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Magnetic Properties of Tetraaquo-bis(μ-hippurato-*O*)-bis(hippurato-*O*)dicopper(II) Tetrahydrate

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In recent years there has been much interest in the correlation between the structural features and the magnetic properties of bridged copper(II) dimers. Several groups have postulated such correlations,[1] both qualitative and quantitative, for the cases where the geometry around the copper atom is tetragonal pyramidal or square planar and the bridging atom (frequently oxygen) is in the basal (*xy*) plane. In these cases the orbitals containing the unpaired spin (which lie in the *xy* plane) overlap well with the bridging orbitals. The concepts which have been used successfully in these cases, however, are not applicable in the case of the parallel-planar copper(II) dimers,[2] in which the bridging atom occupies an in-plane coordination site on one copper(II) ion and an apical site of the other copper(II) ion, or in the case of the paired trigonal-bipyramidal systems. In both of these latter situations the molecules can be envisaged as pyramids or bipyramids which share an equatorial-to-apical edge.[3] For these geometries, the overlap is very different; in the extreme case for which the Cu–L–Cu angle is 90°, the s and p orbitals on the bridging atom are orthogonal to the orbital on one copper which contains the unpaired spin. Hence, for such systems the magnitude of the singlet–triplet splitting, 2*J*, should be much smaller than in the previous examples, and this has been demonstrated for some 2:1 pyridine-*N*-oxide–copper(II) dimers. In both bis[dinitratobis(pyridine-*N*-oxide)copper(II)], $[Cu(pyO)_2(NO_3)_2]_2$,[4] and bis[dinitratobis(4-methoxypyridine-*N*-oxide)copper(II)], $[Cu(4\text{-}MeOpyO)_2(NO_3)_2]_2$,[5] the bridging oxygen atoms are in apical positions and the 2*J* values measured are +10 cm^{-1} [6] and −2 cm^{-1},[7] respectively.

The compound tetraaquo-bis(μ-hippurato-*O*)-bis(hippurato-*O*)dicopper tetrahydrate, $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2{\cdot}4H_2O$,[8] has distorted [4 + 1] tetragonal-pyramidal geometry and is bridged through two carboxyl oxygen atoms of the hippurate ions. Each bridging oxygen atom simultaneously occupies an equatorial position on one copper atom and an apical position on the other copper atom in the dimer; the Cu–O–Cu angle is 101.0°. It appeared, therefore, that the magnitude of 2*J* for this compound should also be small. To test this hypothesis and to gain further understanding of the magnetic properties of compounds of this structural type, we have obtained magnetic susceptibility data in the range 1.7–121° for this complex and have determined the value of the singlet–triplet splitting. The results of these studies are reported herein.

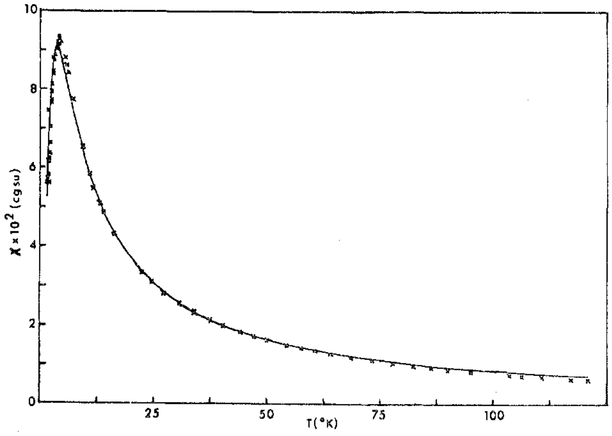

Figure 1. Plot of the magnetic susceptibility of $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2{\cdot}4H_2O$ per dimer as a function of temperature. The solid line represents the values calculated from the magnetization expression with $g = 2.13$, $2J = -4.3$ cm^{-1}, and $\gamma = -1.9$.

Experimental Section

Preparation. The complex $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2{\cdot}4H_2O$ was prepared by the method of Brown et al.[9] The light blue crystals obtained gave satisfactory analyses.

Magnetic Measurements. Magnetic susceptibility measurements were made on a powdered sample of $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2{\cdot}4H_2O$ using a Foner-type vibrating-sample magnetometer[10] operating at 10 kG as described elsewhere.[11] Mercury tetrathiocyanatocobaltate(II)[12] was used as a susceptibility standard. Measurements were made in the temperature range 1.7–121°K. The temperatures were measured with a calibrated Ga–As diode. Above 4.2°K and below 10,000 G the diode is independent (<0.01°K) of the field strength. Below 4.2°K the diode becomes field dependent, but recent careful measurements[13] on $[Cu(2,2'\text{-}bpy)_2(tu)](ClO_4)_2$ indicate that the error is not excessive since the data for this magnetically dilute system obey the Curie–Weiss law to 1.6°K with $\Theta = -0.020$°K. Susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants[14] and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60 × 10^{-6} cgsu/Cu atom).

Results and Discussion

The temperature variation of the magnetic susceptibility of $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2{\cdot}4H_2O$ is plotted in Figure 1. A maximum in this plot is observed at approximately 4°K, and the data are approximated by the Bleaney–Bowers equation[15]

$$\chi_m = \frac{Ng^2\beta^2}{3k(T-\Theta)}[1 + {}^1/_3 \exp(-2J/kT)]^{-1} \qquad (1)$$

The best least-squares fit of the data to this equation with $\Theta = 0.0$° gives a singlet–triplet splitting, 2*J*, of −4.3 cm^{-1} with $g = 1.97$; the mean fractional deviation (MFD), defined as $\sum[(|\chi_{obsd} - \chi_{calcd}|)/\chi_{obsd}]/NO$, where NO is the number of observations (68 in the present case), of a data point from the theoretical curve is 0.074. The inclusion of the interdimer interaction parameter θ improves the fit considerably, yielding a 2*J* value of −3.2 cm^{-1} with $g = 2.14$ and $\Theta = -2.2$° and lowering the MFD to 0.043.

However, the small value of 2*J* obtained indicates that eq 1 may not be appropriate since in the Bleaney–Bowers equation the approximation is made that $2J >> g\beta H$; for $H = 10$ kG, $g\beta H = 1.0$ cm^{-1}. For cases where 2*J* is of the same order of magnitude as $g\beta H$ it is necessary to use the magnetization expression[16]

$$M = \frac{Ng\beta \sinh (g\beta H/kT)}{\exp(-2J/kT) + 2 \cosh (g\beta H/kT) + 1} \qquad (2)$$

A best least-squares fit of the data to this equation gives $g = 1.98$ and $2J = -4.38$ cm^{-1}, MFD = 0.067. At this point, an attempt was made to improve the agreement by taking into account the weak-exchange interaction between pairs in the molecular field approximation using the method of Friedberg and coworkers.[16] By setting $H = H_0 + \gamma M$, where H_0 is the external field and H is the effective field, eq 2 becomes a self-consistent equation that may be solved by repeated iteration. A best least-squares fit to this equation gives a $2J$ value of -4.3 cm^{-1} with $g = 2.13$ and $\gamma = -1.9$. This g value is more reasonable for copper(II) than the value of 1.98 obtained when only the external field is considered and is in good agreement with the average value of 2.17 obtained from EPR studies.[17] By using the equation[16,18]

$$J' = \gamma N g^2 \beta^2 k / 2Z$$

where Z is the number of nearest neighboring dimers (in this case there are four) a value of -0.20 cm^{-1} is obtained for the lattice interaction parameter J'. Small values of J' are common for copper(II) dimers.[19] The theoretical curve for this model, where $\chi_m = M/H_0$, is indicated by the solid line in Figure 1; the MFD for this fit is 0.041.

The results of this investigation, therefore, support the hypothesis that the value of the singlet–triplet splitting, $2J$, is small for dimeric systems in which the bridging atom occupies an apical site on the metal and demonstrate the necessity of using the magnetization expression for cases where $2J$ is of the same order of magnitude as $g\beta H$.

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Registry No. $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2 \cdot 4H_2O$, 40215-14-3.

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Study of the Ring Conformations in Tris(ethylenediamine)metal Complexes Using Solid-State Vibrational Spectroscopy

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One of the most interesting features of chelate–metal complexes is the possibility of conformational isomerism for the five-membered ring systems found in such compounds. The relatively simple tris(ethylenediamine) complexes, for example, have four possible conformers, and because of the chiral metal center each of these four has an enantiomeric partner. There are then eight allowed isomers: $\Lambda\delta\delta\delta$, $\Lambda\delta\delta\lambda$, $\Lambda\delta\lambda\lambda$, $\Lambda\lambda\lambda\lambda$, $\Delta\lambda\lambda\lambda$, $\Delta\lambda\lambda\delta$, $\Delta\lambda\delta\delta$, $\Delta\delta\delta\delta$.[2] Absolute configuration about the metal has been designated Λ or Δ where the view down the threefold axis of the complex forms a left-handed or right-handed propeller, respectively. In the Λ configuration, the δ ring conformation is achieved when the carbon–carbon bond is nearly parallel to the threefold axis and the λ ring conformation is assigned where this bond forms an obtuse angle with the C_3 axis. Due to identical conformational stabilities of their mirror image set, the following discussion will be limited to only the first set of four conformers in the above list.

Corey and Bailar[3a] first calculated the relative energies of the $\Lambda\delta\delta\delta$ and $\Lambda\lambda\lambda\lambda$ conformations based on a comparison of the nonbonded interactions in the systems and predicted the $\Lambda\delta\delta\delta$ form to be 1.8 kcal mol^{-1} lower in energy. A more complete study which included entropy effects by Gollogy, Hawkins, and Beattie[3b] suggested that $\Lambda\delta\delta\lambda$ would be nearly equal in stability with the $\Lambda\delta\delta\delta$ conformation. In agreement with these theoretical arguments, the large majority of X-ray structure determinations on tris(ethylenediamine)metal complexes have revealed $\Lambda\delta\delta\delta$ while only a few, as indicated in Table I, have shown $\Lambda\lambda\lambda\lambda$ or one of the mixed conformer ring systems. Thus far, the structural differences in these isomers have been detected only by arduous experiments requiring complete X-ray techniques. In this work we have attempted systematically to identify the individual conformer ring systems for tris(ethylenediamine) complexes using the solid-state vibrational spectroscopy of compounds whose ring conformations have been determined by X-ray methods.

Experimental Section

Preparation of Compounds. Several of the compounds used in this study were prepared following standard synthetic procedures. Among these are $[Co(en)_3]Cl_3 \cdot 3H_2O$,[15a] $[Cr(en)_3]Cl_3 \cdot 3.5H_2O$,[15b] and $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$.[15c] Synthesis of the compounds $[Cr(en)_3][Co(CN)_6] \cdot xH_2O$,[16] $[Co(en)_3][Cr(CN)_5NO] \cdot 2H_2O$,[13] $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$,[17] $[Ni(en)_3][(C_6H_5)_4B]_2$,[18] and $[Ni(en)_3](C_2H_3O_2)_2 \cdot 2H_2O$[19] followed recent literature references and resulted in good yields. The infrared spectra from 4000 to 600 cm^{-1} were obtained for each of these compounds and were in good agreement with literature values. Other methods of characterization for some of the compounds included conductivity measurement, elemental and hydrate analysis, and X-ray crystallographic determination.

Spectroscopic Studies. All infrared spectra were obtained as Nujol mulls on NaCl plates using a Beckman IR-10 or a Perkin-Elmer 180 spectrophotometer. Duplicate and triplicate spectra were taken to ensure reproducibility. We were able to achieve greater resolution on the Perkin-Elmer instrument as illustrated in Figure 1 where the same sample has yielded spectrum 1c on the IR-10 and spectrum 1d on the Model 180. Hence, all other spectra shown in Figure 1 and those in Figure 2 were obtained on the Perkin-Elmer 180.

Raman wave number shifts were recorded on a Cary 82 laser Raman spectrophotometer using the 5145-Å exciting line of an argon ion laser. Thermal decomposition of the highly colored solids due