01 Jan 1972

Structural and Magnetic Properties of $[(CH_3)_3NH]\ CuCl_3 2H_2O$

D. B. Losee

J. N. McElearney

A. Siegel

Richard Lewis Carlin

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/chem_facwork/1598

Recommended Citation

D. B. Losee et al., "Structural and Magnetic Properties of $[(CH_3)_3NH]\ CuCl_3 2H_2O$," *Physical Review B*, American Physical Society (APS), Jan 1972.
The definitive version is available at https://doi.org/10.1103/PhysRevB.6.4342

PHYSICAL REVIEW B VOLUME 6, NUMBER 11 1 DECEMBER 1972

Structural and Magnetic Properties of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$

D. B. Losee, J. N. McElearney, A. Siegel, and R. L. Carlin
Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680

and

A. A. Khan
Department of Geological Sciences, University of Illinois at Chicago Circle, Chicago, Illinois 60680

and

J. P. Roux and W. J. James
Department of Chemistry and Graduate Center for Materials Research, University of Missouri—Rolla, Rolla, Missouri 65401

(Received 14 April 1972)

The crystal structure at room temperature and the low-temperature heat capacity and magnetic susceptibilities of single crystals of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ are reported. The monoclinic crystals belong to the space group $P2_1/c$ with $a = 7.479(10)$ Å, $b = 7.864(11)$ Å, $c = 16.730(23)$ Å, $\beta = 91.98(3)°$, and $Z = 4$. The structure consists of chains of edge-sharing $[CuCl_4(OH_2)_2]$ octahedra running along the a axis. Each copper atom is coordinated in a square plane by two water molecules and two chlorine atoms, with two more chlorine atoms at a longer distance. The susceptibility data can be fitted adequately between 1.5 and 20 °K by a Curie–Weiss law $[g_a = 2.08 \pm 0.01$, $g_b = 2.02 \pm 0.01$; $g_{c'} = 2.11 \pm 0.01$; $\theta_a = (0.38 \pm 0.03)$ °K, $\theta_b = (0.36 \pm 0.03)$ °K, $\theta_{c'} = (0.41 \pm 0.03)$ °K], but the susceptibility parallel to the chain can be better fitted as an Ising linear chain. Measurements perpendicular to the chain are not as well fitted by the Ising model. The heat capacity, which consists primarily of a lattice contribution above 3 °K, begins to rise as the temperature falls below 3 °K, but long-range order does not set in above 1 °K, the lowest temperature attained in this work. Both Ising and Heisenberg linear-chain models fit the low-temperature data with $|J/k| < 1$ °K. The results are compared with those reported for the compounds $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2NC_5H_5$.

I. INTRODUCTION

Three copper salts, $CuCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2NC_5H_5$, and $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$, have surprisingly similar crystal structures. They all contain chemical chains consisting of a series of distorted octahedra each sharing an edge with each of two neighbors. The octahedra are successively linked through two chlorine atoms while either *trans*coordinated water or pyridine molecules complete each octahedron. The similarity, however, does not extend beyond the presence of the common $(-CuCl_2-)_n$ chains since the three compounds have these chains isolated from adjacent chains to a varying extent. In this paper the crystal structure of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$, which is named trimethylammonium catena-di-μ-chloro-diaquocopper(II) chloride, is reported along with its magnetic properties, which are then compared with those of $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2NC_5H_5$.

II. EXPERIMENTAL

Single crystals similar in appearance to that depicted by Groth[1] were grown from a 1 : 1 mixture of $[(CH_3)_3NH]Cl$ and $CuCl_2 \cdot 2H_2O$ in water at room temperature. Some crystals grew containing occluded solution and were readily identified and discarded. A single crystal weighing 0.109 g was used for the three susceptibility measurements while a crystal weighing 2.956 g was used for the heat-capacity runs. The crystals which appeared to be stable analyzed as follows: calc. Cu = 23.88 wt%, C = 13.54 wt%, H = 5.30 wt%, N = 5.26 wt%, Cl = 39.98 wt%; found Cu = 22.40 wt%, C = 13.67 wt%, H = 5.17 wt%, N = 5.47 wt%, Cl = 41.03 wt%.

The near-zero-field magnetic susceptibilities were measured on a Cryotronics 17-Hz mutual inductance bridge using techniques previously described.[2] The experimentally determined magnetic susceptibilities for $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ are shown in Fig. 1 from 1.5 to 20 °K where measurements have been made parallel to the a, b, and c' crystallographic directions. The c' axis is defined as the axis perpendicular to the ab plane. The a and c axes have been interchanged relative to the morphological description given by Groth. The error bars given in Fig. 1 for these measurements are the same for each point and amount to ± 0.0042 emu/mole. A more detailed picture of the data is illustrated in Fig. 2.

Zero-field specific-heat measurements were made using a calibrated germanium resistance

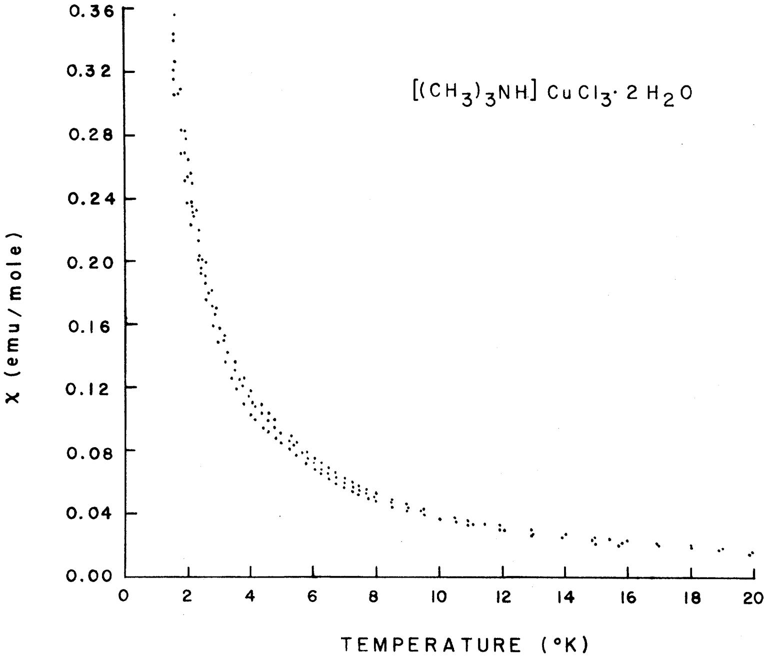

FIG. 1. Magnetic susceptibilities of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ parallel to the a, b, and c' axes. Below 10 °K, $\chi_{c'} > \chi_a > \chi_b$; otherwise, the measurements are isotropic within experimental error.

thermometer and standard heat-pulse techniques appropriate to adiabatic calorimetry. The results of these measurements are shown in Fig. 3. Two separate runs were made on the same crystal, one from 1 to 11 °K and the other from 4.5 to 35 °K. In the region where the two runs overlapped, the reproducibility was within 2%. The behavior of the data between 5 and 6 °K suggests the presence of an inconsequential magnetic impurity.

The crystal symmetry, approximate cell parameters, and space group of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ were determined from precession photographs. Several crystals selected because of their spherical shape and small size revealed double spots in-

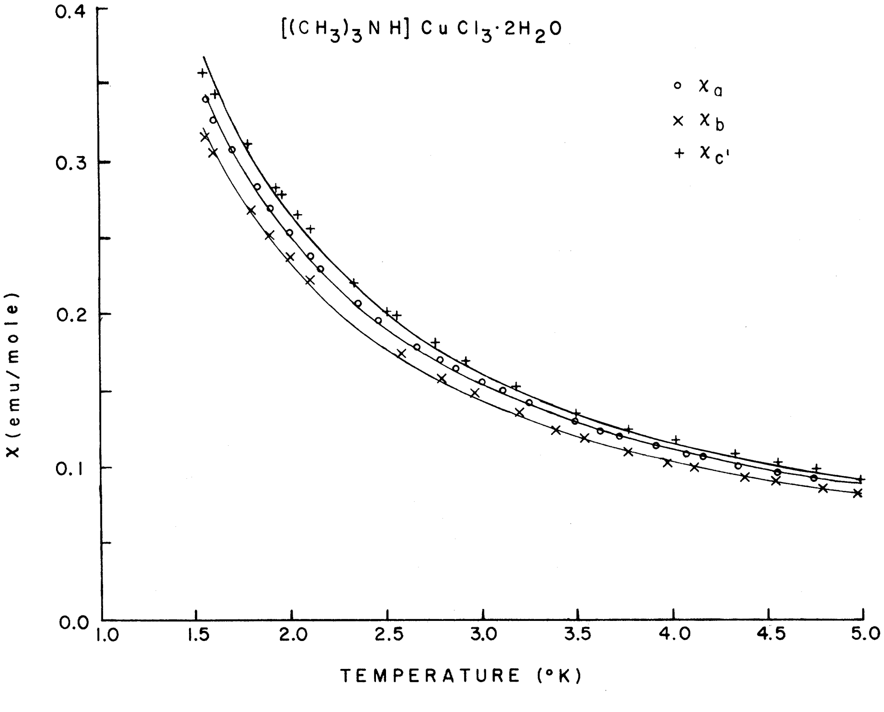

FIG. 2. Magnetic susceptibilities of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ parallel to the a, b, and c' axes, with the Curie–Weiss-law fit illustrated. The parameters are listed in the text. Error bars are represented by the size of the symbols.

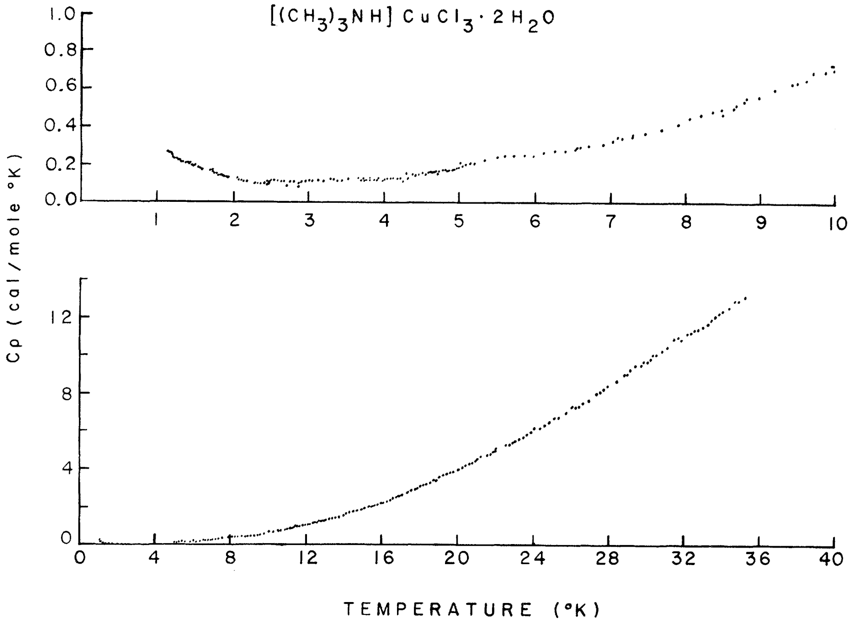

FIG. 3. Heat capacity of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ between 1 and 36 °K (bottom) and 1 and 10 °K (top).

stead of single diffraction peaks on the precession photographs. In order to obtain diffraction patterns free of these features, it was necessary to cut bigger crystals showing growth along the needle axis. One such specimen with dimensions $0.3 \times 0.3 \times 0.3$ mm was used for the intensity-data collection on a quarter-circle semiautomatic diffractometer using Mo $K\alpha$ radiation. Lattice parameters were determined from 24 carefully centered reflections. Intensity data up to $(\sin\theta)/\lambda = 0.48\,\text{Å}^{-1}$ were collected, and each reflection was measured only once. Observed structure factors were calculated by applying the Lorentz-polarization and -absorption corrections.

III. CRYSTAL-STRUCTURE ANALYSIS

$[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ is monoclinic and belongs to the space group $P2_1/c$ with $a = 7.479\ (10)$ Å, $b = 7.864\ (11)$ Å, $c = 16.730\ (23)$ Å, and $\beta = 91.98\ (3)°$; formula weight = 265.92, $Z = 4$, measured density $D_m = 1.78\ \text{g cm}^{-3}$, calculated density $D_c = 1.80\ \text{g cm}^{-3}$. The linear mass-absorption coefficient for the Mo $K\alpha$ radiation is $\mu_{\text{Mo}\,K\alpha} = 30.69\ \text{cm}^{-1}$. The axial ratios quoted by Groth[1] for this compound as $a'' : b'' : c'' = 1.0617 : 1 : 0.9583$ ($\beta = 91.83°$) compare well with the axial ratios $c : 2b : 2a = 1.0637 : 1 : 0.9510$ determined from the present cell parameters.

The crystal structure was determined by Patterson, Fourier, and least-squares methods. The R factor with the individual isotropic temperature factors converged to 13.7%. However, some of the temperature factors were negative, and a comparison of the observed and calculated structure factors revealed that the observed intensities were affected by extinction. An extinction correction[3] reduced the R to 0.088, and all the temperature factors were also positive and of usual magnitudes. No attempt was made to locate the H atoms or to refine the structure with anisotropic temperature factors. Such an effort was considered not worthwhile in view of the limited accuracy of the observed data. A list of observed and calculated structure factors is available on request.

Scattering factors for Cu, Cl, O, C, and N atoms were taken from the International Tables.[4] The computer programs were the same as those used by Baur and Khan.[5]

IV. DESCRIPTION OF THE STRUCTURE

Positional and thermal parameters of the atoms in $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ are listed in Table I. In Table II, some selected interatomic bond lengths and bond angles are given. A view of the complete structure parallel to [010] is shown in Fig. 4 and a view of a part of the structure along the [001] direction in Fig. 5. The most significant feature of the structure is the chains of edge-sharing $[CuCl_4(OH_2)_2]$ octahedra running along the a axis. There are two nonequivalent Cu atoms but both are coordinated similarly. Each Cu atom is coordinated in a square plane by two water molecules and two Cl atoms. Two more Cl atoms at a longer distance (see Table II) complete the distorted octahedron. The third chlorine atom, Cl(3), situated between the chains, accepts four hydrogen bonds from the water molecules belonging to the chains, and the bonding in the (001) plane is through these O-H-Cl bonds only. These hydrogen-bonded chains, therefore, can be visualized

TABLE I. Coordinates and isotropic temperature factors of atoms in $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$.

	x	y	z	B (Å^2)
Cu(1)	0	0	0	1.7(1)
Cu(2)	0.5	0	0	1.8(1)
Cl(1)	0.2008(8)	0.9225(8)	0.1004(3)	2.1(2)
Cl(2)	0.7144(7)	0.9954(7)	0.0993(3)	1.9(2)
Cl(3)	0.7544(8)	0.4980(7)	0.0830(4)	2.3(2)
O(1)	0.466(2)	0.245(2)	0.022(1)	2.1(4)
O(2)	0.038(2)	0.247(2)	0.027(1)	2.1(3)
C(1)	0.744(3)	0.987(3)	0.335(1)	4.0(6)
C(2)	0.082(3)	0.255(3)	0.231(1)	3.0(6)
C(3)	0.411(3)	0.238(3)	0.227(1)	3.3(6)
N	0.241(2)	0.298(2)	0.184(1)	2.6(5)

TABLE II. Selected bond lengths and bond angles in $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$.

Cu(1)–O(2)	2.013(14) Å
Cu(1)–Cl(1)	2.296(6) Å
Cu(1)–Cl(2)	2.751(5) Å
Cu(2)–O(1)	1.982(15) Å
Cu(2)–Cl(2)	2.268(5) Å
Cu(2)–Cl(1)	2.910(6) Å
O(2)–Cl(3)	3.064(15) Å
O(1)–Cl(3)	3.083(15) Å
O(1)–Cl(3)	3.106(15) Å
O(2)–Cl(3)	3.168(15) Å
N–C(2)	1.49(3) Å
N–C(3)	1.51(3) Å
N–C(1)	1.52(3) Å
Cl(2)–Cu(1)–Cl(1)	93.2(2)°
Cl(2)–Cu(1)–Cl(2)	180.0°
Cl(1)–Cu(1)–O(2)	90.4(4)°
N–O(2)	3.01(2) Å
N–O(1)	3.26(2) Å
N–Cl(1)	3.28(2) Å

as forming layers of composition $(CuCl_3 \cdot 2H_2O)$ situated at heights 0 and $\frac{1}{2}$ along the c axis. The $[(CH_3)_3NH]^+$ groups occupy the space between these layers. The interlayer bonding appears mainly of the van der Waals type.

The structure is similar to that of the cobalt analog[6] which, historically, was determined first.

V. MAGNETIC MEASUREMENT RESULTS

A Curie–Weiss law $\chi = Ng^2\mu_B^2 S(S+1)/3k(T-\theta)$ with $S=\frac{1}{2}$ was used to fit the susceptibility data from 1.5 to 20 °K on the UICC IBM 370/155 computer using a least-squares procedure. The resulting values with the field parallel to the a and b axes are $g_a = 2.08 \pm 0.01$, $\theta_a = (0.38 \pm 0.03)$ °K, and $g_b = 2.02 \pm 0.01$, $\theta_b = (0.36 \pm 0.03)$ °K. All of the errors quoted herein represent confidence limits based on the degree to which a variation in one parameter in the fit affects the other parameters. In both instances, as shown in Fig. 2, the fits are within the experimental error over a 20-deg region except at the very lowest temperature where long-range exchange effects are probably contributing. In the case of the measurement made along the c' direction, which can also be taken as along the c axis since $\beta = 91.98°$, the Curie–Weiss fit is not quite as good, giving $g_{c'} = 2.11 \pm 0.01$ and $\theta_{c'} = (0.41 \pm 0.03)$ °K. However, this measurement was made on the same crystal almost a year after the two previous measurements. With this in mind it is encouraging to see how well the data can be fit.

Since the crystal structure clearly reveals chemical chains parallel to the a axis, the susceptibility

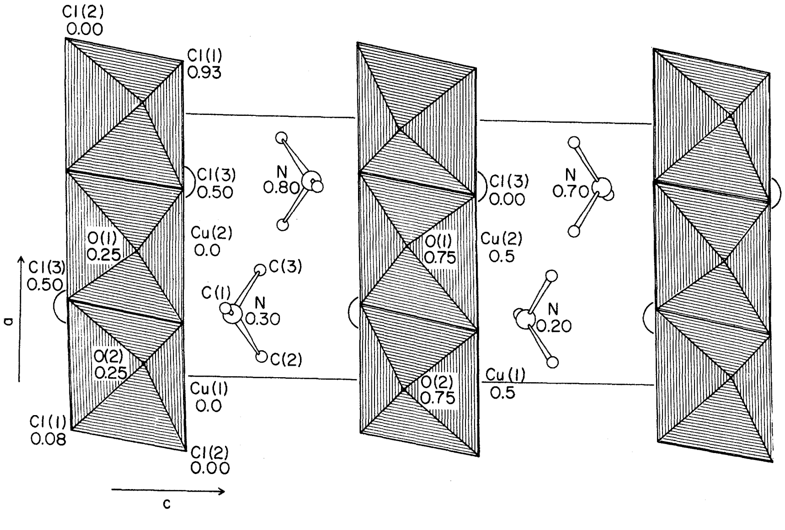

FIG. 4. Crystal structure of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ viewed parallel to [010]. Heights of atoms including the copper atoms within the octahedra are given as fractions of b.

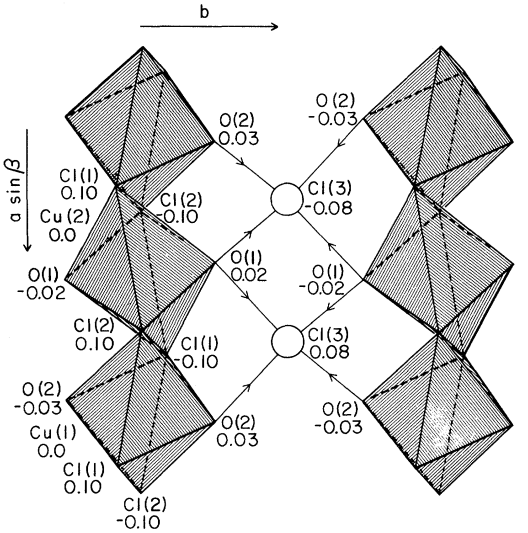

FIG. 5. Hydrogen-bonded chains, which form layers of composition ($CuCl_3 \cdot 2H_2O$) in $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$, viewed parallel to [001]. Only one layer is shown. Heights of atoms including the copper atoms within the octahedra are given as fractions of c and the arrows indicate the hydrogen bonds.

in this direction was also fit to the Ising linear-chain equation[7] given by $\chi_{\parallel} = (N\mu_B^2 g_{\parallel}^2/4kT)e^{2J/kT}$. The parameters $g_{\parallel} = 2.080 \pm 0.005$ and $J/k = (0.210 \pm 0.005)$ °K gave a slightly better fit over the entire temperature region than the Curie–Weiss law for this direction.

In a similar manner Fisher's equation[7] for the perpendicular susceptibility of an Ising linear chain, $\chi_{\perp} = (N\mu_B^2 g_{\perp}^2/8J)[\tanh(J/kT) + (J/kT)\,\mathrm{sech}^2(J/kT)]$, was applied to both the b and c' directions. Although these directions are obviously perpendicular to the chemical chains, the perpendicular-Ising-chain equation did not fit the data as well as the Curie–Weiss law fit.

Preliminary attempts at fitting the data to an isotropic Heisenberg ferromagnetic chain as given by Bonner and Fisher[8] have shown that this may also give a reasonable fit. With these observations in mind, little significance can be placed on the parameters derived from any of the models involving exchange unless more clearly defined characteristics appear in the susceptibility at lower temperatures. This is especially true since a clear choice between simple Curie–Weiss behavior and the other susceptibility results derived for interaction along a chain cannot be made.

The heat capacity is featureless above 3 °K, as anticipated from the susceptibility results, and is attributed to a lattice contribution alone. The rise observed in the heat capacity at the lowest temperatures achieved in this experiment suggests a magnetic-exchange contribution. Ising[9] and Heisenberg[8] models for extended linear chains have been used to fit the data from 1 to 5 °K. It is assumed that in this temperature region there are only two contributions to the heat capacity, namely, the magnetic one plus a lattice term of the form $C_{\mathrm{lat}}/R = aT^N$. A least-squares fit of the data to the Ising linear-chain model for spin $\frac{1}{2}$ using the equation[9] $C/R = (J/2kT)^2\,\mathrm{sech}^2(J/2kT) + aT^N$ gave values of $a = 0.0008 \pm 0.0001$ deg^{-3}, $N = 2.97 \pm 0.01$, and $|J/k| = (0.9 \pm 0.1)$ °K. A good fit to 3 °K was also achieved by a graphical procedure using Bonner and Fisher's calculation[8] for the isotropic Heisenberg linear chain with a value $J/k = (-0.50 \pm 0.05)$ °K. Notice should be taken of the sign of J which suggests an antiferromagnetic interaction. This appears contrary to the susceptibility results reported above, although again it is more likely a case of insensitivity in this temperature region.

A binary-cluster model has been found[10] to describe adequately $Cu(NO_3)_2 \cdot 2.5H_2O$ in a comparable temperature region, even though this compound revealed[11] crooked chains running along the b axis. This model was also used to fit the present data with $C/R = \frac{3}{2}(J/kT)^2 e^{-J/kT}/(1 + 3e^{-J/kT})^2 + aT^N$. In this case a clear choice could be made in favor of the chain models over the binary-cluster model as a better representation of the data. Assuming the possibility of simple three-dimensional magnetic interactions, attempts at fitting the data to a simple $C/R = aT^N + b/T^2$ form were made but were not successful.

VI. DISCUSSION

It is interesting to compare the magnetic behavior observed for this compound with that of $CuCl_2 \cdot 2H_2O$ and $CuCl_2 \cdot 2NC_5H_5$. A variety of low-temperature techniques[12] have been used to study the magnetic properties of $CuCl_2 \cdot 2H_2O$. These have revealed a typical dilute antiferromagnet displaying a transition to an ordered state at 4.3 °K. The crystal structure[13,14] consists of chains similar to those found in $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ extending along the c axis (Harker's setting[13]). These chains are connected by the hydrogen bonds formed between the water molecules of one chain and the chlorine atoms of the neighboring chains. The atomic distances within the distorted octahedra are[14] Cu-Cl = 2.290 Å, Cu-O = 1.957 Å, and Cu-Cl = 2.940 Å. It has been established by NMR[15] and neutron-diffraction[16] studies that the antiferromagnetic transition in $CuCl_2 \cdot 2H_2O$ results in sheets of ferromagnetically ordered spins in the a-b planes with antiparallel alignment in adjacent a-b planes. The susceptibility measured in the a direction as reported by van der Marel *et al.*[17] goes through a broad maximum at about 4.5–5.5 °K. The other two directions, in particular the c direction, are not well characterized above the transition. Although there is no clear experimental proof of magnetic chain behavior along the *c* axis other than the presence of short-range order, several theoretical calculations[18,19] have estimated the exchange in this direction. Hewson *et al.*[19] using a Green's-function method report a value of $J_c/k = -6.78$ °K which is in fair agreement with the value of $J_c/k = -7.63$ °K estimated by them from the early susceptibility results.[20] Friedberg's measurement[21] of the heat capacity suggests substantial short-range order above the Néel temperature since only about 60% of the magnetic entropy has been acquired at the transition temperature. Moriya[22] has postulated a canted antiferromagnetic structure below T_N which has recently been confirmed by Umebayashi *et al.*[23] from neutron-scattering experiments at 1.7 °K.

In the case of $CuCl_2 \cdot 2NC_5H_5$,[24] square coplanar units (Cu-Cl = 2.28 Å, Cu-N = 2.02 Å) aggregate into nearly isolated antiferromagnetic chains parallel to the *c* axis by weaker Cu-Cl bonds (3.05 Å) which complete the distorted octahedron about each copper. The two nonequivalent Cu-Cl bond distances differ more in this structure than those in either $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ or $CuCl_2 \cdot 2H_2O$. This compound exhibits[25] a broad maximum at 17.5 °K in the susceptibility which is characteristic of a magnetic linear chain. There is no indication of long-range order down to 1.3 °K. The susceptibility begins to diverge at the lowest temperature from the theoretical Heisenberg isotropic-chain model with $|J/k| = 13.6$ °K used to fit the data. The low-temperature specific-heat measurements yield a value of $|J/k| = 11.6$ °K using the same model.

An interesting feature of these three compounds is the relative magnitude of the exchange within the chemical chains. As mentioned above the values for the exchange parameters are as follows: $|J/k| < 1$ °K for $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$, $J/k \simeq -7$ °K for $CuCl_2 \cdot 2H_2O$, and $|J/k| \simeq 13$ °K for $CuCl_2 \cdot 2NC_5H_5$, where the values have all been derived from a Heisenberg model. It appears that the compound with the most asymmetry in the $(-CuCl_2-)_n$ unit, i.e., $CuCl_2 \cdot 2NC_5H_5$, has the largest exchange while the least asymmetric unit, $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$, displays clearly the least amount of exchange along the chemical chain. It is likely that the exchange interactions in $CuCl_2 \cdot 2H_2O$ causing the transition itself will in some way influence the exchange along the chain. However, it is also perhaps likely that the nearest-neighbor interaction as reflected in the asymmetry will make the largest contribution in determining this exchange. This seems to be the case.

The question remains whether or not the chains in $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ are separated enough so that the exchange along the chemical chain is the predominant mode of exchange. At some low temperature the exchange between chains is expected to result in long-range order, perhaps with a canting of the spins within the chain. Since there are no inversion centers between the copper ions in the chain, a Moriya[22] interaction is allowed on symmetry grounds.

This study has shown that $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$ has a lower transition temperature than $CuCl_2 \cdot 2H_2O$. If the transition in $CuCl_2 \cdot 2H_2O$ is assumed to be largely determined by the exchange within the *a*-*b* plane then the lower transition temperature of the trimethylammonium compound can be hypothesized to be the result of the intervening anionic chloride ions between the chains, which reduce the predominant mode of such exchange. This exchange possibility has been all but eliminated in $CuCl_2 \cdot 2NC_5H_5$ because of the insulating (diluting) effects of the pyridine molecules. Spence and coworkers[26,27] in recent NMR studies comparing the exchange interactions in $MnCl_2 \cdot 2H_2O$ and $KMnCl_3 \cdot 2H_2O$ have pointed out the extremely delicate balance there is between the geometry and exchange effects. The bond distances within the coordinating octahedron in $MnCl_2 \cdot 2H_2O$ are $(\text{Mn-Cl}_1) = 2.592$ Å, $(\text{Mn-Cl}_1') = 2.515$ Å, and (Mn-O) = 2.150 Å, while in $KMnCl_3 \cdot 2H_2O$ they are $(\text{Mn-Cl}_1) = 2.594$ Å, $(\text{Mn-Cl}_1') = 2.570$ Å, and (Mn-O) = 2.18 Å. From the NMR studies, the spins in $MnCl_2 \cdot 2H_2O$ were found to order antiferromagnetically in chains, while the spins in $KMnCl_3 \cdot 2H_2O$ are ordered ferromagnetically within dimeric units even though both compounds have the same basic octahedral edge-sharing coordination. In any event, very small changes in the coordination geometry are associated with profound changes in the exchange to the point where even the sign of the exchange has been reversed.

It is then reasonable to suggest that small changes in the coordination geometry for this series of copper compounds cause the unanticipated effects observed in the magnitude of the exchange along the chemical chain. It is obvious that studies at lower temperatures are necessary for a better understanding of the magnetic properties of $[(CH_3)_3NH]CuCl_3 \cdot 2H_2O$.

ACKNOWLEDGMENT

This research was supported in part by the National Science Foundation under Grant No. GP 12106. We acknowledge the Computer Centers at both the University of Illinois at Chicago Circle and the University of Missouri–Rolla for computation facilities.

---

[1] P. Groth, *Chemische Kristallographie* (Wilhelm Englemann, Leipzig, 1908), Vol. 1, p. 375.

[2] J. N. McElearney, D. B. Losee, S. Merchant, and R. L. Carlin, J. Chem. Phys. 54, 4585 (1971).

[3] W. H. Zachariasen, Acta Cryst. 16, 1139 (1963).

[4] *International Tables for X-Ray Crystallography*, Vol. II (Kynoch, Birmingham, England, 1959).

[5] W. H. Baur and A. A. Khan, Acta Cryst. B26, 1584 (1970).

[6] P. J. Cresswell and W. T. Robinson (unpublished).

[7] M. E. Fisher, J. Math. Phys. 4, 124 (1963).

[8] J. C. Bonner and M. E. Fisher, Phys. Rev. 135, A640 (1964).

[9] J. W. Stout and R. C. Chisholm, J. Chem. Phys. 36, 979 (1962).

[10] S. A. Friedberg and C. A. Raquet, J. Appl. Phys. 39, 1132 (1968).

[11] B. Morosin, Acta Cryst. B26, 1203 (1970).

[12] C. J. Gorter, Rev. Mod. Phys. 25, 332 (1953).

[13] D. Harker, Z. Krist. 93, 136 (1936).

[14] A. Engberg, Acta Chem. Scand. 24, 3510 (1970).

[15] N. J. Poulis and G. E. G. Hardeman, Physica 18, 201 (1952); 18, 315 (1952); 19, 391 (1953).

[16] G. Shirane, B. C. Frazer, and S. A. Friedberg, Phys. Letters 17, 95 (1965).

[17] L. C. van der Marel, J. van den Broek, J. D. Wasscher, and C. J. Gorter, Physica 21, 685 (1955).

[18] W. Marshall, J. Phys. Chem. Solids 7, 159 (1958).

[19] A. C. Hewson, D. ter Haar, and M. E. Lines, Phys. Rev. 137, A1465 (1965).

[20] J. van den Handel, H. M. Gijsman, and N. J. Poulis, Physica 18, 862 (1952).

[21] S. A. Friedberg, Physica 18, 714 (1952).

[22] T. Moriya, Phys. Rev. 120, 91 (1960).

[23] H. Umebayashi, B. C. Frazer, D. E. Cox, and G. Shirane, Phys. Rev. 167, 519 (1968).

[24] J. D. Dunitz, Acta Cryst. 10, 307 (1957).

[25] K. Takeda, S. Matsukawa, and T. Haseda, J. Phys. Soc. Japan 30, 1330 (1971).

[26] R. D. Spence and K. V. S. Rama Rao, J. Chem. Phys. 52, 2740 (1970).

[27] R. D. Spence, W. J. M. de Jonge, and K. V. S. Rama Rao, J. Chem. Phys. 54, 3438 (1971).