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Magnetic Properties of Binuclear Copper(II) Complexes with One Hydroxo Bridge

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There has been continuing interest in the magnetic exchange properties of dihydroxo-bridged copper(II) complexes [1–3]. For some six complexes, a linear relationship has been noted between the bridge angle, Cu–O(H)–Cu, and the exchange parameter, J (*i.e.*, parameter in spin Hamiltonian – $2J\hat{S}_1 \cdot \hat{S}_2$). The most ferromagnetic interaction ($2J = +172$ cm^{-1}) was found for $[Cu(bipy)(OH)]_2(NO_3)_2$, where bipy is 2,2′-bipyridine. This compound has a bridge angle of 95.6(1)°. The largest bridge angle, 104.08(17), is seen in $[Cu(tmen)(OH)]_2Br_2$, where tmen is N, N, N′,N′-tetramethylethylenediamine. This second compound exhibits the most antiferromagnetic interaction with $2J = -509$ cm^{-1}. To date, no copper(II) complexes have been reported with one hydroxo bridge. A considerable antiferromagnetic interaction would be expected for such a complex as a consequence of a relatively large Cu–O(H)–Cu bridge angle. The crystal structure of μ-hydroxo-bis[pentaamminechromium-(III)] does show a Cr–O(H)–Cr bridge angle of 165.6(9)° [4]. In this paper, we report the preparation and magnetic properties of the first two μ-hydroxo-bridged copper(II) complexes.

The addition of an aqueous solution of either $NaClO_4$ or KPF_6 to an aqueous solution of Cu(tren)(OH)$^+$ results in the precipitation of microcrystalline $[Cu_2(tren)_2(OH)](ClO_4)_3 \cdot H_2O$ or $[Cu_2(tren)_2(OH)](PF_6)_3$, respectively. Variable-temperature magnetic susceptibility, infrared, and EPR data have been obtained for these two compounds and these data indicate the presence of binuclear copper(II) complexes bridged by a single hydroxo bridge.

The KBr-pellet IR spectrum of either of the $[Cu_2(tren)_2(OH)]X_3$ compounds shows a relatively sharp and medium intensity band in a region where an O–H stretch would be expected [5]. The PF_6^- compound has a band at 3601 cm^{-1}, whereas the ClO_4^- compound has a band at 3571 cm^{-1}. No IR band is seen in this same region for $[Cu_2(tren)_2(CN)]X_3$, X = PF_6^- or ClO_4^- [6]. The assignment of the O–H stretch was substantiated for the PF_6^- compound by preparing the corresponding deuterated compound, $[Cu_2(tren\text{-}d_6)_2(OD)](PF_6)_3$. The O–H band shifted from 3601 cm^{-1} to 2656 cm^{-1}, giving a ν_{OH}/ν_{OD} ratio of 1.36. Similar shifts were observed for the N–H bands. In the case of the non-deuterated compound, N–H stretches are seen at 3321 and 3381 cm^{-1} with a relatively strong N–H bend at 1601 cm^{-1}. The deuterated compound shows N–D stretches at 2440, 2452, and 2530 cm^{-1} and a N–D bend at 1201 cm^{-1}.

The Q-band EPR spectrum (either room-temperature or liquid-nitrogen temperature) of a powdered sample of $[Cu_2(tren)_2(OH)](PF_6)_3$ exhibits a single derivative feature at g = 2.128. The spectrum for the ClO_4^- compound also shows only a derivative at g = 2.132. This is the same type of Q-band EPR signal observed for the $[Cu_2(tren)_2(CN)]X_3$ compounds [6]. Empirically, the presence of such a single-derivative signal points to a relatively strong magnetic exchange interaction. Exchange averaging between two Cu(tren)$^{2+}$ moieties which are not magnetically aligned could lead to a single-derivative spectrum.

The variable-temperature magnetic susceptibility data provide further conclusive evidence for the presence of hydroxo bridges. Figure 1 illustrates the data obtained for $[Cu_2(tren)_2(OH)](PF_6)_3$. At 285.5 °K, the μ_{eff}/Cu ($0.77\mu_B$) for this compound is already considerably below the spin-only value of $1.73\mu_B$. The solid lines in Figure 1 represent the least-squares fit of the data to the Bleaney–Bowers equation [7] for isotropic exchange in a binuclear copper(II) complex. The fitting parameters are $2J = -700$ cm^{-1} and g = 2.05. The increase in χ_M at very low temperatures is due to a small amount of a monomeric paramagnetic impurity; in the fitting the χ_m for the impurity was taken as $\chi_M = 8.0 \times 10^{-3}$ cgsu at 4.2 °K. A more limited data set was obtained for the ClO_4^- compound; the data set runs from 285.5 °K where $\mu_{eff}/\text{Cu} = 0.64\mu_B$

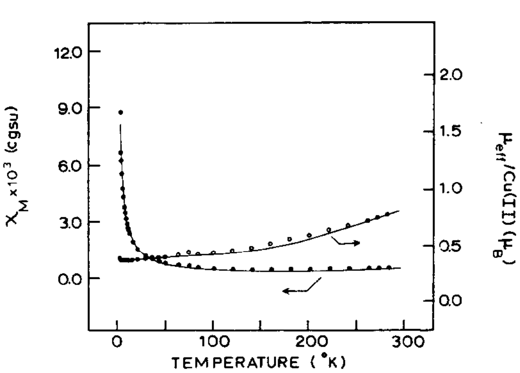

Figure 1. Corrected molar paramagnetism per binuclear complex, χ_M, and effective magnetic moment per copper(II) ion, μ_{eff}/Cu, plotted as a function of temperature. The solid lines result from least-squares fitting the data to the Bleaney– Bowers equation.

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to 203.7 °K where μ_{eff}/Cu = 0.40μ_B. Fitting the ClO_4^- data gave 2J = –760 cm^{-1} and g = 2.120.

Both of the $[Cu_2(tren)_2(OH)]X_3$ compounds exhibit antiferromagnetic interactions that are considerably stronger than the strongest antiferromagnetic interaction (2J = –509 cm^{-1}) seen for the dihydroxo-bridged copper(II) complexes. This is as expected because a single hydroxo bridge would lead to an appreciably larger Cu–O(H)–Cu bridge angle. However, the antiferromagnetic interactions present in the $[Cu_2(tren)_2(OH)]X_3$ are not as great as would naively be expected from the established [1, 2] correalations of 2J and angle for dihydroxo-bridged species. This is also expected, because the copper(II) ion ground states in $[Cu_2(tren)_2(OH)]X_3$ are d_{z^2}, whereas the dihydroxo-bridged copper(II) complexes are all square pyramidal and have $d_{x^2-y^2}$ ground states. A change in the coper(II) ground state can have a pronounced effect on the magnitude of a magnetic exchange interaction propagated by some bridging species [8]. A crystal structure of one or both of the two $[Cu_2(tren)_2(OH)]X_3$ compounds would be very desirable. The difference in O–H stretching frequencies between the two compounds could reflect a change in the bridge angle. Well-formed crystals of the ClO_4^- compound have been obtained.

Experimental

Compound Preparations

Samples of $[Cu_2(tren)_2(OH)](X)_3$ where X = PF_6^- or ClO_4^- and tren is 2,2′, 2″-triaminotriethylamine (Ames) were prepared by the following procedure. To an aqueous solution (40 ml) of *ca.* 1.0g (4 mmol) of $CuSO_4 \cdot 5H_2O$ was added *ca.* 0.6 ml of tren followed by an aqueous solution of *ca.* 0.08g (2mmol) of NaOH. To the filtered solution, an aqueous saturated solution of KPF_6 or $NaClO_4$ was added which resulted in the precipitation of microcrystalline blue solids. The perchlorate salt precipitates as a hydrate, $[Cu_2(tren)_2(OH)](ClO_4)_3 \cdot H_2O$. Recrystallization of the latter from water yields well-formed crystals of the anhydrous form. *Anal.* Calcd for $C_{12}H_{37}N_8OCu_2P_3F_{18}$: C, 16.55; H, 4.25; N, 12.86; Cu, 14.59. Found: C, 16.68; H, 4.01; N, 12.99; Cu, 14.43. Calcd for the hydrate, $C_{12}H_{39}N_8O_{14}Cu_2Cl_3$: C, 19.15; H, 5.18; N, 14.88; Cu, 16.88 Found: C, 19.28; H, 4.90; N, 15.08; Cu, 16.96.

The preparation of $[Cu_2(tren\text{-}d_6)_2(OD)](PF_6)_3$ was carried out in the same way as the non-deuterated compound was prepared, except D_2O was used as the reaction solvent.

Physical Measurements

Infrared spectra were obtained with a Perkin-Elmer Model 467 spectrophotometer. Samples were prepared as 13-mm KBr pellets. The EPR instrumentation and procedure for variable-temperature magnetic susceptibility determination have been previously described [9]. The magnetic susceptibility data were least-squares fit with an adapted version of the computer function minimization program known as STEPT [10].

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