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A Redetermination of the Crystal Structure of NH_4CuCl_3 and a Magnetic Study of NH_4CuX_3 (X = Cl, Br)

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As part of our study of the structural and magnetic properties of copper(II) halide salts, the crystal structure of NH_4CuCl_3 has been reinvestigated. The original determination [1] (based on a two-dimensional X-ray data, and so inherently inaccurate) showed the salt to be isomorphous with $KCuCl_3$. Both contain dimeric $Cu_2Cl_6^{2-}$ anions, which stack to form chain systems. Magnetic investigations have been carried out for $KCuCl_3$ [2] and $KCuBr_3$ [3]. Both salts show behavior characteristic of antiferromagnetically coupled dimer systems. No corresponding magnetic investigations have been carried out for the ammonium salts, so these measurements were pursued in our laboratory.

Single cyrstals of NH_4CuCl_3 were accidentally grown while trying to prepare $C_3H_5NH_3CuCl_3$, ammonium ion being the by-product of the copper catalyzed decomposition of the cyclopropylammonium ion. Systematic extinctions confirmed the previously determined space group ($P2_1/c$). Lattice constants, from 12 accurately centered reflections (λ = 0.71067 Å for Mo-K_α radiation) gave a = 4.0344(7) Å, b = 14.206(2) Å, c = 8.992(2) Å, and β = 96.43(2)°.

Intensity data were collected on a Picker diffractometer with θ–2θ scan technique. A total of 1847 independent reflections were obtained, of which 1214 had intensity greater than 3σ. Refinement, based on positional parameters previously determined, converged to an $R(= \Sigma|F_{obs}|-|F_{calc}|/\Sigma|F_{obs}|)$ of 0.067. The major problem in the refinement was extinction, which was not corrected, and is the cause of the high R value. Hydrogens were located from difference maps. Final parameters are given in Table I, and pertinent bond distances and angles in Table II. An illustration of the structure is given in Fig. 1.

TABLE II. Bond Distances and Angles for NH_4CuCl_3.

Cu–Cl(1)	2.261(2)	Cl(1)–Cu–$Cl(2)^a$	92.77(8)
Cu–$Cl(2)^a$	2.280(2)	Cl(1)–Cu–$Cl(3)^b$	92.02(8)
Cu–$Cl(3)^c$	2.308(2)	Cl(1)–Cu–$Cl(3)^c$	175.77(9)
Cu–$Cl(3)^c$	2.314(2)	$Cl(2)^a$–Cu–$Cl(3)^b$	172.57(10)
		$Cl(2)^a$–Cu–$Cl(3)^c$	91.45(8)
		$Cl(3)^a$–Cu–$Cl(3)^c$	83.76(8)
		Cu–Cl(3)–Cu^c	96.24(8)
		Interdimer	
Cu–$Cl(2)^d$	2.951(3)	Cl(1)–Cu–$Cl(2)^d$	93.25(8)
Cu–$Cl(3)^e$	3.168(3)	Cl(1)–Cu–$Cl(3)^e$	90.44(8)
		$Cl(2)^a$–Cu–$Cl(2)^d$	100.10(8)
		$Cl(2)^a$–Cu–$Cl(3)^e$	80.74(8)
		$Cl(3)^b$–Cu–$Cl(2)^d$	85.27(8)
		$Cl(3)^b$–Cu–$Cl(3)^e$	93.56(8)
		$Cl(3)^c$–Cu–$Cl(2)^d$	86.13(8)
		$Cl(3)^c$–Cu–$Cl(3)^e$	90.11(8)
		Cu–$Cl(2)^d$–Cu^f	100.10(8)
		Cu–$Cl(3)^e$–Cu^f	93.56(8)
		Cu–$Cl(3)^e$–Cu^f	93.56(8)
		Cu^c–$Cl(3)^e$–Cu^f	89.89(8)
		Nitrogen–Chlorine	
N–$Cl(1)^g$	3.183(9)		
N–Cl(1)	3.214(9)		
N–$Cl(2)^h$	3.250(10)		
N–$Cl(2)^a$	3.284(10)		
N–$Cl(2)^i$	3.334(9)		
N–$Cl(3)^j$	3.435(9)		
N–$Cl(1)^k$	3.498(10)		
N–Cl(1)	3.506(10)		

Coordinates transformed by: [a] $x, -1 + y, z$; [b] $-1 + x, y, -1 + z$; [c] $1 - x, -y, 1 - z$; [d] $-1 + x, -1 + y, z$; [e] $x, y, -1 + z$; [f] $x, y, 1 + z$; [g] $1 + x, ½ - y, ½ + z$; [h] $1 - x, 1 - y, 1 - z$; [i] $2 - x, 1 - y, 1 - z$; [j] $x, ½ - y, -½ + z$; [k] $1 + x, y, z$.

TABLE I. Final Positional and Thermal Parameters.[a]

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.2340(2)	0.04865(7)	0.1526(1)	0.0345(9)	0.00178(6)	0.0056(2)	0.0014(1)	−0.0030(2)	−0.0005(1)
Cl(1)	0.2676(6)	0.1942(1)	0.2550(2)	0.0387(15)	0.00186(10)	0.0080(3)	0.0011(3)	−0.0037(5)	−0.0005(1)
Cl(2)	0.6666(6)	0.9934(2)	0.3141(2)	0.0354(14)	0.00240(10)	0.0061(2)	0.0006(3)	−0.0016(4)	0.0005(1)
Cl(3)	0.8218(6)	0.0962(1)	0.9648(2)	0.0396(14)	0.00192(9)	0.0060(2)	0.0013(3)	−0.0025(4)	−0.0003(1)
N	0.783(2)	0.1691(6)	0.5517(11)	0.045(6)	0.0032(4)	0.0089(10)	−0.0037(12)	0.000(2)	0.0003(5)

[a] Thermal parameters defined by $T = \exp - (\beta_{11}h^2\beta_{22}k^2 + ... = 2\beta_{23}kl)$.

The structure contains nearly planar centrosymmetric $Cu_2Cl_6^{2-}$ anions. The bridging Cu–Cl distances are slightly longer (2.31 Å, average) than the terminal distances (2.27 Å, average). The briding Cu–Cl–Cu angle is 96.24°. The dimers stack in chains, with each copper ion completing its 4 + 2 coordination sphere by long Cu–Cl interactions (2.295 Å and 3.136 Å). The ammonium ions stack between the chains, hydrogen bonding to the chloride ions, and forming a three-dimensional structural network. Further structural details are contained in reference 1.

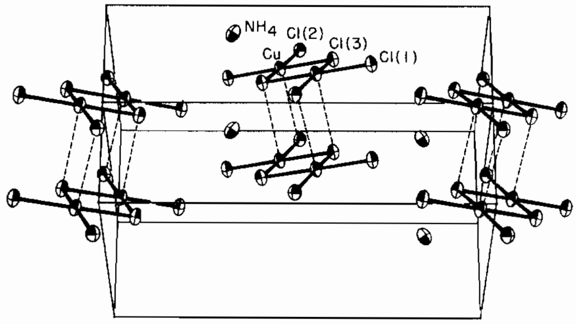

Fig. 1. A unit cell view of the structure of NH_4CuCl_3.

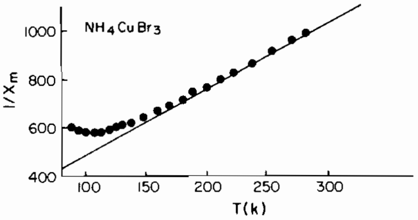

Fig. 2. A plot of inverse susceptibility (△△△) and χ_mT (•••) *versus* temperature for NH_4CuCl_3.

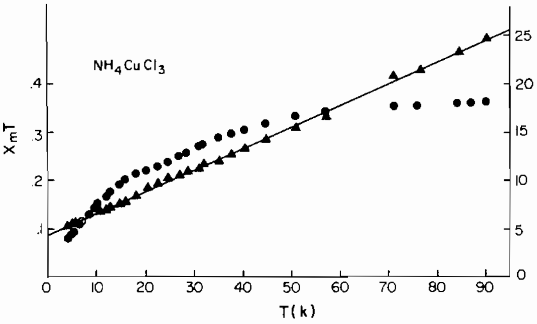

Fig. 3. A plot of inverse susceptibility *versus* temperature for NH_4CuBr_3.

The magnetic data for NH_4CuCl_3 and NH_4CuBr_3 are shown in Figs. 2 and 3, respectively. The chloride salt shows simple Curie–Weiss behavior with C = 0.45 (g = 2.19) and θ = –44 K. Thus the interdimer exchange coupling is sufficiently strong to obscure the individual intradimer interactions. This behavior is in contrast to that of the isostructural $KCuCl_3$ salt, the data for which show well defined antiferromagnetic coupling, with a singlet–triplet energy separation of $\Delta E/k$ = 55 K. Thus, the ammonium ion must provide much more substantial superexchange pathways than the potassium ion. The data for the bromide salt shows a maximum in susceptibility (a minimum in $1/\chi$) at ~110 K, characteristic of dimeric systems. Samples were plagued with impurities, both paramagnetic and diamagnetic, and so a detailed analysis could not be made. The high temperature data obeyed the Curie–Weiss law with C = 0.36 and θ = –206, the low value of the Curie constant being due to the presence of diamagnetic impurities. The temperature at which the susceptibility is a maximum for the dimer system occurs at $\Delta E/kT_{max}$ = 1.6. Thus a value of $\Delta E/k$ ~ 180 K can be estimated from the data. This is in good agreement with the results for $KCuBr_3$, where $\Delta E/k$ = 190 K.

The magnetic behavior of these two salts confirm the general conclusion that the antiferromagnetic exchange coupling in $Cu_2X_6^{2-}$ salts is much stronger for X = Br than for X = Cl.

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