recovery was not quantitative. It appears that excess dithionite may result in some reduction of the ligand, in qualitative agreement with the work of Fallab.

In a final experiment the blue component was heated to 70 °C, under an inert atmosphere. On subsequent cooling, only a small increase in the 670-nm band was observed, unlike Fallab's results. On oxygenation, the 670-nm band disappeared, but quantitative recovery of the 630-nm band was not observed. These results may be due to simple reduction of Fe(III) (with ligand oxidation). Alternative exposure to high vacuum, over two freeze–thaw cycles, did *not* result in spectral changes. We believe these results are more consistent with high-temperature reduction than an oxygenation–deoxygenation cycle.

In summary, the available data support the contention of Weber and Busch[4,7] that $Fe^{II}PTS$ is irreversibly oxidized by air in aqueous solution and that a dioxygen complex is not formed. This conclusion is consistent with all other known examples of model iron–dioxygen complexes which are stabilized in nonaqueous solvents at low temperatures; for these complexes dimerization must be excluded for reversibility.[2]

Registry No. $Fe^{II}PTS$, 59784-64-4; dioxygen, 7782-44-7; $Fe^{III}PTS$, 62521-18-0.

References and Notes

(1) (a) Supported by Grant No. A-259 from the Robert A. Welch Foundation. (b) Texas A&M University Health Fellow, 1974–1976.

(2) (a) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976); (b) F. Basolo, J. Ibers, and B. M. Hoffman, *Acc. Chem. Res.*, **8**, 384 (1976).

(3) D. Vonderschmitt, K. Bernauer, and S. Fallab, *Helv. Chim. Acta*, **48**, 951 (1965).

(4) J. Weber and D. H. Busch, *Inorg. Chem.*, **4**, 469 (1965).

(5) K. Bernauer and S. Fallab, *Helv. Chim. Acta*, **34**, 1287 (1961).

(6) J. Weber, personal communication.

(7) Weber and Busch[4] also noted possible dioxygen adduct formation in the solid state. The present results deal only with aqueous solution and do not preclude interaction in the crystal (or in any other medium).

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Magnetic Exchange Interaction in the Chloro-Bridged Copper(II) Complex *N,N,N',N'*-Tetramethylethylenediammonium Hexachlorodicuprate(II)

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Within recent years, extensive studies of the structural and magnetic properties of dimeric and polymeric copper(II) complexes have provided insight into the features responsible for magnetic exchange interactions. For the most thoroughly studied case, that of hydroxy-bridged copper(II) dimers, it is now possible to accurately predict both the sign and magnitude of the exchange integral from knowledge of the structural parameters of the bridge.[2]

Unfortunately, similar correlations have not proven possible for the analogous case of chloride-bridged copper(II) dimers. This arises largely from the paucity of structural and magnetic data on such species but also because of the variety of structural types adopted by those materials which have been characterized. We have engaged in a program designed to synthesize and characterize chloride-bridged copper(II) dimers in order to determine if correlations between structural and magnetic properties are possible. We report here on the synthesis and characterization of tetramethylethylenediammonium hexachlorodicuprate(II) and compare the properties of this material with the structurally characterized compound potassium trichlorocuprate, $KCuCl_3$.[3]

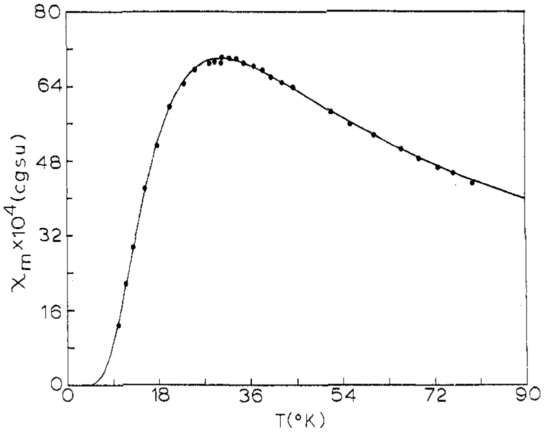


Figure 1. Magnetic susceptibility as a function of temperature in the range 8–80 K. The solid line was generated by the Van Vleck equation for exchange-coupled $S = {}^1/_2$ ions with $2J = -33.7$ cm^{-1} and $g = 2.12$.

Experimental Section

Preparation of Tetramethylethylenediammonium Hexachlorodicuprate. Tetramethylethylenediamine dihydrochloride (3.05 g, 0.016 mol) (prepared by the reaction of tetramethylethylenediamine and concentrated hydrochloric acid) and 6.9 g (0.040 mol) of cupric chloride dihydrate were dissolved in 30 mL of 3 M HCl. The solution was heated to boiling and evaporated at the boiling point until the volume was approximately 15 mL. The solution was cooled, and the bronze-colored needle-shaped crystals which formed were filtered, washed briefly with cold 3 M HCl, and vacuum-dried; yield 0.65 g (9%). Anal. Calcd for $[(CH_3)_2NHCH_2CH_2NH(CH_3)_2]Cu_2Cl_6$: C, 15.73; H, 3.96; Cu, 27.75. Found: C, 15.77; H, 3.96; Cu, 27.80. Further crops of product could be obtained by reduction in the solution volume. Attempted precipitation of the product by addition of acetone led exclusively to the monomeric complex $[(CH_3)_2NHCH_2CH_2NH(CH_3)_2]CuCl_4$.[4]

Physical Measurements. Magnetic susceptibility measurements were made on powdered samples using a Foner-type vibrating-sample magnetometer[5] operating at 10 kG. Nickel metal was used as a susceptibility standard. Measurements were made in the temperature range 8–80 K. Temperatures were measured using a calibrated Ga–As diode.[6] Susceptibilities were corrected for the diamagnetism of the substitutent atoms using Pascal's constants[7] and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/copper atom).

EPR spectra were obtained at room temperature using a Varian E-3 spectrometer. Electronic spectra were obtained at room temperature in the region 4000–30 000 cm^{-1} using the mull transmittance technique on a Cary 17 spectrometer.

Analyses were by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Results

The magnetic susceptibility data for $[tmenH_2]Cu_2Cl_6$ in the temperature range 8–80 K are shown in Figure 1. By assuming the exchange Hamiltonian $H = -2J\hat{S}_1 \cdot \hat{S}_2$, for the pair of interacting spins, the familiar singlet–triplet susceptibility equation

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

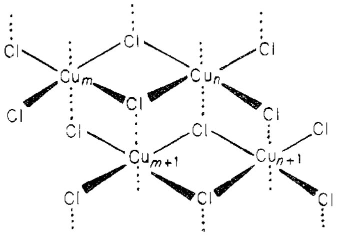
results. This equation, which is written per copper ion, may be fitted to the experimental data yielding a value for the exchange energy $2J$ of -33.7 cm^{-1} with $g = 2.12$.

The electronic absorption spectrum of a sample of the compound mulled in mineral oil exhibited bands at 11 400 (broad and featureless), 19 200, and 25 300 cm^{-1} where the latter two bands occur as shoulders on an intense high-energy band. There was no discernible structure of the low-energy side of the low-energy band, nor were there any low-energy bands in the 4000–6000-cm^{-1} region.

The EPR spectrum consisted of a broad symmetrical signal centered at $g = 2.094$ with a peak-to-peak width of 656 ± 5 G.

Discussion

Although several materials with the empirical formula $A^+CuCl_3^-$ (or $A^{2+}Cu_2Cl_6^{2-}$) are known, only a few have been shown to contain discrete $Cu_2Cl_6^{2-}$ ions. Both tetraphenylarsonium[8] and tetraphenylphosphonium[9] trichlorocuprate have been examined crystallographically and shown to contain dimeric $Cu_2Cl_6^{2-}$ ions in which copper adopts a distorted tetrahedral geometry and the dimer comes about by two distorted tetrahedra showing an edge. In contrast, potassium trichlorocuprate forms dimeric $Cu_2Cl_6^{2-}$ ions in which copper adopts a square-planar geometry.[3] The coplanar dimers are stacked in the following manner



The magnetic behavior of these materials is distinctly different. The first two materials have been shown to exhibit intradimer ferromagnetic interactions and have triplet ground states with $2J = +46$ cm^{-1} [10] and $2J = +85$ cm^{-1},[11] respectively. The magnetic properties of $KCuCl_3$ have been the subject of several studies.[3,12,13] The careful work by the Japanese showed conclusively that there is a strong antiferromagnetic intradimer interaction ($2J = -35$ cm^{-1}) with a sizable interdimer interaction as expected from the structural results.

The physical appearance of tetramethylethylenediammonium hexachlorodicuprate, $(tmenH_2)Cu_2Cl_6$, is striking, the material crystallizing as shiny bronze-colored needles. By was of contrast, tetramethylethylenediammonium tetrachlorocuprate, which may be precipitated from the same solutions used to form $(tmenH_2)Cu_2Cl_6$ by addition to acetone, is bright yellow.[4] A red or red-brown color has been claimed[14] to be characteristic of chloride-bridged copper dimers, and on this basis $(tmenH_2)Cu_2Cl_6$ is undoubtedly similar to those materials which have been established as containing the di-μ-chloro-tetrachlorodicuprate(II) anion. However, both the planar[14] and tetrahedral[8] $Cu_2Cl_6^{2-}$ exhibit a band near 20 000 cm^{-1}, hence the reddish color. It has been claimed that crystals of planar $Cu_2Cl_6^{2-}$ exhibit pleochroism when examined with a polarizing microscope, whereas those of tetrahedral $Cu_2Cl_6^{2-}$ do not, and on that basis $(tmenH_2)Cu_2Cl_6$ is expected to be planar, since it exhibits pleochroism similar to that of $KCuCl_3$. However, $(C_6H_5)_4PCuCl_3$, which contains tetrahedral $Cu_2Cl_6^{2-}$, also exhibits this pleochroism,[9] so that existence of pleochroism is not an adequate demonstration of planarity. The most convenient method of distinguishing geometries comes from near-infrared spectra, since planar $Cu_2Cl_6^{2-}$ has d–d absorptions at 12 900 cm^{-1} (broad) and 10 500 cm^{-1} (shoulder)[14] whereas tetrahedral $Cu_2Cl_6^{2-}$ exhibits well-resolved absorptions at 12 200 and 8930 cm^{-1}.[8] On this basis $(tmenH_2)Cu_2Cl_6$, which exhibits an extremely broad absorption band centered about 11 400 cm^{-1} with no low-energy band, may be assigned a square-planar geometry.

Hara et al.[13] were able to describe the magnetic properties of $KCuCl_3$ in terms of the Hamiltonian

$$H = -2J_a\vec{S}_m\cdot\vec{S}_n - g\beta(\vec{S}_m + \vec{S}_n)\cdot H - g\beta(\vec{S}_m\cdot\vec{H}_m{}^{M} + \vec{S}_n\cdot\vec{H}_n{}^{M})$$

where $\vec{H}$ is the external magnetic field and $\vec{H}_m{}^{M}$ is the molecular field. Using this Hamiltonian the susceptibility may be written as

$$\chi_m = \frac{Ng^2\beta^2}{kT[3 + \exp(-2J_a/kT)] - 4zJ_b}$$

with the term $4zJ_b$ arising from the Weiss coefficient in the molecular field model, where z is the number of nearest neighbors to a copper ion being considered and J_b is the exchange integral between copper ions in adjacent dimers.[15] For $KCuCl_3$ J_b/J_a was found to be 0.05.

If this formulation for magnetic susceptibility is applied to the data for $[tmenH_2]Cu_2Cl_6$, there is no improvement to the fit with finite values of J_b, thus leading to the conclusion that there are no significant intermolecular interactions. The similarity in magnetic properties of $KCuCl_3$ and $[tmenH_2]Cu_2Cl_6$ indicates that the chlorocuprate complex in the latter compound is very similar to the $Cu_2Cl_6^{4-}$ unit in $KCuCl_3$ but that the stacking arrangement may not exist.

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Registry No. $[tmenH_2]Cu_2Cl_6$, 62154-35-2.

References and Notes

(1) (a) University of Vermont. (b) University of North Carolina. (c) Participant in Summer Undergraduate Research Participation Program supported by the National Science Foundation and the Kenan Endowment to the University of North Carolina Chemistry Department.
(2) D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975); W. E. Hatfield, *ACS Symp. Ser.*, **5**, 108 (1974).
(3) R. O. Willett, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, **38**, 2429 (1963).
(4) D. B. Brown, V. H. Crawford, J. W. Hall, and W. E. Hatfield, *J. Phys. Chem.*, in press.
(5) S. Foner, *Rev. Sci. Instrumen.*, **30**, 548 (1959).
(6) D. B. Losee and W. E. Hatfield, *Phys. Rev. B*, **10**, 212 (1974).
(7) E. Konig, "Magnetic Properties of Transition Metal Compounds", Springer-Verlag, Berlin, 1966.
(8) R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, **30**, 207 (1974).
(9) M. Textor, E. Dubler, and H. R. Osuald, *Inorg. Chem.*, **13**, 1361 (1974).
(10) C. Chow, R. Caputo, R. D. Willett, and B. C. Gerstein, *J. Chem. Phys.*, **61**, 271 (1974).
(11) W. E. Estes, personal communication.
(12) G. J. Maass, B. C. Gerstein, and R. D. Willett, *J. Chem. Phys.*, **46**, 401 (1967).
(13) K. I. Hara, M. Inoue, S. Emori, and M. Kubo, *J. Magn. Reson.*, **4**, 337 (1971).
(14) R. D. Willett and O. L. Lines, Jr., *Inorg. Chem.*, **6**, 1666 (1967).
(15) A. P. Ginsberg and M. E. Lines, *Inorg. Chem.*, **11**, 2289 (1972).

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Thallium Derivatives of *closo*-Carboranes. 1. Pyrolysis of $Tl_2R^1R^2C_2B_9H_9$ Species

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Heterocarboranes derived from main-group elements have received relatively little attention in comparison to those derived from transition metals.[1] However, the reported examples of non-transition-metal heterocarborane syntheses and