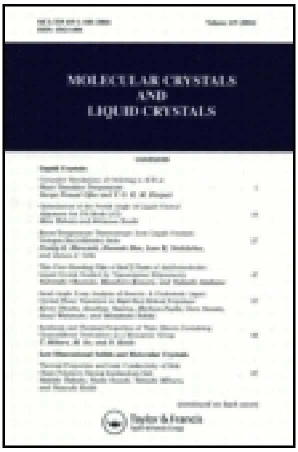

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Low-Temperature X-ray Structure Determinations, and Single Crystal Magnetic Susceptibility and EPR Studies on (3-Chloroanilinium)$_8$[CuCl$_6$]Cl$_4$

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LOW-TEMPERATURE X-RAY STRUCTURE DETERMINATIONS, AND SINGLE CRYSTAL MAGNETIC SUSCEPTIBILITY AND EPR STUDIES ON (3-CHLOROANILINIUM)$_8$[CuCl$_6$]Cl$_4$

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Abstract A recent X-ray diffraction study has shown that (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$ contains compressed [CuCl$_6$]$^{4-}$ octahedra. Low temperature studies reported here do not obviate such a conclusion, and so, questions concerning disorder and dynamics still remain. Down to 110 K, the [CuCl$_6$]$^{4-}$ ions are arranged in a quasi-linear chain. SQUID-based temperature-dependent magnetic susceptibility data exhibit a maximum near 17 K. The Bonner-Fisher model yields an antiferromagnetic Heisenberg exchange of $J = -9.3$ cm^{-1}. Magnetic field-dependent susceptibility measurements on single crystals with the chain-axis aligned parallel to the field, show a marked field dependence below 9 K and suggest weak ferromagnetism due to spin canting. Single crystal EPR measurements at room temperature yield $g_{\|} = 2.035$ and a *single* $g_{\perp} = 2.202$; at 4 K, $g_{\|} = 2.041$ with $g_{\perp 1} = 2.200$ and $g_{\perp 2} = 2.168$. Line widths in all orientations at 4 K are very narrow, ranging from 0.5 to 2.0 mT.

INTRODUCTION

The compound 3-chloroaniline reacts with a hydrochloric acid solution of copper(II) chloride to yield bright yellow needle-like crystals with the composition (3-chloroanilinium)$_8$CuCl$_{10}$.[1] The compound consists of discrete [CuCl$_6$]$^{4-}$ ions. The first crystal structure (293 K) revealed a tetragonally-compressed octahedron with four long Cu-Cl bonds of 2.61 Å and two short Cu-Cl bonds of 2.28 Å. The[CuCl$_6$]$^{4-}$ ions form a quasi-linear chain through apical Cl---Cl contacts of 3.99 Å between the [CuCl$_6$]$^{4-}$ ions. The copper-copper separation along the chain is 8.55 Å. We report that an independent X-ray determination at 298 K has reproduced this apparent compression.[2]

In D_{4h} the ground state is $^2A_{1g}$ for tetragonally compressed d^9 complexes and $g_{\|} = 2.0$ is expected. The powder EPR spectrum (298K)[1] for [CuCl$_6$]$^{4-}$ is indeed reversed, that is $g_{\|} < g_{\perp}$, thus suggesting compression.[3] Slight deviation from $g_{\|} = 2.0$ arises from low-symmetry crystal field components mixing excited states into the ground state, or, from the dynamic Jahn-Teller effect.[4] An alternative explanation is that the apparent compression is due to disordered elongation: if the true pair of long bonds and one pair of short bonds were disordered, one obtains the appearance of four 'long' bonds of intermediate length. In such a way, the 'compressed' $g_{\|}$ would be the true $g_{\perp}$ along the nondisordered short bonds, and the 'compressed' $g_{\perp}$ would be the average of the true $g_{\perp}$ and $g_{\|}$ of elongated, but disordered, $[CuCl_6]^{4-}$ ions. Preliminary isofield (1.0 T) magnetic susceptibility data[1] exhibited behavior characteristic of antiferromagnetic exchange, possibly along the quasi-chain direction and transmitted through Cl---Cl contacts of 3.99 Å, a distance slightly greater than the van der Waal's contact of 3.60 Å.[5] These possibilities have stimulated additional synthetic, theoretical, spectroscopic, magnetic, and EPR studies. In this article, preliminary results are described.

EXPERIMENTAL

Synthesis of $(3\text{-}Cl\text{-}C_6H_7N)_8[CuCl_6]Cl_4$ $CuCl_2{\cdot}2H_2O$ was reacted with 3-chloroaniline as previously described.[1] A first crop of crystals is readily obtained upon cooling the reaction solution to room temperature. Better quality crystals suitable for physical measurements are obtained from a second crop obtained by slow evaporation.

Structure Determinations Two independent crystal studies were performed. *1)* A yellow needle-shaped crystal (0.18 x 0.18 x 0.8) was mounted on a glass fiber and the x-ray diffraction data were collected at 298 K and at 150 K on a R3m/V Nicolet four circle diffractometer with graphite monochromated MoKα radiation; $\lambda = 0.71073$ Å.[2] For both temperatures, the unit cell parameters and standard deviations were obtained by least squares fit to 25 reflections randomly distributed in reciprocal space and lying in the range 25 - 35°. The structure was solved by full matrix least squares refinement using SHELXTL-PLUS on a Microvax II. *2)* Independently, another crystal was mounted for data collection at 110 K using an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and by using MoKα radiation.[6] Unit cell parameters and standard deviations were obtained by least squares fit to 25 reflections randomly distributed in reciprocal space and lying in the range 30 - 35°. The structure was solved by full matrix least squares refinement using the NRCVAX programs[7].

Relevant structural data for all three structural determinations described in this work are compared in Table I to the previously published[1] room temperature structure. *Crystal data:* $CuC_{48}H_{56}Cl_{18}N_8$, $P\bar{1}$, Z=1, and Table I.

Magnetic susceptibility measurements. Field-dependent magnetic susceptibility data for several single crystals and freshly prepared powder samples were collected in the temperature range 1.7 - 300 K using a Quantum Design SQUID-based magnetometer utilizing modifications and procedures described elsewhere.[8] Data were corrected for temperature independent magnetism (-902 x 10^{-6} emu/mol) using Pascal's constants for the diamagnetic components[9] and a T.I.P. per Cu(II) ion of 60 x 10^{-6} emu/mole. Figures in this paper are based on a molecular weight of 1447 g/mol.

RESULTS AND DISCUSSION

Structural Description. Structural refinements were carried out independently in two laboratories. As seen in Table I, the agreement between the crystallographic data are excellent, although the data at 110 K are less precise. All four crystal structure determinations indicate (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$ consists of discrete 3-chloroanilinium ions, uncoordinated chloride ions, and [CuCl$_6$]$^{4-}$ ions which are linked into a quasi-linear chain by way of apical Cl---Cl interactions. Pertinent bond distances for the [CuCl$_6$]$^{4-}$ ion shown in Figure 1, are given in Table II according to temperature.

TABLE I Unit cell dimensions for (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$.

Unit Cell	Temperature (K)			
Dimension	293	298	150	110
a /Å	8.5488(16)	8.559(3)	8.435(3)	8.418(10)
b /Å	13.964(6)	13.982(5)	13.904(4)	13.851(19)
c /Å	14.273(7)	14.235(5)	14.171(3)	14.114(19)
α/°	82.29(3)	82.34(3)	82.00(2)	81.73(12)
β/°	72.90(3)	72.90(3)	73.00(2)	72.96(10)
γ/°	77.89(3)	77.89(3)	78.10(2)	78.06(10)
reference	1	2	2	6

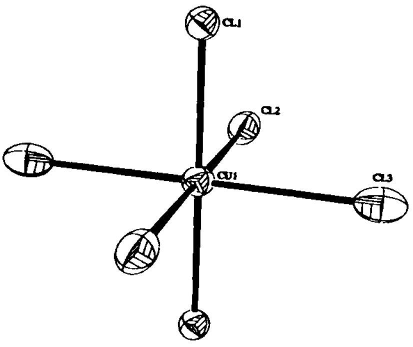

FIGURE 1 [CuCl$_6$]$^{4-}$ tetragonally compressed octahedra; Cu-Cl(1) is the 'short' bond.

TABLE II Copper(II)-chloride distances (Å) in $[CuCl_6]^{4-}$.

Bond	Distance/Å	Temperature	Reference
Cu-Cl(1)	2.2773(11)	293 K	1
	2.282(1)	298 K	2
	2.288(2)	150 K	2
	2.307(6)	110 K	6
Cu-Cl(2)	2.6061(18)	293 K	1
	2.613(2)	298 K	2
	2.608(2)	150 K	2
	2.572(12)	110 K	6
Cu-Cl(3)	2.6086(20)	293 K	1
	2.610(2)	298 K	2
	2.587(2)	150 K	2
	2.586(10)	110 K	6

The packing of the $[CuCl_6]^{4-}$ ions is of considerable importance. The quasi-linear chain is readily apparent in the packing diagram shown in Figure 2. The chain direction is parallel to the a-axis. Antiferromagnetic superexchange interactions along the chain could arise from a -Cl(1')-Cu-Cl(1)----Cl(1')-Cu-Cl(1)- pathway (assuming a d_{z^2} ground state) that is likely to lead to temperature dependent Heisenberg exchange.

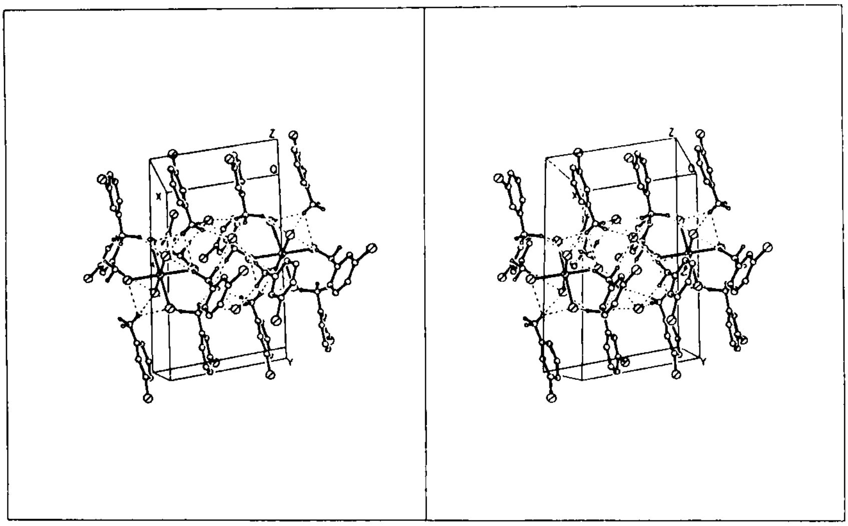

FIGURE 2 Packing diagram showing the quasi-chain structure of compressed $[CuCl_6]^{4-}$ octahedra in which Cu-Cl----Cl-Cu interactions propagate the exchange.

The only close contact to Cl(1) is that to Cl(1') at (-x,-y,1-z) along the chain direction. This contact is temperature dependent (3.995 (293 K) / 3.805 (110 K)) as a result of thermal contraction of the unit cell. The next closest contacts for Cl(1) are to the uncoordinated chlorides at over 4.00 Å. If the structure of the $[CuCl_6]^{4-}$ ion were a time-averaged structure in which four long Cu-Cl bonds were an average of two long Cu-Cl bonds of 2.9 Å and two short bonds of 2.3 Å, then the coordinated-chloro to organo-chloro distance of 3.45 Å may be difficult to explain. However in all structures, the thermal ellipsoids for Cl(2) and Cl(3) are canted relative to the expected directions, and the ellipsoid of the organo-chloro is quite large, indicating that a concerted dynamics or disorder situation may obtain if the octahedra are elongated.

Magnetic Susceptibility. Susceptibility data were collected with applied magnetic fields in the range 0.1 mT to 1.0 T in the temperature range 1.7 to 300 K. The data are plotted in Figures 3 through 5 as χ_m, $1/\chi_m$, and $\mu_{eff} = 2.828(\chi_m T)^{1/2}$. Several dominant features are noteworthy. In Figure 3, χ_m exhibits a susceptibility maximum at a temperature of 16.8 K and μ_{eff} drops from 1.8 B.M at 300 K towards 0.4 B.M near 2 K.

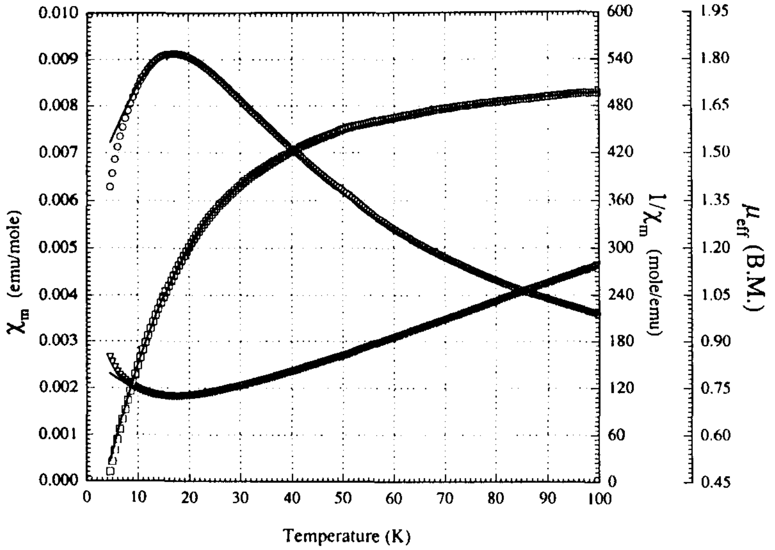

FIGURE 3 Powder susceptibility data (○ – χ_m, ∇ – $1/\chi_m$, □ - μ_{eff}); H = 0.5T.

These data are in qualitative agreement with the previous susceptibility studies (at H = 1.0 T) and suggest the presence of antiferromagnetic exchange interactions. In view of the observation that a quasi-chain structure is maintained upon cooling to 110 K, it is reasonable to fit the susceptibility data to the uniform S = 1/2 Heisenberg spin chain, given by the Hamiltonian $H = -2J_{ij}\sum_{i \le j} \mathbf{S}_i \cdot \mathbf{S}_j$ where J_{ij} is the isotropic intrachain exchange parameter. The theoretical treatment of such a uniform chain was first provided by Bonner and Fisher.[10] Hall[11] later provided a useful analytical expression for the temperature dependence of the magnetic susceptibility as

$$\chi_{\mathrm{BF}} = \left(Ng^2\mu_{\mathrm{B}}^2/k_{\mathrm{B}}T\right)\left[A+Bx+Cx^2\right] \Big/ \left[1+Dx+Ex^2+Fx^3\right] \qquad (1)$$

where A = 0.25, B = 0.14995, C = 0.30094, D = 1.9862, E = 0.68854, F = 6.0626, and x = $|J|/k_BT$. Interchain interactions can be accounted for by a applying a molecular field correction to the χ_{BF} expression, thus obtaining

$$\chi_{\mathrm{corr}} = \chi_{\mathrm{BF}}\Big/\left(1-2zJ'\,\chi_{\mathrm{BF}}/Ng^2\mu_{\mathrm{B}}^2\right) \qquad (2)$$

where J' is the interchain exchange parameter and z is the number of nearest neighbors. A best-fit of the χ_{corr} expression to the χ_m data using nonlinear regression[12] yielded J = -9.3 cm^{-1}, zJ' = -0.95 cm^{-1}, and g = 2.126. The solid line in Figure 3 is generated with these parameters; it is in excellent agreement with the temperature dependence and the position of the maximum as calculated according to the Bonner-Fisher model.

Below 10.0 K, the χ_{corr} expression exhibits increased deviation with respect to the data in Figure 3. Such deviation is often indicative of phase transitions which are easily affected by moderately large applied magnetic fields. To investigate this further, low-field measurements were carried out on both powder and single crystal samples. As a typical example, an applied field of H = 1.0 mT led to the powder data shown in Figure 4, where marked field dependence below 9 K becomes quite evident.

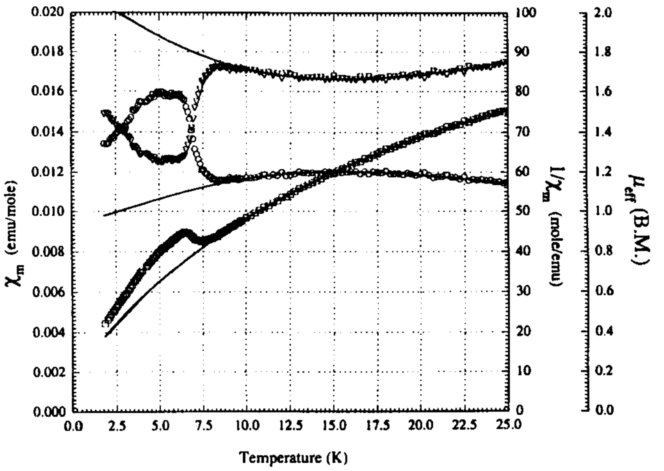

FIGURE 4 Magnetic data (o – χ_m, ∇ – $1/\chi_m$, □ - μ_{eff}); H = 1.0 mT.

The solid lines through the data in Figure 4 are drawn using the parameters for the Bonner-Fisher model described above. The sharp divergence in the susceptibility at *ca.* 7 K becomes better defined at lower field values, whereas at higher field values (H > 0.1 T) it becomes increasingly subdued, as in Figure 3. Such a divergence is usually associated with a magnetic phase transition, particularly when zJ' is nonzero and of the same order of magnitude as J. Although a dramatic increase in magnetization is generally associated with ferromagnetic interactions, the magnitude in Figure 4 is too small to be due to LRO ferromagnetism. For a compound which exhibits predominantly antiferromagnetic interactions, such as (3-chloroanilinium)$_8$[CuCl$_6$]Cl$_4$, apparent ferromagnetism can arise from canted antiferromagnetism because there is no net compensation of all spins.

Field-dependent, single crystal susceptibility data are shown in Figure 5 with the applied magnetic field parallel to the chain axis. Increased magnetic fields suppress the divergence of the susceptibility; low fields enhance it. In contrast, when the field is applied along any direction perpendicular to the chain axis, field dependence is not observed and the susceptibility data display a rounded maximum typical of a chain that conforms to the Bonner-Fisher model. Additional experiments are required to further elucidate the structure of such hidden canting and the exact nature of the short or long range 'ordering' that may be occurring below 8 K.

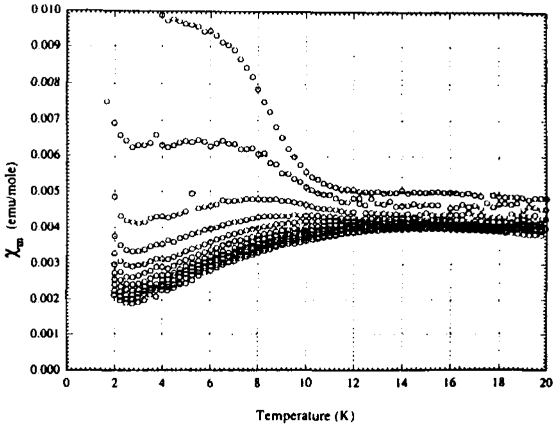

FIGURE 5 Magnetic susceptibility data with various H_{app} parallel to the chain axis.

EPR Studies. Single crystal EPR measurements at room temperature yield $g_{||}$ = 2.035 (parallel to the chain axis) and *a single* $g_{\perp}$= 2.202 for all orientations in which the applied magnetic field is perpendicular to the chain axis. *Normal g-factor anisotropy is not resolved at room temperature for the perpendicular direction.* The linewidth of the resonance line at room temperature is completely independent of orientation and is *extremely* narrow, even for an exchange-coupled system, at *ca.* 1.0 mT. At 4 K $g_{||}$ = 2.041, and perpendicular to the chain axis a slight anisotropy is indeed resolved: $g_{\perp 1}$ = 2.200 and $g_{\perp 2}$ = 2.168. Linewidths in all perpendicular orientations at 4 K are further narrowed with respect to room temperature and are *ca.* 0.6 mT. In contrast, the resonance along $g_{||}$ has broadened with respect to room temperature to *ca.* 2.0 mT.

CONCLUSIONS

Tetragonally-compressed copper(II) ions are rare,[13] and chain compounds which exhibit phase transitions are equally interesting. Although the low temperature structure studies do not obviate the observed compression for (3-chloro-anilinium)$_8$CuCl$_{10}$, definitive conclusions are still to be reached. For T > 10 K, the EPR and powder magnetic data are consistent with a structurally characterized compressed complex that exhibits canting. However, the single crystal magnetic data may correlate better to a crystallographically characterized compression that is indeed the result of dynamically or statically disordered elongated octahedra. Additional studies in laboratories around the world are ongoing in an effort to yield more information about vibronic coupling, lattice strain, site disorder and delocalization.

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