

# Spectroscopic study of $\text{Cu(II)}$ complexes: crystal field theory essay sample

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The color of coordination compounds of the transition elements is one of their characteristic properties. These colors are due to the absorption and subsequent emission of light in the visible part of the spectrum. Light in this region of the spectrum caused promotion of d-electrons from a lower to a higher energy level. The spectra which result are generally referred to as Electronic Spectra. Note that electronic transitions may also be effected by ultraviolet light. Because of the size of the quanta involved, electronic transitions in molecules are always accompanied by vibrational and rotational changes, and hence a band spectrum is observed. In general, the bands which arise are much broader than bands in an infrared spectrum and are little used for identification purposes.

The crystal field theory of bonding in transition metal complexes has helped appreciably to rationalize many of the physical properties of such complexes. Much of the data required for crystal field theory calculation is obtained from a study of the absorption spectra of transition metal complexes.

Regularly six-coordination is most readily pictured by placing the ligands at the plus and minus ends of the three coordinate axes. An electron in the  $d_{x^2 - y^2}$  and  $d_{z^2}$  orbitals is therefore most effected by the field of the ligands and is raised in energy relative to an electron in the  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals. The combined energy level diagram is therefore composed of two upper orbitals, of equal energy, and three lower orbitals, which are also degenerate (Figure 4. 1). The energy zero is conveniently taken as the weighted mean of the energies of these two sets of orbitals; the lower trio are thus stabilized by  $-\frac{2}{5} \Delta E$  while the upper pair are destabilized by

$\frac{3}{5}\Delta E$ , where  $\Delta E$  is the total energy separation. It is termed the crystal field splitting energy. The  $e_g$  and  $t_{2g}$  symbols are symmetry labels arising from Group theory and are now the most commonly used symbols.

Figure 4. 1 Energy level diagram for the d orbital in an octahedral field. The energy gap  $\Delta E$  is often labeled  $10 Dq$  or  $\Delta_{oct}$

Figure 4. 2 Representation of the electronic spectra of Ti(III) complexes. The full line (—) is a

$3+$

$-1$

representation of the spectrum of  $Ti(H_2O)_6$  with a maximum at  $20,000\text{ cm}^{-1}$ .

The Broken line (---) represents the spectrum of  $TiCl_6^{3-}$ , with a maximum at

$13,000\text{ cm}^{-1}$  The size of  $\Delta E$  is most readily measured spectrochemically by

observing the energy of the electronic transitions between the  $t_{2g}$  and  $e_g$

orbitals. The energy usually lies in the visible or near ultra-violet region of

the spectrum and it is such d-d transitions, which are responsible for

the colors of most transition metal compounds. The magnitude of  $\Delta E$

depends on the ligand and on the nature of the transition metal ion.

Consider the simplest possible case, namely a complex in which there is one

electron in a d level, as in the ion  $[Ti(H_2O)_6]^{3+}$ . The transition from the  $t_{2g}$

to  $e_g$  level of the single electron, give rise to single absorption band in the

visible region (Figure 4. 2). The spectrum appears as a single absorption

band  $20,000\text{ cm}^{-1}$ . The water ligands have split the degeneracy of the free

gaseous ion in two: the  $t_{2g}$  and  $e_g$  level, as described above, and in the

ground state the electron occupies the  $t_{2g}$  level. Irradiation of the complex with light of an appropriate frequency results in excitation of the electron in the lower  $t_{2g}$  level to the higher  $e_g$  level. Knowing that light of frequency  $20,000\text{ cm}^{-1}$  is required the crystal field splitting energy for a  $d^1$  system in an octahedral field of water ligand can be calculated. However, this experiment, we will observe this phenomenon by using copper(II) complexes, due to their vivid colors.

#### Procedures

4. 1 Preparation of Cis-diaquabis(glycinato)copper(II)monohydrate Dissolve about 1. 0 g of copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in 8. 5 ml of 1 M HCl and add 700 mg of glycine ( $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ ). Cautiously warm the mixture in the water bath or on hot plate for 30 minutes, and during this period, slowly add solid  $\text{NaHCO}_3$  to the warm solution until a crystalline precipitate is completely formed (Do not overheat). Filter the solid by suction (filtrate discard at waste container No. 4). Allow the crystal to dry in the oven at  $100\text{ }^\circ\text{C}$ . Record the product. Divided the product for the solution 8 (4. 3), and for IR, NMR studies (4. 4).

#### 4. 2 Preparation of Bis(acetylacetonato)copper(II).

Dissolve 0. 31 g of acetylacetonone ( $\text{CH}_3\text{COCH}_2\text{COCH}_3$ ) in 10 ml of 0. 25 M NaOH. Add a solution of 0. 37 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 15 ml of  $\text{H}_2\text{O}$ . The sparingly insoluble Bis(acetylacetonato)copper(II) is immediately formed as a crystalline precipitate. Filter the product by suction (filtrate discard at waste container No. 5). Allow the crystal to dry at room temperature. Record the product.

\*\*Divided the product for the solution 9 (4. 3), and for IR, NMR studies (4. 4).

#### 4. 3 Absorbance Measurement of Complex Solutions

The following stock solutions will be prepared:

0. 01 M  $\text{Cu}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$  using ultrasonic apparatus (Use for preparation of solution 1-7)

0. 10 M  $\text{NH}_3$  (Use for preparation of solution 2-5)

0. 10 M ethylenediamine (Use for preparation of solution 6 and 7) Then, the Copper(II) complexes solution will be prepared with total volume about 10-15 ml in the different ratios as shown below. For solution 2-5, the solutions should immediately homogeneous mix and then measure the absorbance as soon as possible.

Measure the absorbance of these solutions in the range of 500-850 nm.

Compare the  $\lambda_{\text{max}}$  values obtained when different ligands are used and suggest the spectrochemical series. Solid products discard at waste container No. 8. Solutions of products discard at waste container No. 4. Filter papers discard at waste container No. 7.

#### 4. 4 IR and NMR spectra of copper complexes

IR spectra of free glycine, acetylacetonate and copper complexes (4. 1 and 4. 2) are recorded and assigned in mid IR.

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$^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$ ,  $^{13}\text{C}$  DEPT-135 NMR spectra of free glycine, acetylacetonate and copper complexes are examined and assigned.

Discuss and conclude the structure of complexes using the data from spectroscopic techniques.

#### Prelaboratory Problems

1. Determine the position of maximum absorption and hence calculate the crystal field splitting energy for a d9 system in an octahedral environment of water ligands.
2. What effect does this have on the absorption band ?
3. Predict the position of acetylacetonato ligand in the spectrochemical series, as compared to water ligand. Suggest your reasons.

#### Postlaboratory Problems

1. If  $[\text{Ti}(\text{H}_2\text{O})_4]^{3+}$  can exist, which frequency do you expect in the absorption band of this tetrahedral complex? Moreover, how about the spectrochemical series, the same or different as compare to octahedral environment?
2. Write the structure of Cis-diaquabis(glycinato)copper(II) monohydrate and Bis(acetylacetonato)copper(II) complexes.
3. Does the mole ratio (M: L) effect the frequency of the band ? Why?

#### References

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