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The Interaction of Hydrazine with Copper(II) Chloride in Acidic Solutions.
The Formation, Spectral and Magnetic Properties, and Structures of
Copper(II), Copper(I), and Mixed Valence Species.

By

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Abstract

The reaction of hydrazine with copper(II) chloride in acidic aqueous solution has been shown to produce at least four distinct complexes. Hydrazine behaves as a reducing agent, leading to the white, diamagnetic copper(I) complex $(N_2H_4)CuCl$ and the black paramagnetic mixed-valence copper(I,I,II) complex $(N_2H_5)_2Cu_3Cl_6$. Blue and green copper(II) complexes $(N_2H_5)_2CuCl_4 \cdot 2H_2O$ and $(N_2H_5)CuCl_3$ are also formed. Infrared spectra establish the presence of coordinated hydrazinium ions in the blue, green, and black compounds. Structures are proposed for all of these materials based on spectroscopic and magnetic measurements. Significant exchange interactions are present in the chloride-bridged linear chain complex $(N_2H_5)CuCl_3$. The structure of the complex $(N_2H_5)CuCl_3$ has been determined from single crystal X-ray counter data. The complex crystallizes in the orthorhombic space group $Pnma$ with four molecules in a cell of dimensions $a = 14.439(2)$, $b = 5.705(1)$, and $c = 6.859(1)$ Å. The structure has been refined by full-matrix least-squares techniques to a conventional R-factor (on F) of 0.042 using 538 independent observations. The entire formula unit (with the exception of some of the hydrogen atoms) is constrained to lie on a mirror plane. The structure consists of infinite chains of dichloro-bridged dimers, in which one chloride ligand serves to propagate the chain in both directions while the other two chloride ligands do not. Thus, one chloride ligand is coordinated to three copper atoms with an in-plane distance of $2.297(1)$ Å and two out-of-plane separations of $2.8560(5)$ Å, while the other two chloride ligands are each coordinated to only a single copper center with bond lengths of $2.280(1)$ and $2.298(2)$ Å. The Cu-Cu' separation and bridging Cu-Cl-Cu' angle in the chain are $3.751(1)$ Å and $92.79(3)^\circ$, respectively.

Introduction

Hydrazine, like other polybasic ligands, offers the possibility of several different types of coordination behavior toward transition metals. It can, of course, function as a monodentate ligand, but may also serve as either a bridging or chelating bidentate ligand. Although numerous examples of both monodentate and bridging hydrazine have been demonstrated crystallographically, no verified examples of chelatively bound hydrazine have been reported.² Another coordination possibility exists as well. The mono-protonated hydrazinium cation, $N_2H_5^+$, retains a basic site, and should be capable of coordination. Although postulated in certain cases, the only adequately characterized complexes containing coordinated hydrazinium ion are the series $[M^{II}(N_2H_5)_2(SO_4)_2]_n$, $M = Cr, Co, Ni, Cu, \text{ or } Zn$.³ A further complication, or possibility exists for the interaction of hydrazine with transition metals; hydrazine is a potent reducing agent in aqueous solution, so that depending upon the particular metal ion involved, various redox reactions are possible in addition to the coordination possibilities.

We have been interested in the relationship between the structural properties and magnetic exchange interactions in chloride-bridged dimeric copper compounds.⁴ Since the number of chloride-bridged copper dimers is rather small, we have attempted to prepare new examples of this structural type. The complex di- μ -chloro-bis[dichloro-(guaninium)copper(II)] dihydrate is known to be a chloride bridged dimer,⁵ and it is also one of the few structurally characterized examples of a transition-metal complex containing a positively-charged ligand. We reasoned that complexes of similar stoichiometry, and possibly comparable geometry, might be available from the reaction of copper salts with a variety of polybasic ligands under conditions where monoprotonation of the ligand is expected. We report here our results on the reactions between hydrazine and copper(II) chloride in acidic media, reactions which appear to involve redox reactions as well as coordination of both neutral and protonated hydrazine.

Experimental

Preparation of Complexes

In general, it appears that most of the complexes discussed in this work may be formed under a wide variety of reaction conditions, and in fact most reactions led to mixtures of products. The preparative details outlined here are those which we believe to be the most facile routes which lead reproducibly to pure products.

Hydrazinium trichlorocuprate(II). Addition of 4.6 g (44 mmoles) of $N_2H_4 \cdot 2HCl$ to a solution of 7.5 g (44 mmoles) of $CuCl_2 \cdot 2H_2O$ in 25 ml of 3M HCl produced an immediate light green precipitate which was filtered from the solution. Upon refrigeration the filtrate deposited bright green crystals of product.

Anal. Calcd. for $(N_2H_5)CuCl_3$: Cu, 31.31; N, 13.80; H, 2.48. Found: Cu, 31.19; N, 13.52; H, 2.52.

Bishydrazinium tetrachlorocuprate(II) dihydrate. The initially formed light green precipitate (see above) was added to 40 ml of 3 M HCl and heated to 45°C for a few minutes. Following filtration the solution was refrigerated; shiny blue crystals deposited.

Anal. Calcd. for $(N_2H_5)_2CuCl_4 \cdot 2H_2O$: Cu, 20.66; N, 18.22; H, 4.59; Cl, 46.12. Found: Cu, 20.42; N, 18.24; H, 3.68; Cl, 46.20.

Bishydrazinium hexachlorotricuprate(I,I,II). A solution of 3.5 g (20 mmoles) of $CuCl_2 \cdot 2H_2O$ and 2.2 g (20 mmoles) of $N_2H_4 \cdot 2HCl$ in 30 ml of 3M HCl was heated to 75°, with stirring, for approximately five minutes. Upon cooling to room temperature black crystals formed which were filtered, washed with 3M HCl and acetone, and air-dried. (If the solution is allowed to remain in contact with the air prior to isolation of the product, a green crust forms on the surface).

Anal. Calcd. for $(N_2H_5)_2Cu_3Cl_6$: Cu, 40.61; N, 11.94; H, 2.15; Cl, 45.31. Found: Cu, 40.39; N, 11.58; H, 2.18; Cl, 45.40.

Hydrazinechlorocuprate(I). A solution of 8.0 g (47 mmoles) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 4.8 g (46 mmoles) of $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ in 45 ml of 1 M HCl was heated to near boiling for approximately 10 minutes. Upon standing at room temperature the solution deposited shiny white crystals. The solution was filtered in a nitrogen-filled glove bag and washed with water to remove traces of a black impurity which was commonly present.

Anal. Calcd. for $\text{N}_2\text{H}_4\text{CuCl}$: Cu, 48.49. Found: Cu, 48.42. The instability of this complex (see text) precluded other meaningful microanalyses.

Measurements

Magnetic susceptibilities as a function of temperature and applied field were measured as has been described previously.⁶ Data were corrected for diamagnetism of the constituent ions and for temperature independent paramagnetism, (TIP), estimated to be 60×10^{-6} cgsu for Cu(II).

Electronic spectra in the visible and near-infrared regions were obtained using a Cary 14 spectrophotometer. Samples were prepared as Nujol mulls on filter paper. The quality of the spectra was limited by thermal decomposition of the materials in the spectrometer light path.

Infrared spectra for samples prepared as both KBr pellets and Nujol mulls on KBr plates were obtained using a Beckman IR-20A spectrophotometer. Low-frequency ($500\text{-}100\text{ cm}^{-1}$) spectra of Nujol mulls on polyethylene plates were obtained using a Digilab FTS-14 FT interferometer.

Room-temperature EPR spectra were obtained using a Varian E-3 spectrometer. The magnetic field was determined directly from the calibrated chart paper. This technique was checked with a Magnion G-502 precision gaussmeter, a Hewlett-Packard 5245 L frequency counter, and a DPPH sample; the results indicated that the accuracy was better than 1%.

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

Results and Discussion

There have been a number of reports of the reaction of copper complexes with hydrazine. In aqueous solution, reaction of copper(II) salts with hydrazine hydrate leads to complexes $\text{Cu}_2(\text{N}_2\text{H}_4)_2\text{X}_2$, which have been characterized as containing bridging hydrazine by analogy to the Mn^{+2} and Zn^{+2} analogs.² Distinct dihydrates^{7,8} (for $\text{X}_2 = \text{SO}_4^{2-}$ and $\text{X} = \text{Br}^-$) and two monohydrates^{7,9} (for $\text{X} = \text{I}^-$ and $\text{X} = \text{Cl}^-$) of this general formula have also been reported, and solution equilibrium measurements have indicated the existence of $\text{Cu}(\text{N}_2\text{H}_4)_y^{+2}$, $y = 1, 2, 3, 4, 5$.¹⁰ If copper chloride is neutralized to $\text{pH} = 7$ prior to reaction with hydrazine, a diamagnetic complex, presumed to be a diimide complex of copper(I), is formed.¹¹ Oxidation of substituted hydrazines by cupric salts in aqueous solution leads to isolable and well-characterized diazine complexes,¹²⁻¹⁴ e.g., $(\text{CH}_3\text{N}=\text{NCH}_3)\text{Cu}_2\text{Cl}_2$. Distinct hydrazine complexes of copper(I)^{15,16}, as well as mixed-valence copper(I,II) complexes with substituted hydrazines,^{17,18} have also been reported. There has apparently been only one report of the reaction between copper(II) complexes and hydrazine in acid solutions.¹⁹ Although no characterization other than analytical formulations was provided, three of the complexes reported (the blue, green, and black complexes) appear to be identical to those found in our study.

The course of the reaction between hydrazine hydrochloride and copper(II) chloride in hydrochloric acid solution, and hence the identity of the products isolated, is highly dependent upon the specific conditions used - reagent and acid concentrations, reaction temperatures, duration of reaction, and crystallization temperatures. In fact, in a typical reaction all of the products (hereafter referred to as the blue, green, black, and white complexes) to be discussed are formed, but in varying yields and purity. The conditions outlined in the experimental section are simply those which we have found to be most likely to lead to the pure complexes in reasonable yield. In investigations of the kinetics of oxidation of hydrazine by various reagents, it has been claimed that cupric ion does not react

at an appreciable rate with hydrazine in acid solution.²⁰ However, under the conditions of high concentration and elevated temperature used in our preparative work, redox reactions are facile, as judged by both the extensive gas (presumably nitrogen) evolution observed and the isolation of distinct copper(I) containing products.

Although all of the products are sufficiently stable that they may be readily isolated and characterized, color changes indicate that, over long periods of time, most undergo some reaction. The variety of color changes which do occur suggest that several more stable copper-hydrazine phases may exist. Indeed, instability is not surprising for complexes containing both oxidizing and reducing agents. The white complex, $(N_2H_4)CuCl$, is readily air-oxidized, and unless it is isolated in an inert atmosphere the resulting product is gray or black in color. Based on EPR spectra, the black material which forms upon exposure of the white complex to air is not the black mixed-valence complex discussed in detail below. Over long periods of time, the formation of a green color is observed as well. The specifics of the color changes observed for the Cu(II) complexes are somewhat unexpected. Upon standing open to the air for a period of several months, the green complex $(N_2H_5)CuCl_3$ turns black, although samples in closed vials retain their green color. In contrast, the blacked mixed-valence complex $(N_2H_5)_2Cu_3Cl_6$ develops a green color upon standing in closed vials over a period of a few weeks. Of the complexes examined in this work, only the color of the blue $(N_2H_5)_2CuCl_4 \cdot 2H_2O$ appears to be unchanged with time. It should be emphasized that, based on EPR measurements, these decomposition products do not represent simple interconversions, e.g., the green product derived from decomposition of the black $(N_2H_5)_2Cu_3Cl_6$ is not equivalent to the green complex $(N_2H_5)CuCl_3$.

The sensitivity of these compounds was further demonstrated during our attempts to obtain infrared spectra. Although the white and black complexes yielded KBr pellets readily, grinding the blue complex with KBr produced a green mixture, and

grinding the green complex with KBr produced a light orange mixture which darkened with time. Although such color changes could be indicative of pressure induced decomposition, it is more likely that they represent solid state reactions, either bromide for chloride metatheses or cleavage of bridging halide bonds. That the proper explanation is halogen exchange is suggested by the observation that these color changes do not occur upon grinding with potassium chloride.

These materials which we have prepared are sufficiently different that we will examine them individually in the discussion which follows.

$(N_2H_4)CuCl$. This white complex is quite air-sensitive, turning grey and then black upon exposure to air. Air-oxidation is likely, given its formulation as a copper(I) complex. Also, the static susceptibility measurements and epr spectra are in accord with its formulation as a copper(I) complex. The compound is diamagnetic, and the weak EPR signals, which increase with exposure to air, may be attributed to copper(II) oxidation products.

There have been only a few reports of complexes of hydrazines with copper(I). Reaction of anhydrous hydrazine with anhydrous copper(II) chloride near 0°C gives the white solid $CuCl_2 \cdot 3N_2H_4$ (sic), which was formulated¹⁶ as a mixture of $N_2H_4 \cdot HCl$ and $CuCl \cdot 2N_2H_4$. The same copper complex $CuCl \cdot 2N_2H_4$ was more simply prepared from reaction of copper(I) chloride with anhydrous hydrazine. Based on an observed conductivity in hydrazine which is appropriate for a 1:1 electrolyte, the complex was postulated to be the linear cationic species $[Cu(N_2H_4)]^+Cl^-$.¹⁶ This formulation is somewhat suspect, however, since the reported nitrogen infrared stretching frequency, 959 cm^{-1} , is in the range expected for either bridging hydrazine or monoprotonated hydrazine.²¹ More closely related by empirical formula to the present compound is a white complex of phenylhydrazine, $(C_6H_5NHNH_2)CuI$, which may be prepared from the copper(I) salt.¹² Perhaps the best model for the expected structure of $(N_2H_4)CuCl$ is the analogous species

$(N_2H_4)CuCN$, a material whose structure has been determined crystallographically.¹⁵ In this complex infinite zigzag chains of cyanide bridged copper ions are bridged by hydrazine, forming infinite puckered layers which nest together. We propose a similar structure for $(N_2H_4)CuCl$, based on the following reasoning. First, the physical properties of the crystals are correct. As initially formed, the crystals of $(N_2H_4)CuCl$ have the appearance of mica. This is compatible with a layered structure as observed for $(N_2H_4)CuCN$. Infrared spectra are also compatible with this formulation. Previous work²¹ has shown that ν_{N-N} for unidentate hydrazine falls in the range $931-936\text{ cm}^{-1}$, whereas ν_{N-N} for bridging hydrazine falls in the range $948-980\text{ cm}^{-1}$. The value of 960 cm^{-1} observed here for $(N_2H_4)CuCl$ clearly establishes the presence of bridging hydrazine. This result is again compatible with the proposed structure.

The synthesis of this compound is undoubtedly the least predictable of all the materials examined, and the preparation is very sensitive to reaction conditions. Upon occasion, efforts to synthesize $(N_2H_4)CuCl$ have led to the isolation of $CuCl$, which was identified by analysis, crystal morphology, and lack of air sensitivity. Attempted preparation of the complex in more dilute acid (0.01 M) led to a complex of apparent composition $(N_2H_5)CuCl_2$. This white, diamagnetic, solid decomposes thermally in vacuo to produce hydrazinium chloride. Efforts to reproducibly prepare this material in pure form were unsuccessful.

$(N_2H_5)_2Cu_3Cl_6$. One of the most surprising materials formed in these studies is $(N_2H_5)_2Cu_3Cl_6$, a compound which appears as opaque black crystals. This formulation, which involves protonated hydrazine as either ligand or counterion, requires that copper be present as a mixture in the +1 and +2 oxidation states. Analytically, the only distinction between this formulation and one involving neutral hydrazine (and hence a singly-valent copper(II) complex) would be the hydrogen content. Although it might be argued that the accuracy of the analyses is insufficient to

distinguish these possibilities, the mixed-valence formulation is clearly favored, and a variety of magnetic and spectroscopic evidence provides firm support for the existence of both oxidation states.

Infrared spectra demonstrate the existence of hydrazinium cations and thus provide confirmation of the mixed-valence nature of the complex. The N-N stretching frequencies of hydrazine and its salts and complexes are generally sufficient to distinguish the various coordination possibilities.²¹ The uncoordinated hydrazinium ion has ν_{NN} in the range of 958-965, depending on the counterion, and this may be contrasted to free hydrazine, which has $\nu_{\text{NN}} = 885 \text{ cm}^{-1}$. Although the free hydrazinium ion may be distinguished from bidentate hydrazine ($\nu_{\text{NN}} = 931-936 \text{ cm}^{-1}$), there is some overlap with bridging hydrazine ($\nu_{\text{NN}} = 948-980 \text{ cm}^{-1}$). However, coordinated hydrazinium cation may be distinguished from all other possibilities²² by its high N-N stretching frequency near 1000 cm^{-1} . $(\text{N}_2\text{H}_5)_2\text{Cu}_3\text{Cl}_6$ exhibits $\nu_{\text{NN}} = 1000 \text{ cm}^{-1}$ in Nujol mulls, and a doublet $\nu_{\text{NN}} = 1000, 992 \text{ cm}^{-1}$ in KBr pellets. Although the splitting of the band in KBr pellets may reflect either low symmetry in the complex, solid-state effects, or reaction with KBr, it should be noted that the complexes $\text{M}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$, which have symmetrically disposed hydrazinium ligands, also apparently exhibit a doublet near 1000 cm^{-1} . Thus, the existence of a coordinated hydrazinium ion in $(\text{N}_2\text{H}_5)_2\text{Cu}_3\text{Cl}_6$ is fairly well established by the infrared spectra.

More direct evidence for the existence of a mixed-valence copper complex comes from measurements of the magnetic susceptibility. Over the temperature range 2-60°K, the susceptibility exhibits Curie-Weiss behavior with a molar susceptibility χ_m , corrected for diamagnetic effects, given by

$$\chi_m = \frac{0.446}{T + 2.6}$$

where the susceptibility is calculated per formula unit, e.g., for three copper ions. This susceptibility leads to a room temperature magnetic moment $\mu_{\text{eff}}^{295} = 1.88 \text{ B.M.}$ per formula unit. This value is in the range typically found for isolated copper(II)

ions, and demonstrates that of the three copper ions in the formula unit, only one is copper(II). By comparison, the magnetic moment calculated per copper ion is $\mu_{\text{eff}}^{295} = 1.08$ B.M. Such a value is much too low for non-interacting copper(II) ions, and since the linearity of the reciprocal susceptibility versus temperature plots rules out significant exchange interactions, it must be concluded that two of the three copper ions are present as copper(I), rather than copper(II).

A large number of mixed-valence copper complexes are known.²³ With both amine and halogen ligands, the most commonly encountered formulations are species of the sort $[\text{Cu}^{\text{II}}\text{A}_4][\text{Cu}^{\text{I}}\text{X}_2]_2$. We propose that the complex $(\text{N}_2\text{H}_5)_2\text{Cu}_3\text{Cl}_6$ is a similar species which is most appropriately formulated as $[\text{Cu}^{\text{II}}(\text{N}_2\text{H}_5)_2\text{Cl}_2][\text{Cu}^{\text{I}}\text{Cl}_2]_2$. Unlike the simple amine complexes where the +2 cation results from coordination of four neutral ligands to copper(II), in this case the +2 cation arises from the coordination of two positively charged ligands and two negatively charged ligands to copper(II). Although other formulations are possible, the requirement for coordinated hydrazinium ion, as demonstrated by infrared spectra, the lack of magnetic exchange interactions between copper(II) sites demonstrated by magnetic susceptibility measurements, and the similarity of the empirical formula to known species establishes this as the most likely formulation. Although such an ionic formulation could be verified through the measurement of conductivities, its instability in solution precludes such measurements. The complexes $[\text{CuA}_4][\text{CuX}_2]_2$, which range in color from dark green to dark blue, are claimed to be Class I mixed-valence compounds, e.g., to contain noninteracting copper(I) and copper(II) sites.²³ The deep black color of $(\text{N}_2\text{H}_5)_2\text{Cu}_3\text{Cl}_6$, however, suggests the presence of some interaction, e.g., Class II behavior. Although no specific feature of the electronic spectrum could be assigned as an intervalence transfer transition, the very broad absorption through the entire visible region of the spectrum is consistent with the presence of several unresolved transitions. Weak interaction of copper(I) and copper(II) via bridging chloride seems likely, given both the

proclivity of copper(II) to attain coordination numbers greater than four and also the evidence for interaction via bridging cyanide in $\text{Cu}_3(\text{NH}_3)_4(\text{CN})_4$.²⁴

$(\text{N}_2\text{H}_5)\text{CuCl}_3$. Part of our initial interest in the complexes of hydrazine with copper lay in the possibility of preparing, and then examining magnetically and structurally, chloride-bridged copper(II) dimers. By analogy to the structurally characterized⁵ material di- μ -chlorobis[dichloro(guaninium)copper(II)]dihydrate, the green complex hydraziniumtrichlorocopper(II) appeared to offer the best possibility for observing such behavior. In fact, the evidence shows that the complex is a chloride-bridged polymer, rather than a dimer.

Infrared spectra of $(\text{N}_2\text{H}_5)\text{CuCl}_3$ demonstrate the presence of the coordinated hydrazinium ion. In the N-N stretching region, Nujol mull spectra exhibit a single absorption at 995 cm^{-1} , and KBr pellet spectra exhibit a doublet at 1005 and 992 cm^{-1} . As mentioned previously, there is a color change (from green to orange) upon grinding this complex with KBr, and the apparent substitution reaction may be responsible for the observation of distinct N-N stretching frequencies in KBr pellets. As discussed above for $(\text{N}_2\text{H}_5)_2\text{Cu}_3\text{Cl}_6$, the observation of the N-N stretch in this region unambiguously demonstrates the existence of the coordinated hydrazinium ion.

Although somewhat inconclusive, low-frequency infrared spectra suggest the presence of chloride bridging in $(\text{N}_2\text{H}_5)\text{CuCl}_3$. The complex exhibits doublets at 309 and 300 cm^{-1} and at 268 and 262 cm^{-1} . There is only limited precedent for the assignment of low-frequency infrared spectra of copper-halogen complexes, and apparently no comparison of terminal and bridging copper-chlorine stretching frequencies goes without debate. Published data²⁵ for a series of related complexes suggests that terminal copper-chlorine stretching frequencies fall near 300 cm^{-1} . We have examined the far-infrared spectra of several complexes known to contain bridging chlorides, and find that in addition to absorptions near 300 cm^{-1}

(attributable to terminal Cu-Cl), there are absorptions in the range 260-280 cm^{-1} . Thus, the observed absorptions at 268 and 262 cm^{-1} in $(\text{N}_2\text{H}_5)\text{CuCl}_3$ are suggestive of bridging chloride. For comparison, the complex $(\text{N}_2\text{H}_5)_2\text{Cu}_3\text{Cl}_6$, which apparently contains no chloride bridges between copper(II) ions, exhibits no absorptions in the 200-280 cm^{-1} region.

The presence of multicenter spin-spin interactions, and hence the necessity of chloride bridges, is clearly demonstrated by the magnetic susceptibility. Figure 1 is a plot of susceptibility versus temperature in the range 2-74 K. As can be seen, the susceptibility exhibits a broad maximum centered at 11.4 K, consistent with the presence of antiferromagnetic interactions. The data could be reproduced fairly well using the modified Bleaney-Bowers expression²⁶ (eq. 1) for exchange-coupled copper(II) dimers;

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

which results from a consideration of the eigenvalues of (2), the

$$H = -2J \hat{S}_1 \cdot \hat{S}_2 \quad (2)$$

Heisenberg exchange Hamiltonian. However, the value of one parameter obtained from this fitting procedure is unreasonable. Although the values $2J = -6.5 \text{ cm}^{-1}$ and $g = 2.12$ are in the range commonly encountered for chloride bridged copper(II) ions, the value of $\theta = -15.5 \text{ K}$ casts doubt on the validity of the application of the dimer model to this complex. The parameter θ is an indicator of intermolecular interactions. In this case, then, the results suggest that the intermolecular exchange interactions are significantly larger than the intramolecular exchange interactions, a conclusion which is clearly incompatible with the existence of dimeric $(\text{N}_2\text{H}_5)\text{CuCl}_3$.

In order to understand this unusual magnetic behavior we have carried out a structural determination by single-crystal X-ray diffraction methods. Green, hexagonal plate-shaped crystals were obtained as stated above. On the basis of Weissenberg and precession photographs, the crystals were assigned to the orthorhombic system. The observed systematic absences are $0k1$ for $(k+1)$ odd and $nk0$ for h odd, which suggests that the space group is either $Pnma$ (D_{2h}^{16}) or $Pn2_1a$ (C_{2v}^9). The former (centrosymmetric) choice was verified by the structure refinement (vide infra). The cell constants, obtained by least-squares methods, are $a = 14.439(2)$, $b = 5.705(1)$, $c = 6.859(1)$ Å. The observations were made at a temperature of 22°C with the wavelength assumed as $\lambda(\text{MoK}\alpha_1) = 0.7093$ Å. A density of 2.386 g cm^{-3} calculated for four formula units per cell is in good agreement with the value of $2.41(3) \text{ g cm}^{-3}$ observed by flotation in chloroform/bromoform mixtures. Hence, in space group $Pnma$, the copper atom and at least one chlorine atom are constrained to lie on either an inversion center or a mirror plane; only the latter choice is consistent with the known formulation of the complex.

Diffraction data were collected from a crystal bounded by planes of the forms $\{100\}$, $\{001\}$ and the faces $(01\bar{1})$, $(0\bar{1}1)$, (021) , $(0\bar{2}\bar{1})$. The distances between opposite faces were as follows: (001) to $(00\bar{1})$, 0.13 mm; (100) to $(\bar{1}00)$, 0.09 mm; $(01\bar{1})$ to $(0\bar{1}1)$, 0.22 mm; (021) to $(0\bar{2}\bar{1})$, 0.27 mm. The crystal was mounted approximately parallel to the crystallographic b -axis, and in this orientation intensity data were collected on a Picker four-circle automatic diffractometer using $\text{MoK}\alpha$ radiation and a graphite monochromator. The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω -scan technique and was judged to be acceptable.

Twelve reflections, accurately centered through a narrow vertical slit at a takeoff angle of 1.2° , formed the basis of the least-squares refinement of cell

parameters and orientation using the logic documented by Busing and Levy for the PDP-8/L computer.²⁷

Intensity data were collected at a takeoff angle of 3.3° , with a counter aperture of 5.0 mm x 5.0 mm positioned 32 cm from the crystal. The data were collected by the θ - 2θ scan technique at a scan rate of $2.0^\circ \text{ min}^{-1}$. The peaks were scanned from 0.80° to -2θ below the calculated $K\alpha_1$ peak position to 0.80° in 2θ above the calculated $K\alpha_2$ peak position. Stationary-counter, stationary-crystal background counts of 4s were taken at each end of the scan. The pulse-height analyzer was set for approximately a 90% window, centered on the $\text{MoK}\alpha$ peak.

A unique data set having $3^\circ < 2\theta < 55^\circ$ was collected; a total of 717 intensities was recorded. The intensities of three standard reflections, measured after every 100 reflections, showed appreciable decline during the run, and a linear correction was applied to the data to allow for diminished intensity with cumulative exposure.

Data processing was carried out as described by Corfield *et al.*²⁸ After correction for background, the intensities were assigned standard deviations according to the formula

$$\sigma(I) = [C + 0.25(ts/tb)^2(BH + BL) + (pI)^2]^{1/2}$$

where the value of p was selected as 0.05. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects, and for absorption. The absorption coefficient for this compound for $\text{MoK}\alpha$ radiation is 52.2 cm^{-1} , and for the crystal chosen the transmission coefficients were in the range 0.31 to 0.44 with an average value of 0.40. Of the 717 data collected, 552 were greater than three times their estimated standard deviations; in addition to the exclusion of data with I less than 3σ , fourteen data with counts greater than 1×10^6 , which had flooded the counter, were excluded. Thus 538 data were used in the subsequent structure analysis and refinement.

The structure was solved by direct methods using the highest 145 normalized structure amplitudes (E's) in the program MULTAN.^{29,30} The chosen solution, which had an R_{Karle} of 21.11 and an absolute figure of merit of 1.0557, gave an E map that clearly revealed the location of the copper and three independent chlorine all on the crystallographic mirror plane at $y = 1/4$. A structure factor calculation followed by a difference Fourier synthesis revealed the positions of the two nitrogen atoms, also on the mirror plane. Isotropic least-squares refinement of these 6 positions led to values of the conventional agreement factors $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0| = 0.189$ and $R_2 = [\sum w(|F_0| - |F_c|)^2 / \sum w F_0^2]^{1/2} = 0.276$. All least-squares refinements in this study were carried out on F , the function minimized being $\sum w(|F_0| - |F_c|)^2$, where the weights w were taken as $4F_0^2 / \sigma^2(F_0^2)$. In all calculations of F_c , the atomic scattering factors for nonhydrogen atoms were from International Tables³¹ while those for hydrogen were from Stewart *et al.*³² Subsequent anisotropic least-squares refinement on these atoms gave $R_1 = 0.062$ and $R_2 = 0.077$. The hydrogen atoms were then located in a difference Fourier map. Attempts to refine these hydrogen atom parameters were not successful. An attempt to refine the structure in the non-centrosymmetric space group $Pn2_1a$ [an alternate setting of the conventional $Pna2_1$ (No. 33)] was also unsuccessful in that the y -coordinates of the heavy atoms and their associated thermal parameters oscillated wildly. Least-squares refinement was therefore continued in the centrosymmetric space group $Pnma$, with the hydrogen atoms assigned fixed isotropic thermal parameters which exceeded the isotropic thermal parameter of the atom to which they were bonded by 1.5 \AA^2 . In the final cycles of least-squares refinement, no hydrogen parameter was varied, non-hydrogen atoms were refined anisotropically and the data were corrected for secondary extinction,^{33,34} yielding final values for R_1 and R_2 of 0.042 and 0.059, respectively. In the final cycle of least-squares refinement, no parameter experienced a shift of more than 0.03 σ , which is taken as evidence of convergence. The positional parameters, along with their standard deviations as estimated from the inverse matrix, are listed in Table I. The thermal parameters and a compilation of

of observed and calculated structure amplitudes are available as supplementary material. The final value of the extinction coefficient was $7(2) \times 10^{-8}$.

Description of the Structure

The complex is polymeric in the crystal, the coordination around each copper(II) center being the commonly observed tetragonally elongated (4+2) octahedral. The four in-plane (short) bonds are to the three chloride ligands, Cl(1), Cl(2), and Cl(3) and to the nitrogen atom N(1) of the hydrazinium cation. The out-of-plane (long) bonds are to the basal Cl(1) atoms of the copper atoms above and below. The coordination around a single copper atom is shown in Figure 2, and views of the bridging network and consequent chain structure are shown in Figures 3 and 4. Since the copper and all the in-plane atoms in the complex lie on a crystallographic mirror plane, these five atoms are strictly coplanar. This polymeric structure in which one halide ligand is bound to three adjacent copper atoms while the others are terminal is uncommon, but has been observed before in the bromide-bridged polymers dibromo[2-(2-aminomethyl)pyridine]copper(II) and dibromo(2-methyl-1,2-diaminopropane)copper(II);³⁵ this present complex represents the first such example involving chloride bridges, however.

The interatomic distances and angles observed in the complex are listed in Tables II and III. The in-plane Cu-Cl bond lengths of 2.280(1), 2.297(1), and 2.298(2) Å are similar to those found in a variety of other chloro-bridged copper(II) complexes.^{36,37} The Cu-N bond of 2.061(5) Å is longer than those of 1.971(2) and 1.984(2) Å in $\text{Cu}(\text{NH}_3)_2(\text{CO}_3)$ ³⁸ and in most other copper-amine complexes,³⁹ but is consistent with the reported length of 2.08 Å in the zinc hydrazinium complex $\text{Zn}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$.³

The Cu-Cu separation in the chain is 3.751(1) Å, the out of plane Cu-Cl(1)' and associated Cu-Cl(1)''-Cu' angle being 2.8560(5) Å and 92.79(3)°, respectively.

Thus, the bridging geometry here is different from that in the analogous bromide-bridged chains referred to earlier³⁵ in that the bridging angle here is obtuse while in those earlier structures it was acute. Indeed, in the present case the out-of-plane interaction is stronger than those of 3.109(2) and 3.260(6) Å in the bromide-bridged species (allowing for a difference of 0.15 Å between the radii of Br and Cl) but the larger bridging angle causes the Cu-Cu separation to be comparable with those of 3.866(2) and 3.737(6) Å in these complexes.

The N(1)-N(2) bond length of 1.457(7) Å is not significantly different from the value of 1.451(5) Å in neutral hydrazine and in neutral dimethylhydrazine.⁴⁰ The Cu-N(1)-N(2) bond angle is 119.1(3)°, apparently larger than the value of 110° in the zinc complex.³ Since the hydrogen atom parameters were not varied, it is difficult to make many conclusions concerning the hydrogen bonding in the crystals. It is apparent, however, that there is a strong hydrogen bond between N(2) [which has the additional proton] and the terminal atom Cl(3) of a neighboring chain; the N(2)····Cl(3) distance and associated N(2)-H····Cl(3) angle are 3.111(5) Å and 174°.

(N₂H₅)₂CuCl₄·2H₂O. This bright blue crystalline complex forms upon recrystallization of the green (N₂H₅)CuCl₃. Unlike the other materials, it appears to be stable indefinitely. Although nitrogen, copper, and chlorine analyses are quite good for the formulation given, the value for hydrogen is approximately 20% low. Similarly low, but variable, results were found for other preparations of this material and probably reflect some decomposition pathway which complicates the microanalysis.

Magnetic susceptibility measurements are consistent with the existence of non-interacting copper centers. Over the temperature range 2.4 to 100°K the plot of reciprocal susceptibility vs. temperature is linear, with an intercept of -2°K.

The data provide an excellent fit to the Curie-Weiss law, the susceptibility being given by

$$\chi_m = \frac{0.4605}{T + 1.5} \text{ cgsu.}$$

The effective magnetic moment, 1.92 B.M., is normal for copper(II).

Infrared spectra are again consistent with the presence of coordinated hydrazinium ion in $(N_2H_5)_2CuCl_4 \cdot 2H_2O$. Observation of a single N-N stretching frequency at 1008 cm^{-1} in KBr pellets (1016 cm^{-1} in Nujol mulls) rules out uncoordinated hydrazinium ion such as is observed in $(N_2H_5)_2CdCl_4$.⁴¹

Based on the similarity in color and in empirical formula, it is tempting to expect similar structures for this material and the previously characterized $(N_2H_5)_2Cu(SO_4)_2$. This latter complex has a linear chain structure with bridging bidentate sulfate groups and trans hydrazinium ligands. Although magnetic exchange interactions are extremely weak in $(N_2H_5)_2Cu(SO_4)_2$,⁴² an analogous structure involving chloride bridges would be expected to show magnetic behavior comparable to $(N_2H_5)CuCl_3$. Since the complex appears to follow the Curie-Weiss law down to very low temperature, the magnetic measurements appear to preclude such a structure. On the basis of the available evidence, then, we suggest that the most probable structure for $(N_2H_5)_2CuCl_4 \cdot 2H_2O$ involve 6-coordinate monomeric copper complexes trans-bis(hydrazinium)tetrachlorocopper(II).

Conclusion

We have demonstrated that the reaction of hydrazine with copper(II) chloride in acidic solutions gives rise to a range of products differing significantly from those obtained in neutral solutions. The results indicate that protonated hydrazine reacts as both a reducing agent and as a ligand, the specific products formed being sensitive to conditions. Experiments designed to determine if this behavior is also

characteristic of substituted hydrazines have just been initiated; preliminary evidence suggests that a series of complexes is formed.

Acknowledgments

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Supplementary Material: A listing of observed and calculated structure amplitudes (3 pages) and a table of anisotropic thermal parameters, U_{ij} . Ordering information is given on any current masthead page.

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Table I. Positional Parameters for $[(N_2H_5)CuCl_3]$

Atom	x	y	z
Cu	0.4532 (1)	0.2500	0.1477 (1)
Cl1	0.5391 (1)	0.2500	-0.1341 (2)
Cl2	0.3754 (1)	0.2500	0.4370 (2)
Cl3	0.3191 (1)	0.2500	-0.0329 (2)
N1	0.5706 (3)	0.2500	0.3186 (7)
N2	0.6611 (3)	0.2500	0.2245 (7)
H11 ^a	0.575	0.130	0.375
H12	0.663	0.397	0.216
H13	0.711	0.250	0.309

^a Hydrogen atom positions were not varied

Table II. Interatomic Distances (\AA) in $(\text{N}_2\text{H}_5)\text{CuCl}_3$

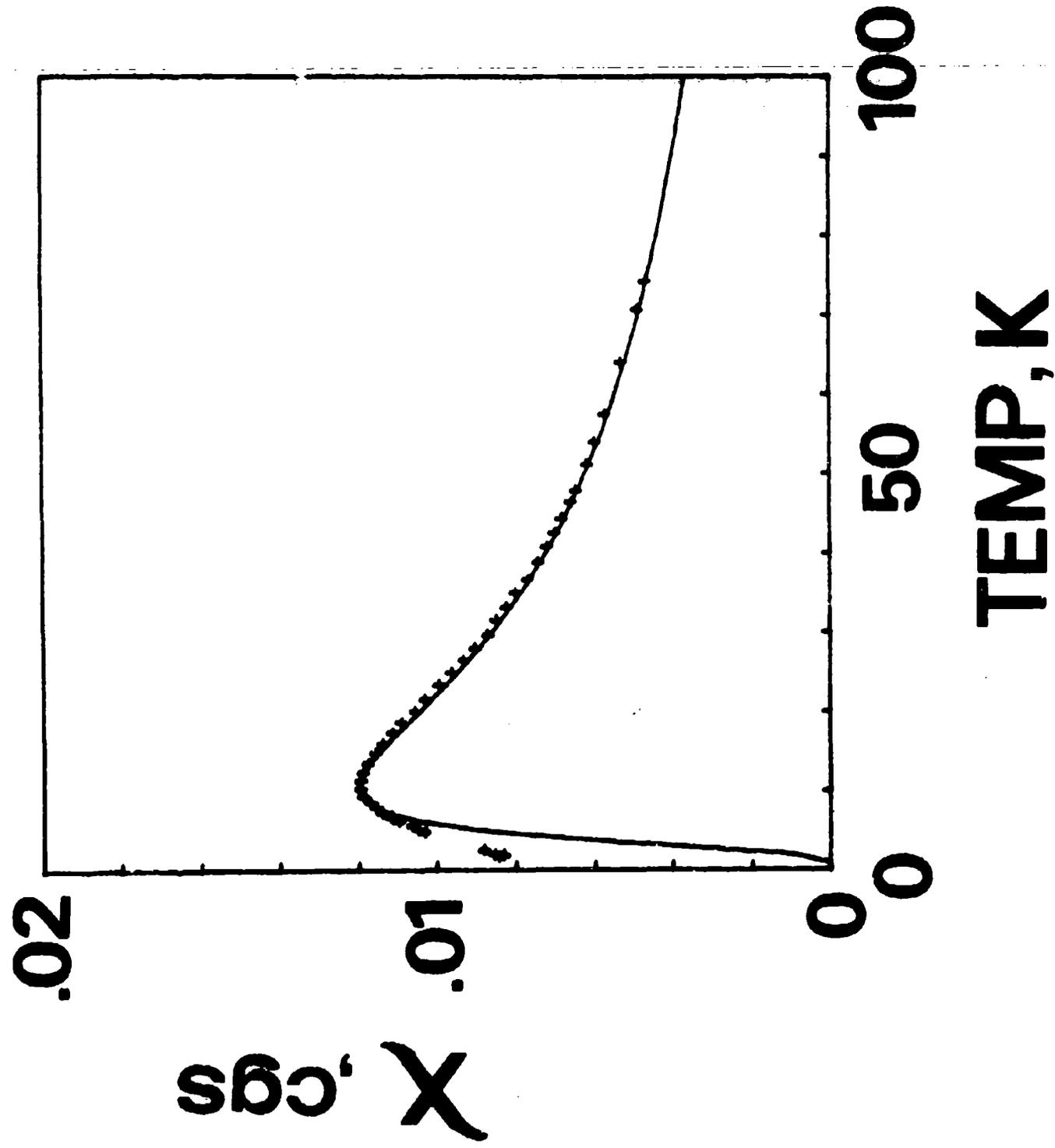
<u>Bond</u>	<u>Distance</u>
Cu-Cu	3.751(1)
Cu-CL1	2.297(1)
Cu-CL1'	2.856(1)
Cu-CL2	2.280(1)
Cu-CL3	2.298(2)
Cu-N1	2.061(5)
N1-N2	1.457(7)

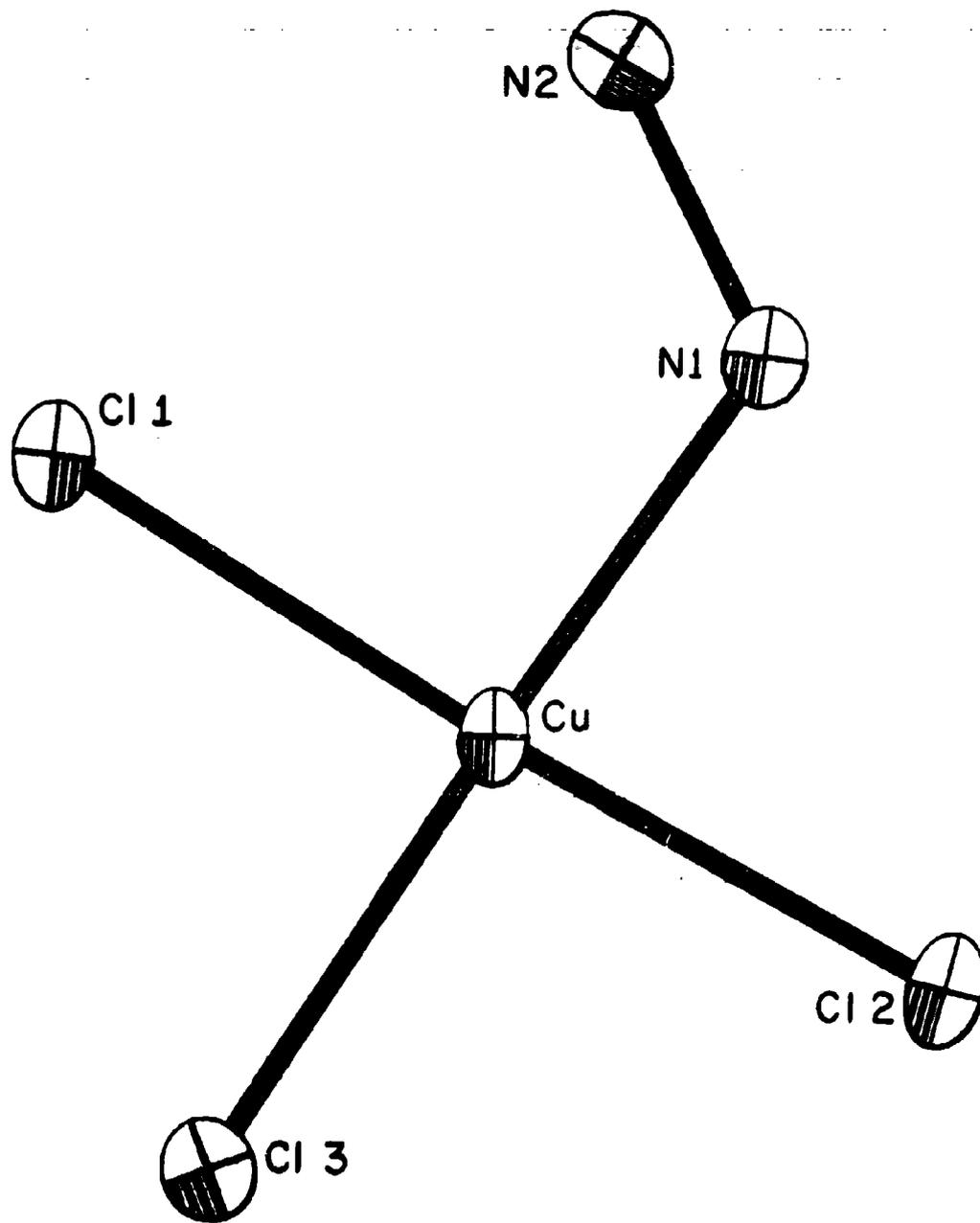
Table III. Interatomic Angles (Deg) in $(\text{N}_2\text{H}_5)\text{CuCl}_3$

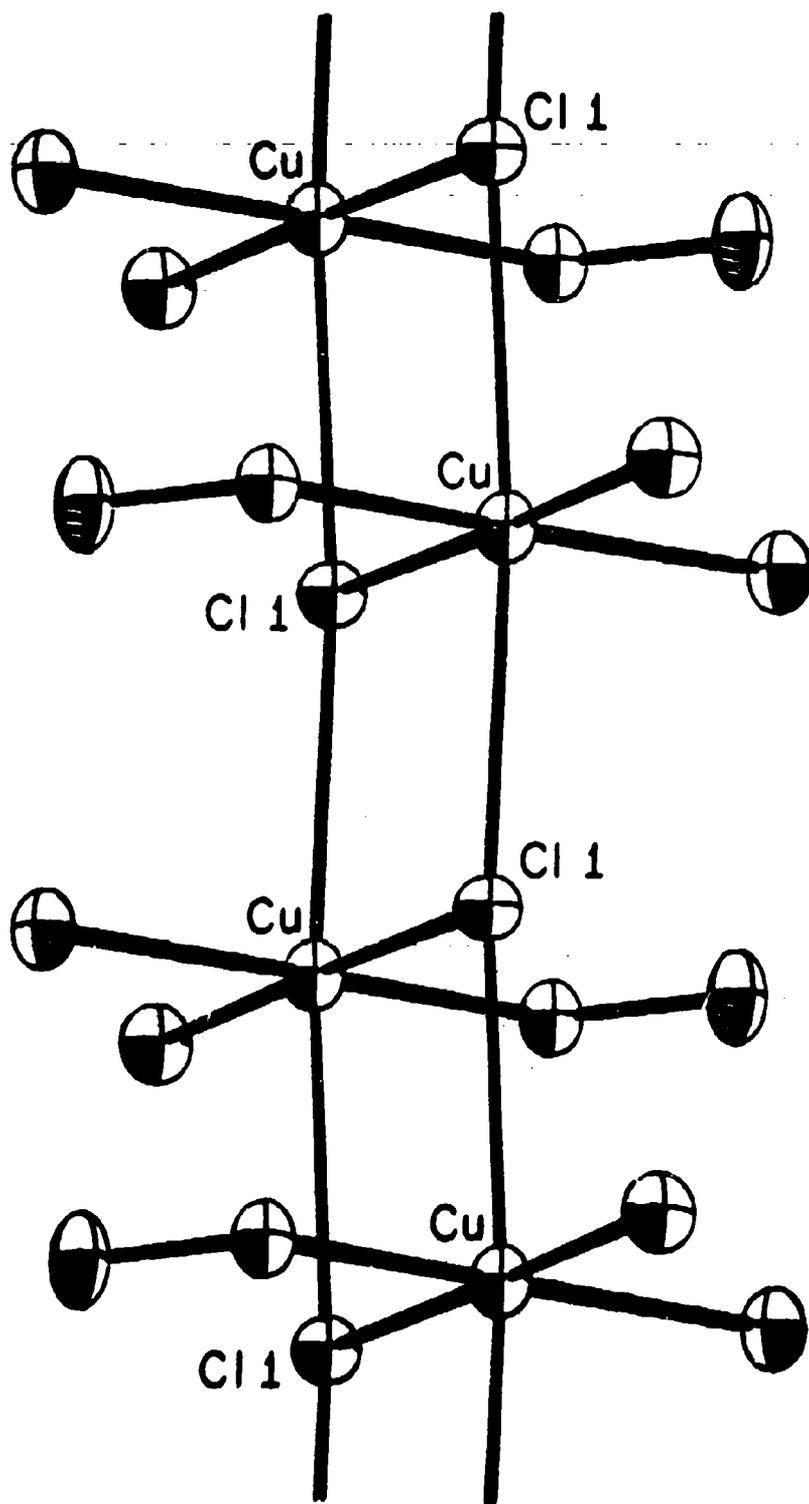
<u>Atoms</u>	<u>Angle</u>
Cu-CL1-Cu'	92.79(03)
CL1-Cu-N1	91.95(14)
N1-Cu-CL2	84.84(14)
CL2-Cu-CL3	93.12(06)
CL1'-Cu-CL2	92.74(03)
CL1'-Cu-CL3	90.87(03)
CL1'-Cu-N1	89.23(03)
CL1'-Cu-CL1''	174.15(07)
N2-N1-Cu	119.06(31)

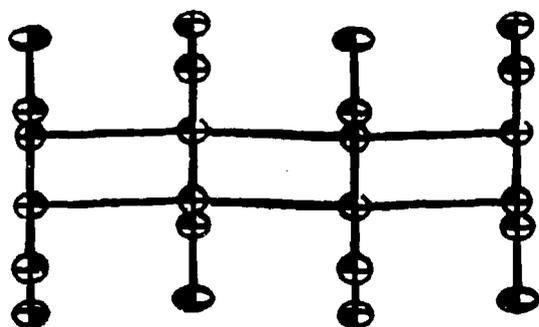
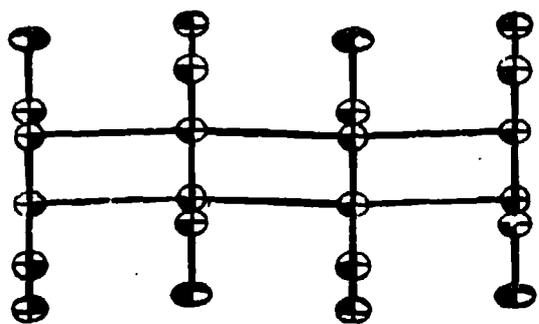
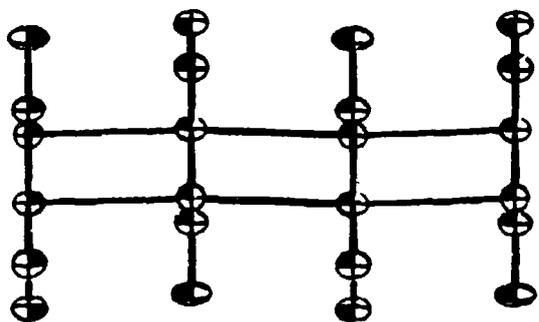
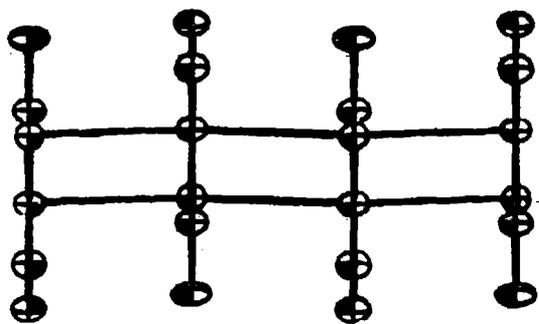
CAPTIONS FOR FIGURES

- Figure 1. Magnetic susceptibility as a function of temperature for Cu(hydrazinium)-Cl₃. The solid line was calculated from the modified Bleaney-Bowers equation with the parameters $2J = 6.5 \text{ cm}^{-1}$, $g = 2.12$, and $\theta = -15.5^\circ\text{K}$.
- Figure 2. View of a single formula unit of Cu(N₂H₅)Cl₃. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.
- Figure 3. View of the bridging network in Cu(N₂H₅)Cl₃. The unlabeled atoms are nitrogen atoms.
- Figure 4. View of the packing of the formula units in the polymeric Cu(N₂H₅)Cl₃ structure.









SUPPLEMENTARY MATERIAL

Anisotropic Thermal Parameters (U_{ij}) for $[(N_2H_5)CuCl_3]$

Atom	U_{11} (or U)	U_{22}	U_{33}	U_{13}
Cu	0.0179 (7)	0.0335 (5)	0.0131 (9)	0.0002 (2)
Cl1	0.0232 (10)	0.0285 (8)	0.0160 (7)	0.0012 (4)
Cl2	0.0268 (10)	0.0393 (8)	0.0157 (7)	0.0044 (5)
Cl3	0.0197 (8)	0.0408 (8)	0.0208 (7)	-0.0016 (5)
N1	0.0213 (25)	0.0311 (25)	0.0203 (18)	-0.0019 (20)
N2	0.0214 (33)	0.0484 (30)	0.0276 (26)	-0.0041 (20)
H11	0.036			
H21	0.072			
H23	0.072			

The form of the anisotropic thermal ellipsoid is

$$\exp[-2\pi^2(U_{11}h^2a^*2 + U_{22}k^2b^*2 + U_{33}l^2c^*2 + 2U_{13}hla^*c^*)]$$

SUPPLEMENTARY MATERIAL

Observed and calculated structure amplitudes (electrons X 10) for $[(N_2H_5)CuCl_3]$

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	2	199	124	1	5	6	126	124	3	0	5	427	414
0	0	4	744	687	1	6	1	232	202	3	0	6	466	452
0	0	6	416	389	1	6	3	326	285	3	0	7	280	275
0	0	8	83	83	1	6	4	195	178	3	0	8	340	335
0	1	3	45	37	2	0	1	388	337	3	1	1	160	155
0	1	5	329	318	2	0	2	606	546	3	1	2	499	527
0	1	7	88	84	2	0	3	687	643	3	1	3	698	679
0	2	2	129	134	2	0	4	1093	1018	3	1	4	362	349
0	2	4	556	589	2	0	5	415	384	3	1	5	157	144
0	2	6	347	341	2	0	6	416	392	3	1	6	242	224
0	2	8	78	75	2	0	7	70	77	3	1	7	298	295
0	3	1	593	554	2	0	8	225	236	3	1	8	292	290
0	3	3	35	46	2	1	1	359	397	3	2	1	343	371
0	3	5	201	220	2	1	2	767	813	3	2	2	722	777
0	3	7	69	73	2	1	3	222	229	3	2	3	690	723
0	4	2	91	95	2	1	4	73	71	3	2	4	500	520
0	4	4	389	393	2	1	5	181	176	3	2	5	335	351
0	4	6	236	234	2	1	6	56	40	3	2	6	390	393
0	4	7	60	0	2	1	7	308	296	3	2	7	236	242
0	5	1	291	264	2	1	8	165	161	3	2	8	295	298
0	5	5	118	113	2	2	1	348	382	3	3	1	87	92
0	6	0	818	720	2	2	2	430	449	3	3	2	362	378
0	6	2	66	53	2	2	3	495	506	3	3	3	437	453
0	6	4	254	226	2	2	4	807	846	3	3	4	227	242
0	7	1	130	107	2	2	5	332	332	3	3	5	117	119
1	0	2	46	21	2	2	6	340	341	3	3	6	180	187
1	0	4	668	602	2	2	7	58	71	3	3	7	202	220
1	0	5	69	63	2	2	8	202	211	3	3	8	206	223
1	0	6	516	504	2	3	0	571	638	3	4	1	236	236
1	0	7	748	712	2	3	1	273	289	3	4	2	458	464
1	1	1	235	250	2	3	2	450	451	3	4	3	470	466
1	1	2	84	72	2	3	3	129	132	3	4	4	337	337
1	1	3	38	29	2	3	4	48	46	3	4	5	223	237
1	1	4	618	572	2	3	5	111	111	3	4	6	260	272
1	1	5	238	208	2	3	7	225	235	3	4	7	162	173
1	1	6	322	299	2	3	8	124	127	3	5	1	63	60
1	1	7	258	255	2	4	0	507	529	3	5	2	197	191
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1	2	3	794	830	2	4	3	317	308	3	5	5	78	78
1	2	4	499	515	2	4	4	547	549	3	5	6	126	125
1	2	5	73	67	2	4	5	220	222	3	6	1	142	127
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10	0	6	265	260	11	4	4	71	67					

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