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

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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 tricopper(2I,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 on the basis of 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 the bridging Cu–Cl–Cu′ angle in the chain are 3.751 (1) Å and 92.79 (3)°, 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 monoprotonated 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 $[M^{II}(N_2H_5)_2(SO_4)_2]_n$, where M = Cr, Co, Ni, Cu, 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 Section

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 mmol) of $N_2H_4{\cdot}2HCl$ to a solution of 7.5 g (44 mmol) of $CuCl_2{\cdot}2H_2O$ in 25 mL of 3 M 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.

Bis(hydrazinium) 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. After 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.

Bis(hydrazinium) Hexachlorotricuprate(2I,II). A solution of 3.5 g (20 mmol) of $CuCl_2{\cdot}2H_2O$ and 2.2 g (20 mmol) of $N_2H_4{\cdot}2HCl$ in 30 mL of 3 M HCl was heated to 75 °C, with stirring, for ap-

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proximately 5 min. When the solution cooled to room temperature, black crystals formed which were filtered, washed with 3 M 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.

(Hydrazine)chlorocopper(I). A solution of 8.0 g (47 mmol) of $CuCl_2{\cdot}2H_2O$ and 4.8 g (46 mmol) of $N_2H_4{\cdot}2HCl$ in 45 mL of 1 M HCl was heated to near boiling for approximately 10 min. Upon standing at room temperature, the solution deposited shiny white crystals. The solution was filtered in a nitrogen-filled glovebag and washed with water to remove traces of a black impurity which was commonly present. Anal. Calcd for N_2H_4CuCl: 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 by a vibrating-sample magnetometer, and the 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), as described previously.[6]

Electronic spectra in the visible and near-infrared regions were obtained with 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 with a Beckman IR-20A spectrophotometer. Low-frequency (500–100 cm^{-1}) spectra of Nujol mulls on polyethylene plates were obtained with a Digilab FTS-14 FT interferometer.

Room-temperature EPR spectra were obtained with 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, NC.

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 the complexes $Cu_2(N_2H_4)_2X_2$, which have been characterized as containing bridging hydrazine by analogy to the Mn^{2+} and Zn^{2+} analogues.[2] Distinct dihydrates[7,8] (for $X_2 = SO_4^{2-}$ and $X = Br^-$) and two monohydrates[7,9] (for $X = I^-$ and $X = Cl^-$) of this general formula have also been reported, and solution equilibrium measurements have indicated the existence of $Cu(N_2H_4)_y^{2+}$, $y = 1-5$.[10] If copper chloride is neutralized to 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., $(CH_3NNCH_3)Cu_2Cl_2$. 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 with 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 complexes 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. On the basis of 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 black 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. For the complexes examined in this work, only the color of the blue complex $(N_2H_5)_2CuCl_4{\cdot}2H_2O$ appears to be unchanged with time. It should be emphasized that, on the basis of 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 compexes 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 formulated[16] 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. On the basis of 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 $(N_2H_4)CuCl$, on the basis of 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 work[21] has shown that ν_{N-N} for unidentate hydrazine falls in the range 931–936 cm^{-1}, whereas ν_{N-N} for bridging hydrazine falls in the range 948–980 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 elemental 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 cm^{-1}, depending on the counterion, and this may be contrasted to free hydrazine, which has ν_{NN} 885 cm^{-1}. Although the free hydrazinium ion may be distinguished from unidentate hydrazine (ν_{NN} 931–936 cm^{-1}), there is some overlap with bridging hydrazine (ν_{NN} 948–980 cm^{-1}). However, coordinated hydrazinium cation may be distinguished from all other possibilities[22] by its high N–N stretching frequency near 1000 cm^{-1}. $(N_2H_5)_2Cu_3Cl_6$ exhibits ν_{NN} 1000 cm^{-1} in Nujol mulls and a doublet, ν_{NN} 1000 and 992 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 $M(N_2H_5)_2(SO_4)_2$, which have symmetrically disposed hydrazinium ligands, also apparently exhibit a doublet near 1000 cm^{-1}. Thus, the existence of a coordinated hydrazinium ion in $(N_2H_5)_2Cu_3Cl_6$ 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

$$\chi_m = 0.446/(T + 2.6)$$

where the susceptibility is calculated per formula unit, e.g., for three copper ions. This susceptibility leads to a room-temperature magnetic moment $\mu_{eff}^{295} = 1.88\ \mu_B$ 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 $\mu_{eff}^{295} = 1.08\ \mu_B$. Such a value is much too low for noninteracting copper(II) ions, and since the linearity of the reciprocal susceptibility vs. 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 $[Cu^{II}A_4][Cu^IX_2]_2$. We propose that the complex $(N_2H_5)_2Cu_3Cl_6$ is a similar species which is most appropriately formulated as $[Cu^{II}(N_2H_5)_2Cl_2][Cu^ICl_2]_2$. 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 $[CuA_4][CuX_2]_2$, 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 $(N_2H_5)_2Cu_3Cl_6$, 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 4 and also the evidence for interaction via bridging cyanide in $Cu_3(NH_3)_4(CN)_4$.[24]

$(N_2H_5)CuCl_3$. 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 characterized[5] material di-μ-chloro-bis[dichloro(guaninium)copper(II)] dihydrate, the green complex hydrazinium trichlorocuprate(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 $(N_2H_5)CuCl_3$ demonstrate the presence of the coordinated hydrazinium ion. In the N–N stretching region, Nujol mull spectra exhibit a single absorption at 995

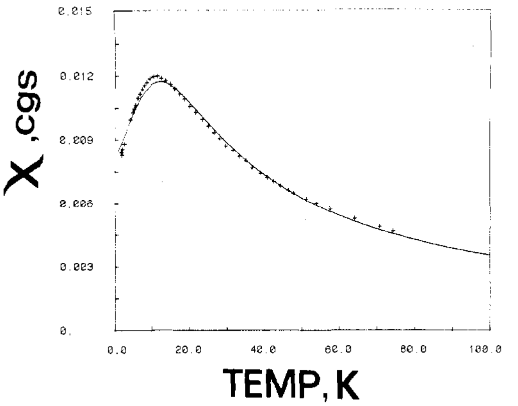

Figure 1. Magnetic susceptibility as a function of temperature for $Cu(N_2H_5)Cl_3$. The solid line was calculated from a modified Heisenberg linear chain equation with the parameters $J = -6.42$ cm^{-1}, $g = 2.07$, and $J' = -2.05$ cm^{-1}.

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 $(N_2H_5)_2Cu_3Cl_6$, 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 $(N_2H_5)CuCl_3$. 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 data[25] 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 found 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 $(N_2H_5)CuCl_3$ are suggestive of bridging chloride. For comparison, the complex $(N_2H_5)_2Cu_3Cl_6$, 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 vs. 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 by using the expression (eq 1) for exchange-coupled copper(II) dimers

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

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

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

the Heisenberg exchange Hamiltonian. However, the value of one parameter obtained from this fitting procedure is unreasonable. Although the values $2J = -6.5$ cm^{-1} and $g = 2.12$ are in the range commonly encountered for chloride-bridged copper(II) ions, the value of $\Theta = -15.5$ K renders the fit meaningless. This difficulty in the analysis of the magnetic susceptibility data led to the X-ray structural determination which is described below in which a ladderlike chain structure was found. Anticipating those results, we note that appropriate theoretical results for the "ladder" structure adopted by hydrazinium copper chloride are not available. However, it is instructive to examine the results of fitting a modified linear-chain model to our data. It is well-known that exchange between copper(II) ions in chains may be described by the Heisenberg Hamiltonian

$$H = -2J\sum_n\{S_z^iS_z^{i+1} + \alpha(S_x^iS_x^{i+1} + S_y^iS_y^{i+1})\} \qquad (3)$$

where $\alpha = 1$. The following closed-formed expression for the magnetic susceptibility of linear chains of $S = {}^1/_2$ ions has been obtained from the numerical results of Bonner and Fisher,[26] where $x = |J|/kT$.

$$\chi_m \approx \frac{Ng^2\beta^2}{kT}\,\frac{0.25 + 0.14995x + 0.30094x^2}{1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3} \qquad (4)$$

There are two identifiable superexchange pathways in hydrazinium trichlorocuprate(II) (see Figure 3); one of these follows the Cl(1)′–Cu–Cl(1)″ bonds and is nearly linear, while the second pathway involves the Cl(1)–Cu–Cl(1)′ bonds and is nearly 90°. Since the unpaired electron on a given copper ion is in a σ^* ($d_{x^2-y^2}$) orbital which is perpendicular to the –Cl(1)′–Cu–Cl(1)″–Cu–... chain, and since the Cu–Cl(1)′ bond distances are rather long (2.856 (1) Å), exchange interactions by this pathway are expected to be weaker than those along the 87.2° Cl(1)–Cu–Cl(1)′ pathway. In the latter case one of the Cl(1)–Cu bonds is short (2.297 Å) and lies in the plane of the σ^* orbital. The geometry of this segment of chain is very similar to that seen in other chloride-bridged copper(II) complexes which exhibit significant intrachain interactions. Thus, we have elected to treat this problem as one involving Heisenberg interactions along a chain with a correction for a second interaction being taken into account and have fit the following expression to our data:

$$\chi_m = \chi_{B\text{-}F}/(1 - 2zJ'\chi_{B\text{-}F}/Ng^2\beta^2) \qquad (5)$$

In this expression $\chi_{B\text{-}F}$ is the susceptibility of an isolated Heisenberg chain, J' is the exchange parameter which includes interactions along the linear Cl(1)–Cu–Cl(1)′ pathway, and z is the number of nearest neighbors; in this case $z = 2$. In the fitting procedures, g, J, and J' were allowed to vary freely, and the best-fit values for the parameters obtained from the nonlinear Simplex routine were $g = 2.07$, $J = -6.42$ cm^{-1}, and $J' = -2.05$ cm^{-1}. These magnetic parameters support the assumptions outlined above concerning the magnitudes of the interactions along the two exchange pathways, but in view of the model used for the analysis they must be used with some caution. A complete calculation of the magnetic susceptibility of a ladderlike chain having two exchange interactions would be a very worthwhile task, albeit a complex one. Magnetic parameters obtained from such a calculation would permit a valid correlation of magnetic and structural features of magnetically condensed systems.

In order to understand the magnetic behavior of $(N_2H_5)CuCl_3$ we 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 $0kl$ for $(k + l)$ odd and $hk0$ 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 $\lambda(\text{Mo K}\alpha_1) = 0.7093$ 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) 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 $\{100\}$ and $\{001\}$ and the faces $(01\bar{1})$, $(0\bar{1}1)$, (021), and $(0\bar{2}\bar{1})$. 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 Mo Kα 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 with 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 × 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° min^{-1}. The peaks were scanned from 0.80° in 2θ below the calculated Kα_1 peak position to 0.80° in 2θ above the calculated Kα_2 peak position. Stationary-counter, stationary-crystal background counts of 4 s were taken at each end of the scan. The pulse-height analyzer was set for approximately a 90% window, centered on the Mo Kα peak.

A unique data set having $3° \leq 2\theta \leq 55°$ 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

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

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 Mo Kα radiation is 52.2 cm^{-1}, and for the crystal chosen the transmission coefficients were in the range 0.31–0.44 with an average value of 0.40. Of the 717 data collected, 552 were greater than 3 times their estimated standard deviations; in addition to the exclusion of data with I less than 3σ, 14 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 145 highest 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 atoms 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 six positions led to values of the conventional agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.189$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.276$. All least-squares refinements in this study were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$, where the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for nonhydrogen atoms were from ref 31 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 noncentrosymmetric 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 Å^2. In the final cycles of least-squares refinement, no hydrogen parameter was varied, nonhydrogen 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 0.03σ, 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 observed and calculated structure amplitudes are available as supplementary material. The final value of the extinction coefficient was 7 (2) × 10^{-8}.

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

atom	x	y	z
Cu	0.4532 (1)	0.2500	0.1477 (1)
Cl(1)	0.5391 (1)	0.2500	−0.1341 (2)
Cl(2)	0.3754 (1)	0.2500	0.4370 (2)
Cl(3)	0.3191 (1)	0.2500	−0.0329 (2)
N(1)	0.5706 (3)	0.2500	0.3186 (7)
N(2)	0.6611 (3)	0.2500	0.2245 (7)
HN(11)[a]	0.575	0.130	0.375
HN(21)	0.663	0.397	0.216
HN(23)	0.711	0.250	0.309

[a] Hydrogen atom positions were not varied.

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-(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 Cu(N-

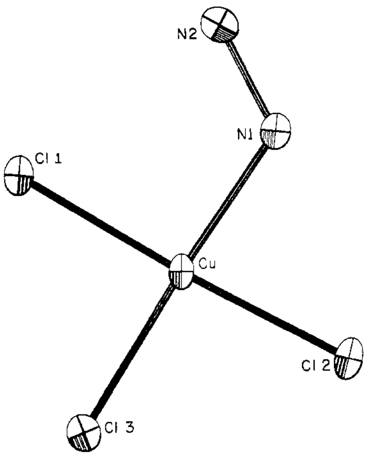

Figure 2. View of a single formula unit of $Cu(N_2H_5)Cl_3$. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

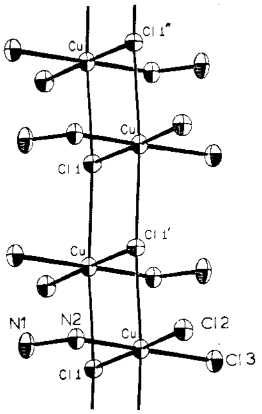

Figure 3. View of the bridging network in $Cu(N_2H_5)Cl_3$.

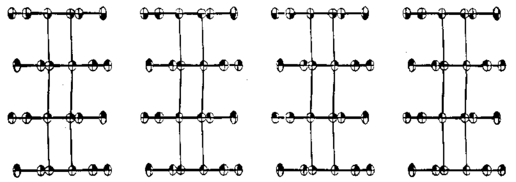

Figure 4. View of the packing of the formula units in the polymeric $Cu(N_2H_5)Cl_3$ structure.

Table II. Interatomic Distances (Å) in $(N_2H_5)CuCl_3$[a]

Cu-Cu	3.751 (1)	Cu-Cl(3)	2.298 (2)
Cu-Cl(1)	2.297 (1)	Cu-N(1)	2.061 (5)
Cu-Cl(1)'	2.856 (1)	N(1)-N(2)	1.457 (7)
Cu-Cl(2)	2.280 (1)		

[a] For designations of atoms see Figures 2 and 3.

$H_3)_2(CO_3)$[38] and those in most other copper-amine complexes[39] but is consistent with the reported length of 2.08 Å in the zinc hydrazinium complex $Zn(N_2H_5)_2(SO_4)_2$.[3]

The Cu-Cu separation in the chain is 3.751 (1) Å, the out-of-plane Cu-Cl(1)′ distance 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 earlier[35] 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 values of 3.866 (2) and 3.737 (6) Å in these complexes.

Table III. Interatomic Angles (deg) in $(N_2H_5)CuCl_3$[a]

Cu-Cl(1)-Cu′	92.79 (03)	Cl(1)′-Cu-Cl(3)	90.87 (03)
Cl(1)-Cu-N(1)	91.95 (14)	Cl(1)′-Cu-N(1)	89.23 (03)
N(1)-Cu-Cl(2)	84.84 (14)	Cl(1)′-Cu-Cl(1)″	174.15 (07)
Cl(2)-Cu-Cl(3)	93.12 (06)	N(2)-N(1)-Cu	119.06 (31)
Cl(1)′-Cu-Cl(2)	92.74 (03)		

[a] For designations of atoms see Figures 2 and 3.

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°, respectively.

$(N_2H_5)_2CuCl_4·2H_2O$. The bright blue crystalline complex $(N_2H_5)_2CuCl_4·2H_2O$ forms upon recrystallization of the green $(N_2H_5)CuCl_3$. 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 noninteracting copper centers. Over the temperature range 2.4-100 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

$$\chi_m = 0.4605/(T + 1.5) \quad \text{cgsu}$$

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

Infrared spectra are again consistent with the presence of coordinated hydrazinium ion in $(N_2H_5)_2CuCl_4·2H_2O$. 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]

On the basis of 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 that of $(N_2H_5)CuCl_3$. 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 $(N_2H_5)_2CuCl_4·2H_2O$ involves six-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 both as 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.

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Registry No. $(N_2H_5)CuCl_3$, 70812-15-6; $(N_2H_5)_2CuCl_4$, 70800-81-6; $(N_2H_5)_2Cu_3Cl_6$, 70775-60-9; $(N_2H_4)CuCl$, 70775-62-1.

Supplementary Material Available: A listing of observed and calculated structure amplitudes and a table of anisotropic thermal parameters (U_{ij}) (4 pages). Ordering information is given on any current masthead page.

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