we have previously used the well-known procedure for preparing the complexes [Cu(NH3)n(H2O)6-n]2+ in solution (1), where n = 0, 1, 2, 3, 4, 5. This procedure has the advantage of yielding similar simple complexes, but extreme care must be taken to guard against the precipitation of Cu(OH)2. Another problem is that the complexes, but extreme care must be taken to guard against the precipitation of Cu(OH)2. 7

This procedure has the advantage of yielding similar simple complexes, but extreme care must be taken to guard against the precipitation of Cu(OH)2. Another problem is that the procedure is not easily made quantitative. The important point that the absorptions are weak, in terms of molar absorptivity, is not directly reinforced. The observation of the "pentammine effect", where the complex with n = 5 has $\lambda_{\text{max}}$ at a higher value (i.e., lower energy) than the complex with n = 4, confuses students considerably and decreases the pedagogical value of the exercise.

An adaptation of the laboratory exercise could be successful if the following points were reinforced: (i) that spectra for d0 (or d1) species are relatively simple; (ii) that the absorptions are weak compared to those observed in ultra-violet spectra of organic compounds; (iii) that the absorptions peaks are very broad; and (iv) that the position of $\lambda_{\text{max}}$ is dependent on the nature of the ligand.

A practical exercise has been devised, which clearly illustrates the above points. In this exercise, pseudo-octahedral copper(II) complexes with O6 and N2O4 donor sets are prepared in solution. Note that the symbol NkOn, where m and n are integers, refers to the nature and number of donor atoms in the coordination sphere. A straightforward preparation yields a complex with an N2O4 donor set. Spectra in solution are measured for each of the complexes. From the spectra, $\lambda_{\text{max}}$ and $\epsilon$ values can be determined and compared. A spectrochemical series, albeit small, can be directly derived.

Experimental Procedure

Preparation of Diaquabis(ethylenediamine)copper(II) iodide: [Cu(en)2(H2O)2]I2

Copper(II) acetate monohydrate (1.9 g, 0.0095 mol) is mixed with water (5 mL), and ethylenediamine (IUPAC name: 1,2-diaminoethane) (2.0 mL, 1.8 g, 0.030 mol) is added dropwise with stirring. Caution: Use fume cupboard. A solution of potassium iodide (4.2 g, 0.025 mol) dissolved in a minimum volume of water is added. The reaction mixture is heated to 60 °C on a water bath. Any undissolved material is removed by vacuum filtration of the hot solution through a sintered filter crucible (porosity 3). The filtrate is cooled in an ice bath. (Fine violet crystals should precipitate; if the complex does not crystallize, ethanol is added.) The crude product is collected on a sintered filter crucible by vacuum filtration. To purify the compound, the crude material is recrystallized from a minimum volume of hot water. The product is collected on a sintered filter crucible and washed with cold ethanol. The complex is dried by continuing to draw air through the filter crucible.

Note that the complex is quite soluble in water. To obtain a reasonable yield, water volumes must be kept to a minimum.

Preparation of Solutions

All masses of solids are determined to the nearest 0.1 mg and solutions are prepared in 100-mL volumetric flasks, using appropriate techniques. Solutions prepared using the suggested masses of solids will have A (absorbance) at $\lambda_{\text{max}}$ between 0.4 and 0.7.

The first solution can be prepared by dissolving a known mass of copper(II) sulfate pentahydrate (approximately 1 g) in water. This solution should contain the hexaaqua copper(II) ion, a six-coordinate copper(II) complex with an O6 donor set.

The second solution is prepared by dissolving a known mass of copper(II) acetate monohydrate (ca. 0.15 g) and sodium dihydrogenethylenediaminetetraacetate (Na2H2EDTA, ca. 0.4 g) in water. This solution should contain the species [Cu(EDTA)]2–, a six-coordinate copper(II) complex with an N2O4 donor set.

The third solution is prepared by dissolving a known mass of diaqua bis(ethylenediamine) copper(II) iodide (ca. 0.5 g) in water. This six-coordinate copper(II) complex has an N2O4 donor set.

Spectra

Spectra are recorded for the range 400–900 nm using a Shimadzu UV2101PC spectrophotometer, calibrated against a water blank. The spectra can be plotted on one graph, to allow direct comparison of the positions of $\lambda_{\text{max}}$. The wavelength of $\lambda_{\text{max}}$ is converted to wavenumber to produce a

<table>
<thead>
<tr>
<th>Solution</th>
<th>Species</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\nu_{\text{max}}$ (cm−1)</th>
<th>$\epsilon$ (cm3·mol−1·L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Cu(H2O)6]2+</td>
<td>810</td>
<td>12300</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>[Cu(EDTA)]2–</td>
<td>735</td>
<td>13600</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>[Cu(en)2(H2O)2]2+</td>
<td>545</td>
<td>18300</td>
<td>64</td>
</tr>
</tbody>
</table>

Figure 1. Spectra (absorbance vs. wavelength) for the species [Cu(H2O)6]2+ (– – – – ), [Cu(EDTA)]2– (– – – ), and [Cu(en)2(H2O)2]2+ (– – – – ).
parameter that is directly proportional to energy of the electronic transition. Using the Beer–Lambert law, the concentration of the copper(II) species in each solution and the value of at λ_max, the value of ε (molar absorptivity) can be determined. Note that for the second solution, Na_2H_2EDTA is in excess, so that the concentration of the complex can be calculated from the mass of copper(II) acetate monohydrate.

Results and Discussion

The results for the experiment are illustrated in Figure 1 and summarized in Table 1.

Copper(II) complexes have been chosen because Cu^{2+} is a d^9 ion (equivalent to d^1 in spectral terms, taking account of the positive-hole formalism); it is spectrally simple, with one broad absorption band observed. The absorption band for the third solution (containing [Cu(en)_2(H_2O)_2]^{2+}) is approximately 7000 cm^{-1} wide at half-height. Note that spectra which arise from d–d electronic transitions are very weak (low molar absorptivities) because the transitions are quantum-mechanically forbidden (Laporte selection rule).

For a particular metal ion, the magnitude of the ligand field splitting parameter for octahedral complexes, Δ_o, depends on the nature of the ligand. It is to be stressed that these complexes can only be considered as approximately octahedral because of the Jahn–Teller distortion expected for a d^9 ion. This distortion has been clearly demonstrated for [Cu(en)_2X_2] complexes in the solid state (3). From many spectral studies, it has been found that it is possible to rank the order of field strength for ligands (which is found to be independent of the metal ion). This ranking list is known as the "spectrochemical series" and a shortened version, adapted from (4), is given below (donor atoms in multatomic ions or molecules are shown in bold):

I^- < Br^- < Cl^- < NO_3^- < F^- < diethylthiocarbamate (S) < OH^- < C_6H_4O_2^- < H_2O < SCN^- < NH_3 = pyridine (N) < ethylenediamine (N) < NO_2^- = 2,2'-bipyridine (N) = CN^- 

There is some correlation of donor atom with position on the spectrochemical series, in that N-donors consistently rank above O-donors. The fact that N-donor ligands usually produce stronger ligand fields than O-donor ligands is illustrated in Table 2, where values of Δ_o for various Ni(II) complexes are given, selected from (5).

This information supports the observation made here, that for a series of complexes of a particular metal ion, the value of Δ_o should increase from an O_6 donor set to N_2O_4 to N_4O_2 to N_6, if it were possible to prepare a series of complexes with ligands chosen to provide the appropriate donor sets. The copper(II) complexes prepared in this exercise, either in the solid state or in solution, are examples of complexes with the first three donor sets (O_6, N_2O_4, and N_4O_2). Unfortunately, it is extremely difficult to prepare Cu(II) complexes with an N_6 donor set (6).

Acknowledgments

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Literature Cited

5. Ibid; p 508.