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# Measurement of the Magnetic Exchange in a Chlorobridged Cu(II) Dimer

*Advanced inorganic experiment employing the  
Faraday magnetic susceptibility system*

Magnetic exchange involves the coupling of electron spins through space (direct exchange) or through bridging groups (superexchange) (1). The spins may couple in a parallel or antiparallel fashion as shown in Figure 1. In the former arrangement the material is said to be ferromagnetic while in the latter arrangement the material is said to be antiferromagnetic. Measurement of the degree of the exchange interaction,  $2J$ , in transition metal dimers and, to a lesser extent, trimers and tetramers have become active areas of research in recent years (2-4). The value of  $2J$  in copper(II) dimers has been correlated with the metal-ligand-metal angle (3) as well as with specific delocalization mechanisms (4). Although a variable temperature magnetic susceptibility measurement is not the only means of measuring the magnitude and sign of the exchange interaction, the method is the most accurate and the one most often employed, and can be used to obtain related magnetic variables (e.g.,  $\bar{g}$  and  $TIP$ , *vide infra*). However, there is no description of an experiment designed for such a determination by students although the experiment may be employed easily and profitably. This paper is intended to supply such a description.

Copper(II) dimers provide theoretically simple models (5) and are pedagogically appealing since the exchange can be related to the two arrangements of the unpaired electron on each copper(II) nucleus shown in Figure 1. Measurements have been made on systems having both types of arrangements; however, the parallel configuration of spins is relatively rare in copper(II) dimers (6-9). Copper(II) dimers containing bridging groups like the alkanoates or Schiff bases provide a rather constant and similar type of orbital overlap between the copper(II) nuclei which is not influenced to any great extent by substituents with the result that within a particular series the magnitudes of the spin exchanges are very similar (2). Consequently, these types of copper(II) dimers would not be very appealing experimentally to the students. A series of copper(II) dimers that has been used with great success in both an undergraduate honors course and a graduate laboratory experiment are the halogen-bridged, copper(II) guaninium dimers having the general formula:  $(\text{Cu}(\text{guaninium})\text{X}_3)_2 \cdot n\text{H}_2\text{O}$ , where  $\text{X} = \text{Cl}$ ,  $n = 2$  and 0;  $\text{X} = \text{Br}$ ,  $n = 0$ ;  $\text{X} = \text{F}$ ,  $n = 2$ ; and guaninium is the protonated form of guanine, Figure 2. These complexes are prepared in virtually pure form and in a simple fashion (10, 11) and have been characterized spectroscopically (10-12). The hydrated, chlorobridged complex, shown in Figure 3 (13), will be the dimeric compound used in the magnetic exchange determination.

The measurement of  $2J$  is interesting and informative to the student in several ways. It is an introduction to a field of research which is presently receiving great attention. It allows

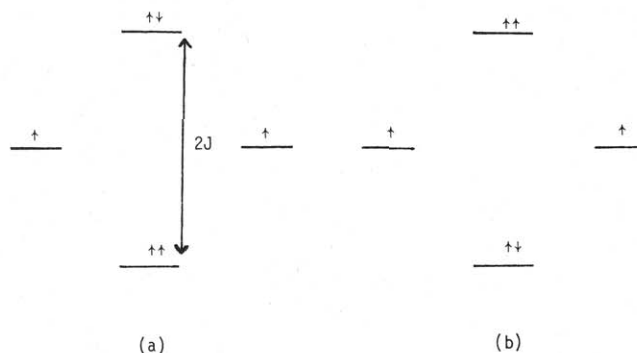


Figure 1. Possible spin coupling of two electronic spins located at two copper(II) ions in a dimer. (a) triplet ground state,  $2J$  positive. (b) singlet ground state,  $2J$  negative.

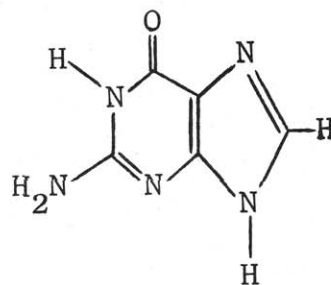


Figure 2. Keto form of neutral guanine.

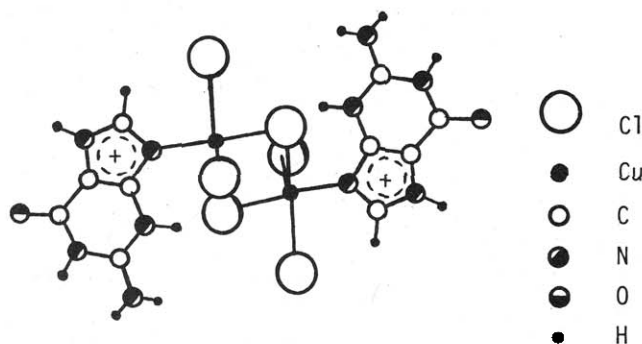


Figure 3. Schematic of the structure of the trichloroguaniniumcopper(II) monohydrate dimer (13).

the determination of the nature of the dimeric ground state as well as the measurement of the strength of the interaction between the metal centers—the primary objectives of the experiment. The student also has a means of checking his preparative techniques since monomeric impurities will yield lower values of  $2J$ . In addition, the student is intrigued by the thought of working with a complex that contains a nucleic acid residue. Since guanine is a major constituent of DNA, and since copper(II) has been shown to have a pronounced effect on the reversible unwinding of DNA (14–17), experimenting with a coordination compound of copper(II) containing a nucleic acid base invariably generates queries as to the role copper(II) plays in the transmission of genetic information. And, lastly, this complex contains a guanine ligand having a positive charge (13)—a relatively rare phenomenon in coordination chemistry.

## Experimental

### Synthesis

The stable, trichloroguaniniumcopper(II) monohydrate dimer is synthesized according to methods previously outlined (10–12). A fourfold excess of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.36 g) is dissolved in aqueous HCl (2 M) with the formation of a light yellow solution. To this, guanine is added (0.3 g) and the mixture vigorously stirred with heat until all the guanine dissolves. Concentrated HCl is added until the solution changes to a dark green color and then is evaporated down to one-third the volume (20 ml). Upon cooling, yellow brown crystals appear which can be easily filtered (m.p. 240–50° dec.).

### Variable Temperature Bulk Magnetic Susceptibility Measurements

The magnetic susceptibility measurements can be obtained in the range 77°–300°K (18) using a Faraday balance setup and  $\text{HgCo}(\text{SCN})_4$  as the standard (19). The most accurate values of  $2J$  are obtained, however, from measurements made between 80° and 120°K. The Faraday setup used in our laboratory is essentially that described by Busch et al (20) except that the BASF catalyst tower, drying tower, cryostat elevator, liquid nitrogen leveling device, and recorders are not utilized. Our cryostat (Air Products, PA) is permanently mounted on a horizontal arm and the electromagnet (Alpha Scientific, 4 in. water-cooled, adjustable-gap) is placed on a trolley and track. This placement allows in-field and out-of-field measurements to be performed in an easy fashion at magnetic fields of about 6000 G. Measurements made out-of-field are accompanied by shut-down of magnet power to assure zero magnetic field. The sample support used is a 50–50 quartz nylon fiber as described by Nelson and Villa (21). Sample sizes range from 10–30 mg and are introduced into specially made (Scanlon Co., CA), high purity, quartz buckets (8 × 3 mm OD; 2 mm ID). The sample support and loaded (or unloaded) bucket are introduced as one unit and suspended from a remote controlled, Cahn G-2 Electrobalance that is covered by a 3-l bell jar employing a rubber, O-ring gasket as a vacuum seal. Helium gas at 1 atm pressure is used as the heat exchanger between sample and cryostat.

### Visible Absorption Measurements

The visible/near-infrared spectrum is obtained as Nujol mulls on Watman #1 filter paper.

### Theory of Exchanged-Coupled Copper(II) Dimers

Van Vleck (22), using a simple quantum mechanical treatment, generated eqn. (1) which could be applied to various magnetic models with different degrees of approximation. This equation sums over a Boltzman distribution

$$\chi = N \sum_{n,j,m} \{[(W_{n,j,m}^{(1)}/kT) - 2W_{n,j,m}^{(2)}] \exp(-W_{n,j,m}^{(0)}/kT)\} / \sum_{n,j,m} \exp(-W_{n,j,m}^{(0)}/kT) \quad (1)$$

of particles in the energy levels populated. In eqn. (1),  $\chi$  is the magnetic susceptibility and  $T$  is the temperature; the subscripts  $n$ ,  $j$ , and  $m$  refer to the principal, rotational, and magnetic quantum numbers, respectively. The superscripts 0, 1, and 2 refer to zeroth, first, and second-order corrections to the energy,  $W$ , respectively;  $N$  and  $k$  refer to Avogadro's number and Boltzman's constant, respectively.

When the magnetic interaction is essentially between two copper(II) ions within a dimer, Hamiltonian (2) is a good de-

scription of the system where  $2J$  is the energy separation between the triplet ( $S = 1$ ) and singlet

$$\hat{H} = -2JS_1 \cdot S_2 \quad (2)$$

( $S = 0$ ) states. Summation over all the magnetic spin states in eqn. (1) yields:

$$\chi = N\bar{g}^2\beta^2[1 + (1/3) \exp(-2J/kT)]^{-1}/3kT + N\alpha \quad (3)$$

where  $\bar{g}$  is the average  $g$ -value of the electron in the complex,  $\beta$  is the Bohr magneton, and  $N\alpha$  is a second-order correction which is usually independent of temperature called the temperature independent paramagnetism (TIP). The magnitude of the  $g$ -factor depends on the ligand field geometry surrounding the copper(II) centers, and will be larger than 2.0023 (the free electron  $g$ -value) because of second-order, orbital angular momentum and spin-orbit coupling effects. A negative value of  $2J$  indicates a singlet ground state (Fig. 1b).

Rearranging and simplifying (3) yields a more useful expression in  $2J$ :

$$-2J = 2.303kT[0.4771 + \log(\mu^2/\bar{g}^2 - 1)] \quad (4)$$

where  $\mu^2 = \mu_{\text{eff}}^2 = 3k\chi_{mc}T/N\beta^2$ , and  $\chi_{mc} = \chi_m - \text{DIAC} - \text{TIP}$  (see eqn. 10). To calculate a value of  $2J$ , therefore, requires a knowledge of  $\bar{g}$  and  $\chi_{mc}$  at each temperature measured (*vide infra*).

### Calculation of $\bar{g}$

$g$ -Values can be assumed to remain constant over the temperature range considered and are obtained easily from EPR measurements. An average  $g$ -value of 2.12 has been determined previously (10) and can be used in lieu of the EPR experiment. By an alternate route, an average  $g$ -value ( $\bar{g}$ ) can be approximated from the visible absorption spectrum by employing the following expressions (23):

$$g_z = 2.0023 \quad (5)$$

$$g_{xy} = 2.0023 - 6\lambda/\Delta E \quad (6)$$

$$\bar{g} = 1/3(g_z + 2g_{xy}) \quad (7)$$

where  $\lambda$  is the spin-orbit coupling constant ( $-823 \text{ cm}^{-1}$  for the free ion), and  $\Delta E$  is the energy of the  $d_{xz,yz} \rightarrow d_{z^2}$  transition which appears at  $\approx 11400 \text{ cm}^{-1}$ . One additional band occurs at  $\approx 8000 \text{ cm}^{-1}$ , and its energy must not be used in the calculation. The  $g$ -value calculated from eqns. (5–7) is considerably larger than that obtained from EPR measurements, because second-order terms in  $\lambda$ , as well as spin-orbit reduction factors, have been ignored.

### Calculation of $\chi$

The steps required in the calculation of the molar susceptibility using the Faraday method have been described elsewhere (20, 24) but are briefly outlined here for convenience. The gram susceptibility,  $\chi_g$ , is obtained using eqn. (8).

$$\chi_g = \chi_r[W_r(\Delta W_s - B)]/[W_s(\Delta W_r - B)] \quad (8)$$

The subscripts  $s$  and  $r$  refer to sample and reference, respectively.  $W$  is the actual weight employed in the measurement,  $\Delta W$  the change in weight (i.e., weight in-the-field minus weight out-of-the-field),  $B$  the diamagnetic correction of the bucket used to introduce sample and reference, and  $\chi_r$  the gram susceptibility of the reference (19) at a specified temperature.

The molar susceptibility is obtained by multiplying (8) by the molecular weight of the sample ( $MW = 680$ ),

$$\chi_m = \chi_s \cdot MW \quad (9)$$

and the corrected molar susceptibility,  $\chi_{mc}$ , which is used in the calculation of  $2J$  (eqn. 4), is found by subtracting the diamagnetic correction of the molecule (metal plus ligand), DIAC, and TIP from  $\chi_m$ ,

$$\chi_{mc} = \chi_m - \text{DIAC} - \text{TIP} \quad (10)$$

The values for DIAC (25) and TIP are  $-400 \times 10^{-6}$  cgs units and  $120 \times 10^{-6}$  cgs units, respectively, per dimer.

**Magnetic and Electronic Data for the Trichloroguaniniumcopper(II) Monohydrate Dimer**

Dimer/2	$-2J^a$ (cm <sup>-1</sup> )	$\bar{g}$	$\mu_{\text{eff}}^b$ (BM)	$\Delta E$ (cm <sup>-1</sup> )	$\chi_{\text{mc}} \times 10^6$ <sup>f</sup> (cgs units)	$T$ (°K)
Cu(G <sup>+</sup> )Cl <sub>3</sub> · H <sub>2</sub> O	85	2.12 <sup>b</sup>	1.80	11400	1420	296
		2.18 <sup>c</sup>			1540	263
		2.29 <sup>d</sup>			1760	198
					2280	141
					2590	111
					2770	87

<sup>a</sup> Calculated using magnetic susceptibility best-fit  $\bar{g}$ -value.

<sup>b</sup> Determined from magnetic susceptibility best-fit.

<sup>c</sup> Determined from EPR.

<sup>d</sup> Determined from visible/near-infrared absorption data.

<sup>e</sup> Room temperature value (from last column).

<sup>f</sup> Per copper(II) ion.

### Calculation of $2J$ and $\bar{g}$ Simultaneously

An iterative procedure using eqn. (4) can be employed to determine both  $2J$  and  $\bar{g}$  for a set of variable temperature susceptibility data. This method involves a computer program DIMFIT which assumes a set of  $2J$  and  $\bar{g}$  values, calculates  $\chi$  and  $T$  and gets the deviation from the experimental  $\chi$ . The iterations continue within reasonable values of  $2J$  and  $\bar{g}$  until an absolute minimum deviation in  $\chi$  is obtained. A copy of the listing of this program with sample output is available upon request. Usually the  $\bar{g}$ -value obtained agrees to within 5% of the EPR values.

### Results

The corrected molar susceptibilities as a function of temperature, room temperature magnetic moment, average exchange integral  $2J$ , and visible absorption maximum for a typical run on the trichloroguaniniumcopper(II) monohydrate dimer is given in the Table (original data found elsewhere (10–12)). The  $2J$  value is negative indicating a singlet ground state ( $\uparrow\downarrow$ ) with a triplet excited state ( $\uparrow\uparrow$ ) 85 cm<sup>-1</sup> above it.

### Discussion

The time required for the experiment depends on the student. The experimental part of the work should not take more than two 3-hr laboratory periods. The time can be most effectively utilized if the first laboratory period is devoted to the sample preparation and electronic absorption measurement, and the second is reserved for variable temperature magnetic susceptibility measurements. The time between successive susceptibility measurements (15 min generally) can be utilized profitably if sample weight changes ( $\Delta W_s$ ) are converted to  $\chi_{\text{mc}}$  values (eqns. 8–10). These calculations are not tedious and

will be required ultimately for the computation of  $2J$  (eqn. 4). One laboratory period is sufficient time to allow six independent  $\Delta W_s$  readings to be performed between 77° and 300°K and includes the time required for the initial calibration of the instrument and the determination of  $\Delta W_s$  (eqn. 8). Students can expect to observe a maximum (Néel point) in the value of the magnetic susceptibility if measurements are made between 80° and 120°K.

Individual reports containing raw data, an average value of  $2J$ , a value of  $\Delta E$ , a discussion, and a small amount of the sample may be submitted. Graphs of the corrected molar susceptibility, inverse corrected molar susceptibility, and magnetic moment (per copper(II) ion) versus temperature can be drawn at the instructor's discretion.

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