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Structure and Magnetic Moment of Pyrrolidinium Copper Trichloride, a Linear Ferromagnet

Pyrrolidinium copper trichloride, (C₄H₈NH₂)CuCl₃, was synthesized in an attempt to find another example of a spin ¹/₂, Heisenberg, linear ferromagnetic copper salt. The pyrrolidinium salt was chosen for its expected similarities to the well-characterized linear-chain compound cyclohexylammonium copper trichloride (CHAC).¹ The latter contains chains of square-pyramidal CuCl₃ polyhedra that share basal plane edges. A folding of the chains along these shared edges leads to bridging Cu–Cl–Cu angles near 85°, a value favoring ferromagnetic coupling.² The –NH₃ moiety of the cyclohexylammonium ion hydrogen bonds to axial chloride ions in adjacent chains, both providing stability to the structure and stabilizing the square-pyramidal coordination geometry. The possibility of the –NH₂ portion of the pyrrolidinium cation performing the same function led to the present investigation. The structure of (C₄H₈NH₂)CuCl₃ was thus determined, and its powder magnetic susceptibility was examined with the result being indeed a ferromagnetic chain but one with much stronger antiferromagnetic interchain coupling than was expected.

The compound was prepared by mixing solutions of hydrated CuCl₂ with solutions of pyrrolidine in dilute HCl. The HCl was always in excess because this seems to help with crystal growth in many of these compounds. Several preparations were done and quantities varied from about 6 to about 15 mmol of CuCl₂; the quantity of pyrrolidine was always at least equivalent to the amount of CuCl₂, and in some cases it was doubled to see if we could form a tetrachlorocuprate (the title compound was the only product observed in any of the preparations). The molar excess of HCl was always about a factor of 2 larger than that required to completely protonate the amine. The components were each dissolved in the minimum amount of water and mixed; the resultant solution was filtered to remove dust and other nucleation centers and set to evaporate slowly in a petri dish. Crystals were collected on a suction filter, washed sparingly with ice cold ethanol and then with ethyl ether, and air-dried. Note that air drying is appropriate in the dry Montana climate but may not be successful when the humidity is high!

A crystal that was a dark red hexagonal prism 0.12-mm thick by 0.48-mm long was mounted on a glass fiber for data collection. Axial photographs showed monoclinic symmetry. Unit cell dimensions were obtained by least-squares refinement using 20 centered reflections for which 27° < 2θ < 33° (graphite-mono-chromatized Mo Kα radiation). Data collection was carried out on a Nicolet R3m/E four-circle diffractometer.³ Three check reflections were monitored every 93 reflections, showing no loss of intensity during the course of data collection. Tables of crystal and refinement data, observed and calculated structure factors, anisotropic thermal parameters, and hydrogen positions are given in the supplementary material (vide infra).

Data reduction,³ including corrections for Lorentz and polarization effects, gave 2448 independent reflections in the range 3° < 2θ < 60°, of which 1264 with I > 3σ(I) were used for structure

Table I. Crystallographic Data for (C₄H₈NH₂)CuCl₃

<i>a</i>	9.3456 (12) Å	<i>fw</i>	242.03
<i>b</i>	6.5097 (7) Å	space group	<i>P</i> ₂ ₁ / <i>n</i> (No. 14)
<i>c</i>	14.1307 (13) Å	radiation, λ	Mo Kα, 0.710 69 Å
β	102.93 (1)°	<i>D</i> _{calc}	1.92 g/cm ³
<i>V</i> _{cell}	837.9	abs coeff	35.0 cm ⁻¹
<i>Z</i>	4	<i>R</i> ^a	0.0412
<i>T</i>	24 °C	<i>R</i> _w ^b	0.0429

$$^a R = \sum (|F_o - F_c|) / \sum |F_o| \quad ^b R_w = \sum \{w(|F_o| - |F_c|)^2\} / \sum \{w|F_o|^2\}$$

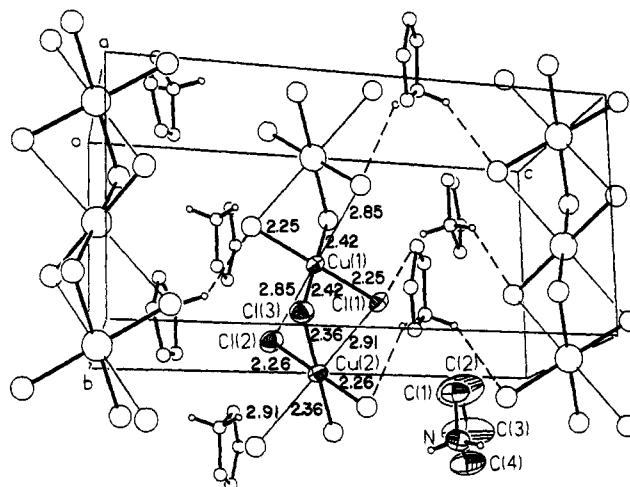


Figure 1. Unit cell, showing the chain structure and probable hydrogen bonding. Bond lengths are given in angstroms.

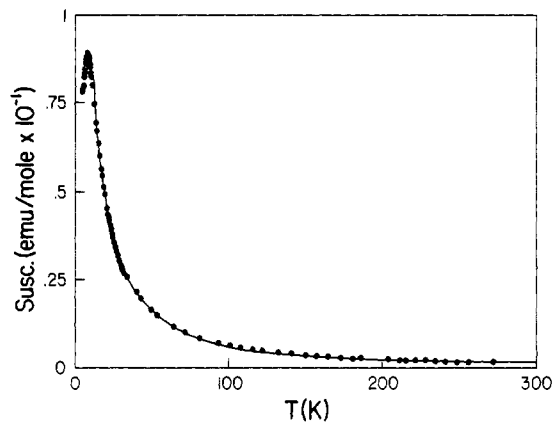


Figure 2. Powder magnetization data (circles) and high-temperature series expansion fit (solid line) with intrachain *J*/*k* = +56 K and interchain *J*'/*k* = -1.2 K.

refinement. A brief summary of unit cell and refinement data is given in Table I; a more complete listing is given in the supplementary material. A Patterson synthesis gave the copper positions, and the remaining non-hydrogen atoms were located by *F*_o–*F*_c difference maps. These positions were refined with anisotropic thermal parameters by blocked-cascade least squares, minimizing *w*Δ², with all 85 parameters refined in each cycle. Not all hydrogen atom positions could be located reliably in the final difference map, and the final cycles of refinement were done with a riding model in which the hydrogens could move about the attached atom but were fixed at 0.96 Å from each carbon and 0.93 Å from each nitrogen. Atomic scattering factors were taken from Cromer and Waber.⁴ Absorption factors were calculated by Gaussian integration using measured distances between indexed crystal faces. Maximum and minimum electron densities in the final difference map were 0.71 and -0.79 e/Å³, respectively. Refined atomic coordinates are given in Table S2 (supplementary

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(3) All crystallographic calculations were performed on a Data General Eclipse computer using the SHELXTL program package by: Sheldrick, G. M. Nicolet Analytical Instruments, Madison, WI, 1983.

(4) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Vol. IV Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–98, 149–150.

material). Bond distances and bond angles for the heavy atoms are given in Tables S3 and S4 (supplementary material). Figure 1 shows a view of part of the unit cell contents that illustrates the chain structure and the probable hydrogen bonding.

A powdered sample of mass 83 mg was mounted on an EG&G Model 155 vibrating-sample magnetometer. Susceptibility data were obtained in an applied magnetic field of 5000 Oe from 4.2 to 273 K. Experimental results are shown as points in Figure 2.

Molar susceptibility from a Pade high-temperature series expansion for a $S = 1/2$ Heisenberg model is given by⁵

$$\chi_P = (C/T)[(1 + 5.7979916K + 16.902653K^2 + 29.376885K^3 + 29.832959K^4 + 14.36918K^5)/(1 + 2.7979916K + 7.008680K^2 + 8.6538644K^3 + 4.5743114K^4)]^{2/3}$$

where $C = N_A g^2 \mu_B^2 / 4k_B$, $K = J/(2k_B T)$, and J is the nearest-neighbor coupling along the chain. To estimate the exchange coupling between the chains, the expression for susceptibility can be modified by the addition of a mean-field correction to account for interchain interactions:⁶

$$\chi = \chi_P / [1 - 2ZJ'\chi_P/C]$$

where J' is the interchain coupling constant between nearest-neighbor chains and Z is the number of nearest-neighbor chains. By minimization of the mean square difference between the calculated and the experimental susceptibility, $J/k_B = 56$ K, $ZJ'/k_B = -1.2$ K, and $g = 2.191$ were found to best fit the data. This result is shown in Figure 2 as a solid line.

The structure consists of chains of face-shared octahedra, with the pyrrolidinium cations spacing these chains. In this particular compound the octahedra are very distorted, with copper displaying its usual 4 + 2 coordination. There are two crystallographically different copper sites in the structure, but they do not appear to be chemically different; both lie on inversion centers. One chlorine atom, Cl(3), forms short symmetrical bonds to both copper sites, forming an infinite zigzag chain in the b direction. Each of the other chlorine atoms forms a short bond to one of the two coppers and a long bond to the other. These short bonds are more than 0.1 Å shorter than those in the symmetric bridges. The long bonds are 2.86–2.91 Å, long even for semicoordinate bonds. The two unsymmetrically bonded chlorines of the chain form nearly symmetric bifurcated hydrogen bonds with the two amine hydrogens of the pyrrolidinium groups. Cl–H distances are 2.42 and 2.49 Å in these bonds; the shortest Cl–H distance to a methylene hydrogen is 2.60 Å. All other Cl–H distances are 2.84 Å or greater. The shortest interchain Cl–Cl distance is 3.71 Å, between Cl(1) and Cl(2). There is no evidence of any structural phase transition between room temperature and 10 K, and since no disorder was observed in the room temperature structure, we believe that the structure is invariant in this range.

The face-sharing chain of distorted CuCl_6 octahedra is related to similar chains observed in a number of ACuCl_3 structures.⁵ One of the structural features of interest is the sense of the relative orientation of the elongated Cu–Cl bonds as one progresses along

the chain. For each copper atom in the chain, the long Cu–Cl bond that links to the copper atom "above" it is projected onto a plane normal to the chain direction. The structural constraints require that the adjacent projected vectors are rotated clockwise by $+60^\circ$ or counterclockwise by -60° . In this structure, the sequence of projected vectors is defined by ..., $+60^\circ$, -60° , $+60^\circ$, -60° , ... (e.g. an antiferrodistortive arrangement of the elongation axes). This repeat sequence is dictated by the length of the crystallographic repeat along the chain axis. A similar sequence has been observed in $[(\text{CH}_3)_2\text{CHNH}_3]\text{CuCl}_3$ (high- T phase),⁶ while the ferrodistorptive version (a helical ..., $+60^\circ$, $+60^\circ$, ... repeat sequence) is found in CsCuCl_3 .⁷ Other sequences have been observed, as well as structural phase transitions involving disorder of the elongated axes.⁵

The unpaired (magnetic) electron on each copper (II) ion is expected to be localized in a $d_{x^2-y^2}$ -type molecular orbital that lies in the plane of its four shorter Cu–Cl bonds. The strongest exchange interaction is thus expected through the symmetric bridges, since the interaction of magnetic orbitals will be greater for this type of bridge. The symmetric Cu–Cl–Cu bond angle is 85.8° , which gives a near-orthogonal overlap at that bridging chlorine and thus predicts a ferromagnetic exchange. The asymmetric bonds have a Cu–Cl–Cu bond angle of 78.3° , which would be expected to cause an antiferromagnetic exchange interaction. However, there is essentially zero unpaired electron density along the long bond in this bridge and this antiferromagnetic exchange is expected to be weak. The ferromagnetic exchange in the short, symmetrical Cu–Cl bridge will dominate. This is consistent with the value of $J/k = +56$ K obtained from the susceptibility data. The susceptibility data indicate an antiferromagnetic coupling between the chains of $J'/k = -1.2$ K. This value is very large if only exchange through the hydrogen-bonded pyrrolidinium groups is considered. However, the large exchange is reasonable if the primary interchain coupling is via Cu–Cl–Cl–Cu bridges.

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Supplementary Material Available: Listings of coordinates for all atoms (Tables S2 and S6), bond lengths and angles (Tables S3 and S4), anisotropic temperature factors (Table S5), and full crystal and refinement data (Table S1) (4 pages); a listing of observed and calculated structure factors (Table S7) (8 pages). Ordering information is given on any current masthead page.

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