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(37) L. K. K. Li Shing Man, and J. Takats, in preparation.
(38) This compound has also been investigated by Whitesides et al.;[15] our values are in reasonable agreement with theirs.
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Two-Dimensional Magnetic Systems. Structural and Magnetic Characterization of Bis(propylene-1,3-diammonium) Tetrachlorocuprate(II)

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The crystal structure and magnetic properties of the compound bis(propylene-1,3-diammonium) tetrachlorocuprate, [H$_3$NC$_3$H$_6$NH$_3$]CuCl$_4$, have been determined. The material crystallizes in the orthorhombic space group *Pnma* ($D_{2h}{}^{16}$) with four formula units in a cell of dimensions $a = 7.200$ (2), $b = 18.246$ (6), and $c = 7.451$ (2) Å. Least-squares refinement of 1209 independent reflections has led to a final R factor (on F) of 0.036. The structure consists of tetragonally distorted [CuCl$_6$]$^{2-}$ units which are chloro bridged to form a two-dimensional layer. Within the two-dimensional network there are two short copper–chloride bond distances of 2.275 (4) Å and two long Cu–Cl distances of 2.946 (4) Å. There are two copper–chloride bonds nearly perpendicular to the bridged network with distances of 2.314 (4) Å. The intralayer bond angles at copper are 87.70 (2) and 92.30 (2)° with the Cu–Cl–Cu bridging angle being 165.70 (4)°. The chlorocuprate sheet is puckered as a result of hydrogen bonding to the propylene-1,3-diammonium ions which lie between the layers. Magnetic susceptibility data collected on powdered and single-crystal samples revealed two-dimensional magnetic interactions with $J/k = 15.4$ K above the three-dimensional ordering temperature of 13.5 K. In the ordered state the preferred direction of the spins is along c (perhaps with some canting) with the next preferred direction apparently perpendicular to the layer. This unusual result reflects the small interlayer separation of 9.123 (3) Å.

Introduction

Compounds of the type [H$_3$NC$_n$H$_{2n+1}$]$_2$MX$_4$ (n = 0, 1, 2, ...; M = Cu, Mn, Fe; X = Cl, Br) have been known for some time to exhibit two-dimensional magnetic behavior at temperatures above T_c,[1] a typical value of the ratio of interlayer J' to intralayer exchange J (J'/J) being less than 10^{-4} for n greater than 2.[2] The pronounced two-dimensional properties arise by the separation of the MX$_4$ layers by the organic alkylammonium groups to give structures similar to K_2CuF_4[3] and Rb_2CuCl_4.[4] The type of two-dimensional ordering observed is in contrast to that for K_2NiF_4 which arises mainly from the symmetry of the body-centered tetragonal lattice,[5] which for the antiferromagnetic NiF_2 sheets leads to a cancelation of the layer–layer interaction.[6]

Although several structural investigations of the copper chloride layers have been carried out,[7-11] single crystals of adequate quality and size of these complexes are difficult to obtain because of the presence of the very weak interlayer interactions, the binding force between layers being only the van der Waals forces between the neighboring alkyl groups.

To overcome this drawback compounds of the formula $[H_3NC_nH_{2n}NH_3]MX_4$, which have the possibility of N–H···X hydrogen bonding between two metal–halogen layers, have been prepared. These types of compounds should still exhibit the two-dimensional layered structures necessary for the anisotropic superexchange interaction between metal centers and also have the advantage of more suitable crystal size and quality necessary for structural and magnetic studies. In this paper, the structural and magnetic parameters of $[H_3NC_3H_6NH_3]CuCl_4$ are presented.

Experimental Section

Crystals of the title compound were prepared by mixing equimolar amounts of propylene-1,3-diammonium chloride and copper chloride in aqueous solution and allowing the resulting mixture to slowly evaporate. The yellow crystals grow as rectangular parallelepipeds, and a crystal measuring 0.030 × 0.007 × 0.093 cm was chosen for preliminary Weissenberg and precession photographs and intensity data collection. From the observed absences of $0kl$ ($k + l = 2n$), and $hk0$ ($h = 2n$) in preliminary film data the space group was assigned as either *Pnma* (D_{2h}^{16}) or its noncentrosymmetric equivalent $Pn2_1a$ of the orthorhombic system. Unit cell parameters and their standard deviations, determined by the least-squares procedure of Busing and Levy[12] on 12 carefully centered reflections, are $a = 7.200$ (2), $b = 18.246$ (6), and $c = 7.451$ (2) Å. The measured density by flotation in benzene and bromoform is 1.92 g cm^{-3} and the calculated density assuming four molecules in the unit cell is 1.909 g cm^{-3}. Hence, with only four molecules in the unit cell the molecules are required to lie in special positions in a centrosymmetric unit cell (vide infra).

The crystal was mounted in a random orientation on a glass fiber. The intensity data were collected using Mo Kα radiation with a graphite crystal monochromator using a θ–2θ scan mode. The takeoff angle used was 1.5°; at this angle the peak intensity of a typical strong reflection was approximately 90% of the maximum value as a function of takeoff angle. Using a scan width of 1.5°, to which was added a dispersion factor to account for the Kα_1–Kα_2 splitting, 1453 independent reflections were examined in the range $2° \leq 2\theta$ (Mo Kα) ≤ 62.5 at a scan rate of 1.0° min^{-1}. At each end of the scan stationary-crystal, stationary-counter background counts were taken for 10 s. Throughout the data collection the intensities of three reference reflections were measured after every 100 reflections to monitor crystal and electronic stability. These standards showed no systematic decline in intensity as a function of x-ray exposure time.[13]

The data were processed by the method Corfield et al.[14] After correction for background, the intensities were assigned standard deviations according to the formula $\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + p^2I^2]^{1/2}$ where the symbols have their usual meaning and the value of p was chosen as 0.04. The intensities were corrected for absorption and for Lorentz–polarization effects.[15] The absorption coefficient of this compound for Mo Kα radiation is 32.37 cm^{-1}, and for the crystal chosen the transmission coefficients were found to range from 0.78 to 0.61. Of the 1453 independent reflections for $2\theta < 62.5°$ for Mo Kα, 1209 were found to have intensities greater than 3 times their estimated standard deviations; only these observed data were used in subsequent least-squares and Fourier calculations.

Solution and Refinement of Structure

The solution of the structure was initiated assuming the centrosymmetric space group *Pnma*, which is shown to be correct by subsequent refinement of the structure. In view of the similarity of the cell constants, a structural model similar to that of the analogous Mn and Fe salts[16] was proposed with the two-dimensional metal–halogen plane assumed to lie perpendicular to the crystallographic b axis. The copper atom was placed at the origin with site symmetry $\bar{1}$, and the two independent chloride ion positions were located from a three-dimensional Patterson map. Subsequent least-squares and Fourier syntheses revealed the locations of all remaining nonhydrogen atoms; atom C(2) [and its associated hydrogen atoms H(21) and H(22)] lie in the mirror at $y = {}^1/_4$, but all other atoms except Cu are in general positions.

Table I. Positional Parameters[a] for $[C_3H_{12}N_2](CuCl_4)$

Atom	x	y	z
Cu	0	0	0
Cl(1)	22 531 (9)	1 696 (4)	21 001 (9)
Cl(2)	−2 007 (9)	12 538 (4)	−4 256 (10)
N(1)	143 (4)	1142 (2)	5 284 (4)
C(1)	−362 (5)	1830 (2)	4 380 (5)
C(2)	289 (8)	2500	5 336 (6)
H(11)	−25 (5)	117 (2)	644 (7)
H(12)	−31 (6)	85 (3)	481 (6)
H(13)	151 (6)	116 (2)	531 (6)
H(21)	15 (5)	174 (3)	336 (8)
H(22)	−168 (6)	176 (2)	435 (5)
H(31)	−19 (7)	250	608 (9)
H(32)	145 (11)	250	528 (9)

[a] Parameters are ×10^5 for chlorine atoms, ×10^4 for other nonhydrogen atoms, and ×10^3 for hydrogen atoms.

Table II. Thermal Parameters for $[C_3H_{12}N_2](CuCl_4)$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	998 (8)	151 (1)	755 (7)	−1 (2)	−208 (6)	13 (2)
Cl(1)	1018 (11)	216 (2)	837 (9)	−1 (3)	−197 (9)	−19 (3)
Cl(2)	1667 (15)	157 (1)	992 (11)	−7 (4)	−97 (10)	21 (3)
N(1)	189 (6)	16 (1)	121 (5)	1 (2)	−5 (5)	−3 (1)
C(1)	192 (7)	18 (1)	115 (5)	−3 (2)	−39 (5)	1 (2)
C(2)	200 (11)	15 (1)	113 (7)	0	−32 (7)	0

Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2
H(11)	4 (1)	H(21)	6 (1)	H(31)	4 (2)
H(12)	5 (1)	H(22)	5 (1)	H(32)	8 (2)
H(13)	5 (1)				

[a] Cu and Cl anisotropic thermal parameters are ×10^5; C and N anisotropic thermal parameters are ×10^4.

In all calculations of F_c, the scattering factors used for the nonhydrogen atoms were from ref 17, and the hydrogen atom scattering factors were from Stewart, Davidson, and Simpson.[18] The effects of anomalous scattering for the Cu and Cl atoms were taken into account in the final cycles of least-squares refinement,[19] the values of $\Delta f'$ and $\Delta f''$ being taken from ref 20. All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ and the weights, w, being taken as $4F_o^2/\sigma^2(F_o)^2$. The weighted and unweighted residuals are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

A difference Fourier map phased on the anisotropic refinement of all nonhydrogen atoms revealed the positions of the hydrogen atoms. The positional and thermal parameters of these atoms were refined in subsequent least-squares cycles.

In the final cycle of least-squares refinement there were 75 varied parameters and 1209 observed reflections which gives a reflection to parameter ratio of roughly 16:1. The final values of R_1 and R_2 were found to be 0.036 and 0.043 and the error on an observation of unit weight was observed to be 1.53. Refinement was considered converged when only one nonhydrogen parameter was shifting by more than 0.50σ. The final value of R_2 showed no dependence on either sin θ or $|F_o|$, which indicates that our assignment of $p = 0.04$ in the weighting scheme was essentially correct. No correction for extinction was deemed appropriate on examination of the final values of $|F_o|$ and $|F_c|$.

The final difference Fourier map showed no peak greater than 0.5 e Å^{-3} except for a peak very near the copper atom and another peak close to the Cl(2) atom. Both of these peaks were less than 1.0 e Å^{-3}.

The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables

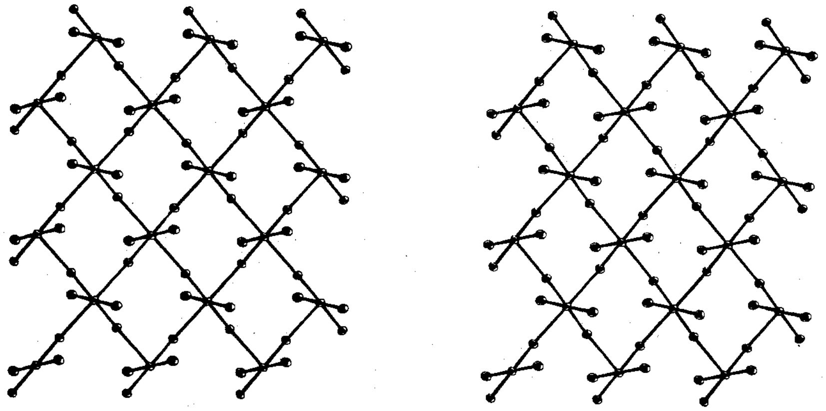

Figure 1. Stereoscopic view of the two-dimensional layers in $[NH_3C_3H_6NH_3](CuCl_4)$. The cations are omitted for clarity.

Table III. Structural Information on Metal-Chloride Layers

Complex	Space group	M-Cl, Å Bridging	 Terminal	M-Cl-M′, deg	Interlayer sepn, Å	Ref
$[NH_4]_2(CuCl_4)$	*Cmca*	2.300 (5)	2.332 (4)	180	7.73 (1)	7
$[CH_3NH_3]_2(CuCl_4)$	*Cmca*	2.793 (5)			9.28	7
$[C_2H_5NH_3]_2(CuCl_4)$	*Pbca*	2.285 (4) 2.975 (5)	2.277 (6)	169.6 (2)	10.59 (1)	8
$[C_3H_7NH_3]_2(CuCl_4)$	*Pbca*	2.29 3.04	2.29	166.6	12.33	9
$[C_6H_4NH_3]_2(CuCl_4)$	*P*2₁/*c*	2.2804 (6) 2.9178 (5)	2.3007 (5)	164.4	15.050 (2)	11
$[Pt(NH_3)_4](CuCl_4)$	*P*2₁/*c*	2.302 (4) 3.257 (4)	2.271 (3)	167.4 (1)	8.057 (2)	23
$[(NH_3CH_2CH_2)_2NH_2](CuCl_4)Cl$	*Pnma*	2.272 (4) 2.876 (4)	2.276 (9)	165.7	11.89 (1)	10
$[NH_3C_3H_6NH_3](CuCl_4)$	*Pnma*	2.275 (1) 2.946 (1)	2.314 (1)	165.70 (4)	9.123 (3)	This work
$[C_3H_7NH_3]_2(MnCl_4)$	*Cmca*	2.629 (5)	2.475 (10)	168.5 (2)	12.97	22
$[NH_3C_3H_6NH_3](MnCl_4)$	*Imma*	2.584 (3)	2.491 (3)	167.7 (1)	9.50 (1)	16
$[NH_3C_3H_6NH_3](FeCl_4)$	*Imma*	2.573 (4)	2.404 (4)	169.1 (1)	9.28 (2)	16

I and II. A table of observed and calculated structure amplitudes is available.[21]

Description of the Structure

The structure consists of $[CuCl_6]^{2-}$ units with the familiar (4 + 2) distorted octahedral geometry and propylenediammonium cations, $[NH_3C_3H_6NH_3]^{2+}$, which are hydrogen bonded to the anions. The anions form a two-dimensional layer structure. Each copper atom is surrounded in the layer by two axial chloride ions [Cl(1)′] and two equatorial chloride ions [Cl(1)], the axial chlorine atoms being equatorial to adjacent Cu atoms, and vice versa. Additionally, each Cu center is coordinated to two terminal equatorial chlorine atoms [Cl(2)] which lie above and below the layer and are not shared by other copper atoms. Hence, in the layer there are two short (equatorial) Cu-Cl(1) bonds of length 2.275 (4) Å and two long (axial) Cu-Cl(1)′ bonds of length 2.946 (4) Å to each copper atom; the terminal Cu-Cl(2) distance is 2.314 (4) Å. A view of the layer is given in Figure 1. These bond lengths, which are compared with those found by other workers for other chloride layers in Table III, are in the range observed by those workers[6-11,16,22,23] and are also similar to bridging and terminal Cu-Cl distances reported in dimeric[24-31] and chain[31-34] complexes.

The intralayer bond angles at copper are 87.70 (2) and 92.30 (2)°. The terminal Cu-Cl(2) bond is not exactly perpendicular to the plane formed by Cu and its four associated Cl(1) atoms (vide infra), the Cl(2)-Cu-Cl(1) (equatorial) and Cl(2)-Cu-Cl(1)′ (axial) angles being 90.24 (2) and 87.40 (2)°, respectively. The Cu-Cl(1)-Cu′ bridging angle is 165.70 (4)°; as can be seen in Table III, this value lies in the wide range of 164.4-180° which has been observed for other layer complexes. The bond lengths and angles found in this complex are summarized in Table IV.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in $[C_3H_{12}N_2](CuCl_4)^a$

Distances			
Cu-Cl(1)	2.275 (1)	N(1)-H(13)	0.98 (5)
Cu-Cl(2)	2.314 (1)	C(1)-H(21)	0.86 (5)
Cu-Cl(1)^{I}	2.946 (1)	C(1)-H(22)	0.96 (4)
N(1)-C(1)	1.470 (4)	C(2)-H(31)	0.65 (6)
N(1)-H(11)	0.90 (5)	C(2)-H(32)	0.84 (6)
N(1)-H(12)	0.71 (5)		

Angles			
Cl(1)-Cu-Cl(1)′ ^{I}	87.70 (2)	N(1)-C(1)-C(2)	113.8 (3)
Cl(2)-Cu-Cl(1)	90.24 (2)	C(1)-C(2)-C(1)′ ^{II}	110.2 (4)
Cl(2)-Cu-Cl(1)′ ^{I}	87.40 (2)		

[a] The superscripts on atoms refer to symmetry operations with respect to Table I: I $(x - {}^1/_2 - z)$; II $(x, {}^1/_2 - y, z)$.

The overall geometry of the Cu-Cl layer network is shown in Figure 1. The general appearance is that of boxes of approximate length 5 Å on a side with chlorine atoms along the edges of the box and copper atoms at the corners. In this view it can be seen how the Cu-Cl layer is not strictly planar in the *ac* plane but shows the familiar puckering effect, also observed in the other copper layers.[7-11] This puckering is brought about by a tipping of the $CuCl_4$ unit by 9.6° in the *c* direction and by 1.6° in the *a* direction, with the octahedra at the corners of the unit cell and those at $({}^1/_2, y, {}^1/_2)$ being tipped in alternating directions as required by symmetry. Besides causing puckering in the layer, this tip of the octahedra consequently slants one of the terminal chlorine atoms toward the center of the box formed by the copper atoms. A similar

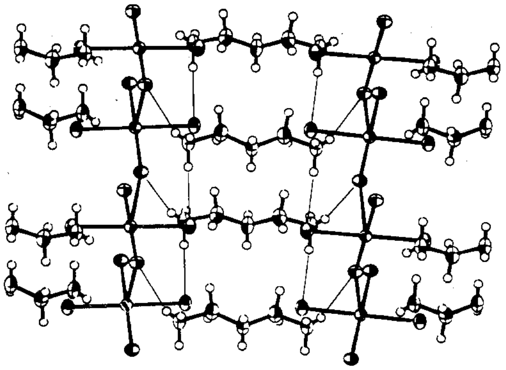

Figure 2. View normal to the ($CuCl_4$) layers showing the geometry of the $[NH_3C_3H_6NH_3]^{2+}$ cations. Hydrogen bonds are shown as thin lines.

Table V. Probable N-H· · ·Cl Hydrogen Bonds in $[NH_3C_3H_6NH_3](CuCl_4)^a$

N	H	Cl	N· · ·Cl, Å	H· · ·Cl, Å	N-H· · ·Cl, deg
N(1)	H(11)	$Cl(2)^{I}$	3.213 (3)	2.34 (5)	161 (3)
N(1)	H(12)	$Cl(1)^{II}$	3.261 (3)	2.58 (4)	160 (6)
N(1)	H(13)	$Cl(2)^{III}$	3.360 (3)	2.38 (4)	178 (5)

[a] Roman superscripts refer to symmetry operations: I ($x, y, 1 + z$); II ($x - {}^1/_2, y, {}^1/_2 - z$); III (${}^1/_2 + x, y, {}^1/_2 - z$).

effect has been observed in related manganese[22,16] and iron salts.[16]

The geometry of the propylenediammonium chain can be seen in Figure 2. The relatively small values of the thermal parameters of these atoms suggest that the cation is not undergoing very much thermal motion. This is presumably because the atoms are involved in extensive hydrogen bonding of the type N–H···Cl between the Cu–Cl layer and the diamagnetic alkylammonium chain. The C–C and C–N bond distances have quite reasonable values of 1.490 (4) and 1.470 (4) Å for single bonds. The N(1)–C(1)–C(2) angle is 113.8 (3)° and the C(1)–C(2)–C(1)′ angle is 110.2 (4)°, where C(1)′ is the C(1) atom reflected through the mirror at $y = {}^1/_4$. Bond distances for hydrogen to nitrogen and carbon show somewhat diverse but not unreasonable values, as would be expected from the nature of this study. These values vary from 0.65 (5) Å for C(2)–H(21) to 0.98 Å for N(1)–H(13) with an average X–H distance of 0.84 (12) Å. The pattern of hydrogen bonding between the chain and layer can be seen in Figure 3, which also shows again the layer puckering. It is obvious from this picture that the hydrogen bonding leads to the tilting of the $CuCl_6$ octahedra to achieve stronger interaction. As is noted by Willett,[22] the NH_3 of C_{3v} symmetry would not hydrogen bond efficiently to the approximately C_{4v} symmetry of a planar CuCl layer, but by tipping the octahedra two axial chlorine atoms are brought toward the NH_3 group. This results in two hydrogen bonds involving H(11) and H(13) and terminal chlorine atoms with H···Cl lengths of 2.34 (5) and 2.38 (5) Å, respectively. Thus each terminal chlorine atom is hydrogen bonded to two hydrogen atoms as shown in Figure 3. The layer chlorine atoms come up out of the plane to form a hydrogen bond to H(12), with a Cl···H separation of 2.58 (4) Å. It is noteworthy that the H(11) atom is positioned such that it always tilts the $CuCl_6$ octahedra along the *c*-axis direction which is the primary direction of tip of the octahedra (vide supra). The H(12) atom is always forcing alternating layer chlorine atoms out of the plane, complementing the effect of the H(11) hydrogen bonds, but the H(13) atom, which hydrogen bonds approximately parallel to the *a* axis, causes very little tilt of the $CuCl_6$ octahedra in the *a* direction. The hydrogen bonding in this complex is summarized in Table V. In comparison of this structure with the $(C_3H_7NH_3)_2(CuCl_4)$ structure it is obvious that in the present complex the layers are allowed to come closer together because of the reduction of nonmagnetic material between the layers and also because of the presence of hydrogen-bonding interactions with both the layer above and that below by the same alkylammonium group. It is also of interest to note that the structures which crystallize in the space group *Pbca*, $[C_3H_7NH_3]_2(CuCl_4)$ and $(C_2H_5NH_3)_2(CuCl_4)$, have metal atoms occupying the face-centered positions in the cell[8,9] and thus the metal atoms in nearest layers do not sit directly over each other. But in the structure reported here and $[(NH_3CH_2CH_2)_2NH_2](CuCl_4)Cl$, which[10] crystallize in space group *Pnma*, the metal atoms do stack directly over each other parallel to the crystallographic *b* axis. The effect of this is to cancel out any dipolar interactions between the metal atoms in the space group *Pbca* but to allow them in the space group *Pnma*.

Magnetic Properties

The magnetic susceptibility results on $[C_3H_{12}N_2](CuCl_4)$ provide an interesting addition to the series of compounds which exhibit predominantly two-dimensional short-range order above some three-dimensional ordering temperature. The magnetic susceptibility data obtained on a polycrystalline sample from 4.2 to 65 K for this structurally two-dimensional compound are shown in Figure 4. The data were collected at a field strength of 500 Oe using the susceptometer system which has been described previously.[35]

It is readily apparent from an inspection of the data that a phase transition to an ordered magnetic configuration occurs at approximately 14 K, since the qualitative behavior of the data is reminiscent of that found for $[(NH_3CH_2CH_2)_2NH_2](CuCl_4)Cl$[35] and $[C_2H_5N]_2(CuCl_4)$.[36] Consequently, the polycrystalline data from 35 to 80 K were fit to the magnetic susceptibility equation which results from the Heisenberg model of two-dimensional ferromagnetism as given by Baker et al.[37] in terms of a series expansion. The best fit to the expression, from a calculation in which both J/k and g were

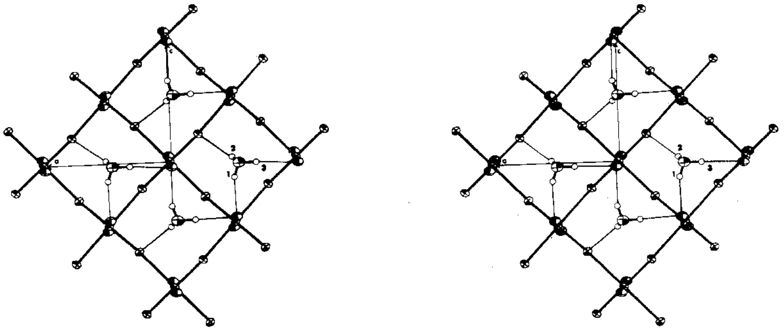

Figure 3. Stereoscopic view showing the hydrogen bonding between the terminal NH_3 groups of the cation and the chlorine atoms. The digits 1, 2, and 3 represent hydrogen atoms H(11), H(12), and H(13), respectively.

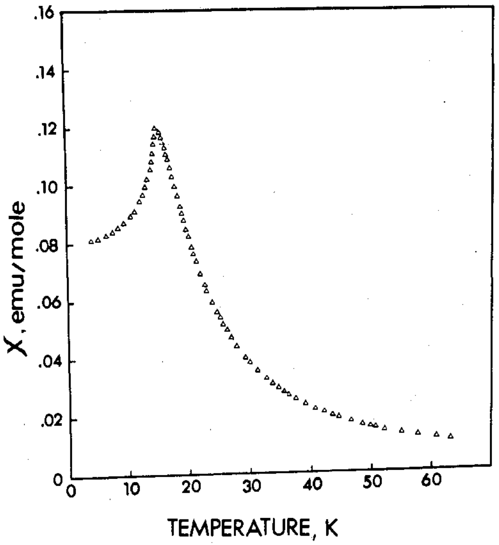

Figure 4. Temperature dependence of the magnetic susceptibility of a polycrystalline sample of $[NH_3C_3H_6NH_3](CuCl_4)$. The data were collected at a field strength of 500 Oe.

varied, resulted in a maximum deviation of any experimental point from the calculated value of 1.2% and yielded parameters of $J/k = 15.2$ K and $g = 2.142$. When the g value was set equal to the powder EPR value of 2.13, a value of $J/k = 15.4$ K resulted, and the maximum deviation was 1.7%. The quality of both fits is excellent over the entire temperature range.

When the simple Curie–Weiss expression for $S = {}^1/_2$ is used to fit the magnetic susceptibility data over the same temperature interval, there are significant deviations between experimental and calculated values of susceptibility as well as poor agreement between the calculated g value and the EPR-determined value. Not unexpectedly, much higher temperature data are required before a meaningful fit to the Curie–Weiss expression can be obtained.

To shed further light on the magnetism of $[C_3H_{12}N_2](CuCl_4)$ single crystal magnetic susceptibilities were collected along the three orthorhombic crystal axes. These measurements were made in a field of 250 Oe on a single crystal weighing 0.05 g. The crystal was first mounted on the sample holder so that measurements could be taken along a and c, and then the crystal was reoriented for measurements perpendicular to the morphologically obvious plate. The results of these measurements from 1.7 to 40 K are shown in Figures 5 and 6.

Although the magnetic behavior of the polycrystalline material appears similar to other examples of two-dimensional systems with $J_f >> J_{af}$, in fact the behavior of $[C_3H_{12}N_2](CuCl_4)$ is quite different. For example, while the measurements along the c axis (Figure 5) yield data which suggest that this axis is the most preferred axis of magnetization, the susceptibility does not decay to zero as the temperature goes to zero. Similarly, while the measurement along b indicates a well-behaved perpendicular susceptibility for an antiferromagnet, χ_a can hardly be called the same. In this regard it should be noted that although the crystal used for the single-crystal study had well-behaved optical properties under the polarizing microscope, it is known from the x-ray size crystals that twinning and stacking faults are common. The deviations from classical antiferromagnetic behavior along the crystal axis may be due to the crystal imperfections. However, this may be a reflection of noncollinear sublattices in the ordered state.

From these measurements a transition temperature of 13.5 (±0.5) K is obtained from the maximum slope of the data taken along c. This can be compared to the temperature of

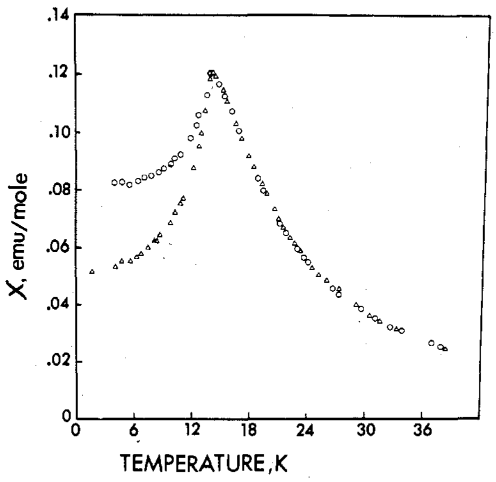

Figure 5. Temperature dependence of the magnetic susceptibility of a single crystal of $[NH_3C_3H_6NH_3](CuCl_4)$, with the measurements being taken along the crystallographic a (circles) and c (triangles) directions.

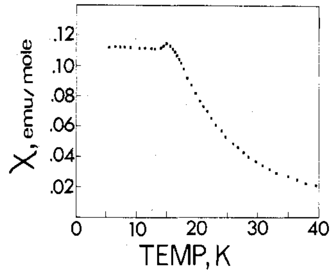

Figure 6. Temperature dependence of the magnetic susceptibility of a single crystal of $[NH_3C_3H_6NH_3](CuCl_4)$ with the measurements being taken along the b crystallographic direction.

14.2 (±0.5) K which is obtained at the susceptibility maximum along c. The corresponding temperature observed in data taken along b is equal to 15.2 (±0.5) K, a substantial difference compared to the c-axis value.

The results of the present magnetic susceptibility experiments on $[C_3H_{12}N_2](CuCl_4)$ indicate a material which has substantial two-dimensional behavior above the transition temperature as indicated by the intralayer exchange constant of 15.4 K. However, the material is far from being an ideal two-dimensional example, and deviations from two-dimensional behavior are manifested both at the transition temperature and below. For instance, at and slightly above the transition temperature, the effects of increased interlayer exchange are reflected by a substantial reduction in the ferromagnetic correlations in the plane compared to the case of the more nearly "isolated" two-dimensional ferromagnets. In these latter cases susceptibility values close to the theoretical values are realized at the transition temperature.[38] These antiferromagnetic interlayer correlations may also be connected with the difference in the temperatures associated with the onset of long-range order which were observed along c and b.

Below 13.5 K the spins lie in the two-dimensional plane, perhaps canted along the c axis. From dipole–dipole considerations this axis is preferred in the layer. However, because of significant antiferromagnetic interactions between layers (9.123-Å separation) the next preferred axis is apparently perpendicular to the layer and lies along b. This may also be a manifestation of anisotropy in the exchange interaction between Cu ions via the asymmetric Cl bridges in the plane, a mechanism which could favor an orientation perpendicular to the plane.

In conclusion, $[C_3H_{12}N_2](CuCl_4)$ appears to be worthy of further study especially when one compares the transition temperature of $[C_3H_{12}N_2](CuCl_4)$ (13.5 K) with that observed for $[CH_3NH]_2(CuCl_4)$ (8.91 K), a 5.5-K increase in transition temperature accompanying a 0.85-Å decrease in interlayer separation. Besides this, there is also a change in the sign of the coupling between the layers. In $[CH_3NH_3]_2(CuCl_4)$ the Cu atoms sit at face-centered positions in the unit cell while in $[C_3H_{12}N_2](CuCl_4)$ the Cu atoms stack one above the other, and, consequently, from symmetry considerations, there is no cancelation of dipolar effects between the layers (vide supra).

Experiments to clarify some of the pecularities observed in $[C_3H_{12}N_2](CuCl_4)$, with particular attention to the anisotropy in this material, are currently under way in this laboratory on x-ray size single crystals using a highly sensitive susceptometer.

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Registry No. $[NH_3C_3H_6NH_3](CuCl_4)$, 60553-51-7.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Synthesis, Properties, and X-Ray Structural Characterization of a Novel Seven-Coordinate Halogenotris(dithiocarbamato) Complex of Ruthenium(IV)

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The synthesis of several new oxidation products of tris(*N*,*N*′-disubstituted dithiocarbamato)ruthenium(III), $Ru(R_2dtc)_3$, where R = C_2H_5 and CH_3 is described. Photolysis of $Ru(Et_2dtc)_3$ in $CHCl_3$ or CH_2Cl_2 or reaction with gaseous HCl in benzene yields two new chlorine-containing compounds. One of the compounds is green and is formulated as $Ru(Et_2dtc)_3Cl$. The crystal structure of this compound has been determined by three-dimensional single-crystal x-ray analysis. The space group is $P2_1/c$ with lattice constants $a = 9.077$ (3) Å, $b = 10.244$ (3) Å, $c = 27.805$ (13) Å, and $\beta = 93.06$ (3)°. The structure was solved by conventional heavy-atom techniques and refined by least-squares methods to a conventional R of 0.055 for 1061 independent reflections. The density of 1.50 g/cm^3 computed from the unit cell volume of 2582 Å^3 on the basis of four $Ru[S_2CN(C_2H_5)_2]_3Cl$ molecules per unit cell agrees well with the 1.53 g/cm^3 determined by flotation methods. The structure consists of well-separated monomeric molecules, each composed of three bidentate Et_2dtc ligands and a chlorine atom with the donor atoms arranged in a distorted pentagonal-bipyramidal configuration around the ruthenium(IV) ion. Two Et_2dtc ligands span equatorial positions while one spans an equatorial and an axial position. The chlorine atom occupies the other axial position. The average Ru–S distance is 2.40 Å and the distances between adjacent sulfur atoms in the equatorial plane are very similar and range from 2.75 to 3.02 Å, all of which are much shorter than the van der Waals contact distance of 3.4 Å. The reaction chemistry of $Ru(Et_2dtc)_3Cl$ is discussed, the most notable reaction being with $AgBF_4$ in acetone solution which yields $[Ru_2(Et_2dtc)_5]BF_4$, thiuram disulfide, and $Ru(BF_4)_3$. The general nature of the oxidation reaction of $Ru(R_2dtc)_3$ is discussed and related oxidation reactions with iodine are described. ^{1}H NMR properties of $Ru(Et_2dtc)_3Cl$ are also discussed in detail.

Introduction

Recently there have been several reports[1-3] of interesting dimeric cationic metal dithiocarbamato complexes with the stoichiometry $M_2(R_2dtc)_5{}^+$ where M = ruthenium(III),[1] cobalt(III),[2] and rhodium(III)[3] and R_2dtc = *N*,*N*′-disubstituted dithiocarbamate. In the case of ruthenium when R = Et (Et = ethyl), a novel triply bridged metal–metal bonded complex I[1,4] is found, whereas the cobalt and rhodium analogues where R = Et and Me (Me = methyl), respectively, have structure II.[2,3] These diamagnetic complexes are syn-