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Structural, EPR, and Magnetic Characterization of (Piperazinium)$_2$CuCl$_6$·MeOH and (1-Methylpiperazinium)$_2$CuCl$_6$

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Received November 14, 1991

The structure and magnetic properties and EPR spectra are reported for two copper chloride complexes of $CuCl_6^{4-}$ stoichiometry. (1-Methylpiperazinium)$_2$CuCl$_6$ belongs to the triclinic space group $P\bar{1}$ with a = 12.448 (8) Å, b = 11.891 (8) Å, c = 6.577 (4) Å, α = 84.16 (1)°, β = 86.74 (1)°, γ = 93.56 (1)°, and Z = 2. The structure contains isolated cations, $CuCl_4^{2-}$ anions, and lattice Cl^- ions. The $CuCl_4^{2-}$ anions have nearly D_{2d} symmetry with an average trans Cl–Cu–Cl angle of 145.8°. The crystals of (piperazinium)$_2$CuCl$_6$·MeOH are tetragonal, of space group $P4_2/n$, with a = 13.597 (8) Å, c = 11.376 (8) Å, and Z = 4. The structure is composed of isolated piperazinium cations, Cl^- ions, and methanol molecules and chains of nearly square pyramidal $CuCl_5^{3-}$ anions. The primary distortion of the $CuCl_5^{3-}$ species away from idealized C_{4v} symmetry involves a small C_{2v} distortion imposed on the basal plane (trans Cl–Cu–Cl angles = 166.8 (1) and 178.2 (1)°, respectively). The basal Cu–Cl distances average 2.313 Å, while the apical Cu–Cl distance is 2.641 (3) Å. These anions are linked together in chains via extremely long interactions of 3.936 (3) Å between the apical Cl of one anion and the Cu atom of its neighbor. Magnetic susceptibility data are indicative of weak antiferromagnetic coupling in this latter compound. Analysis of the EPR line widths is consistent with a two-dimensional magnetic system. These results are interpreted in terms of a two-halide exchange pathway of the type Cu–Cl···Cl–Cu between chains.

Introduction

Copper(II) halide salts exhibit a wide array of interesting structural characteristics with a concomitant diversity in physical properties. Monomeric species normally exist as four-coordinate CuX_4^{2-} anions, which exhibit geometries ranging from slightly compressed tetrahedra to square planar.[1] Monomeric five- or six-coordinate CuX_{2+n}^{n-} anions are much rarer.[2–4] A bewildering array of oligomeric and polymeric species exist,[5–7] in which five- and six-coordination are much more common.

Copper(II) halides possess many interesting physical and chemical properties, including thermochromism[8] and piezochromism,[9] catalysis,[10] mixed-valence behavior,[11] dynamic Jahn–Teller effects,[12] low-dimensional ferro-,[13] antiferro-,[14] and ferrimagnetic[15] behavior, to name some of the more prominent characteristics.

In this paper, we report the crystal structure and electronic properties of two salts with stoichiometries (piperazinium)$_2$CuCl$_4$·MeOH[16] and (1-methylpiperazinium)$_2$CuCl$_6$,[17] respectively. In the original papers, the electronic spectra of both compounds were interpreted in terms of $CuCl_4^{2-}$ anions with coordination geometry close to square planar.

Experimental Section

Samples of (1-MepipzH$_2$)$_2$CuCl$_6$ and (pipzH$_2$)$_2$CuCl$_6$·MeOH, prepared as described in the literature,[16,17] were kindly provided by Prof. R. Battistuzzi. DSC studies were carried out on a Perkin-Elmer Delta Series DSC-7 calorimeter. EPR measurements were made on a Varian E-3 spectrometer. Magnetic measurements were made on an EG&G PARC Model 155 vibrating-sample magnetometer.

Crystals for X-ray analysis were mounted on a Philips PW1100 automated diffractometer in a random orientation: the resulting crystal data and the other details of data collection and refinement are quoted

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Table I. Experimental Data for the Crystallographic Analyses

	$(1\text{-MepipzH}_2)_2CuCl_6$	$(pipzH_2)_2CuCl_6\cdot$ MeOH
formula	$C_{10}H_{28}Cl_6CuN_4$	$C_{13}H_{24}Cl_6CuN_4O$
M_r	480.62	528.62
space group	$P4_2/n$	$P\bar{1}$
a, Å	13.597 (8)	12.448 (8)
b, Å	13.597 (8)	11.891 (8)
c, Å	11.376 (8)	6.577 (4)
α, deg		84.16 (1)
β, deg		86.74 (1)
γ, deg		93.56 (1)
V, Å^3	2103 (2)	965 (1)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.518	1.820
μ, cm^{-1}	18.10	19.85
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.0327	0.0506
$R_w = [\sum w(\Delta F^2)/\sum wF_0^2]^{1/2}$	0.0369	0.0548

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(1\text{-MepipzH}_2)_2CuCl_6$

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
Cu	0.25000	0.25000	−0.08068 (5)	214 (2)
Cl(1)	0.33490 (7)	0.11485 (6)	−0.13583 (9)	395 (3)
Cl(2)	0.11593 (8)	0.16847 (8)	−0.01731 (10)	511 (4)
Cl(3)	0.83894 (8)	0.10533 (8)	−0.28527 (11)	533 (4)
N(1)	0.3590 (2)	−0.0234 (2)	0.2043 (3)	357 (1)
N(2)	0.4614 (3)	−0.2098 (2)	0.2111 (3)	40 (1)
C(1)	0.4304 (3)	−0.046 (3)	0.3009 (4)	39 (1)
C(2)	0.4334 (3)	−0.1562 (3)	0.3221 (3)	40 (1)
C(3)	0.3914 (3)	−0.0738 (3)	0.0941 (4)	44 (1)
C(4)	0.3953 (3)	−0.1832 (3)	0.1123 (4)	45 (2)
C(5)	0.3460 (4)	0.0849 (3)	0.1872 (5)	50 (2)

[a] U_{eq} defined as one-third the trace of the diagonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(pizH_2)_2CuCl_6\cdot MeOH$

atom	x/a	y/b	z/c	U_{eq}, Å^2
Cu	0.22703 (7)	0.22660 (7)	−0.01614 (1)	155 (3)
Cl(2)	0.4144 (2)	0.2267 (2)	−0.0376 (3)	344 (6)
Cl(3)	0.0390 (2)	0.2235 (2)	0.0158 (3)	367 (6)
Cl(4)	0.2392 (2)	0.4180 (2)	−0.0009 (3)	355 (6)
Cl(1)	0.2137 (2)	0.0319 (2)	0.0491 (3)	347 (6)
Cl(5)	0.2284 (2)	0.2301 (2)	−0.4184 (3)	295 (6)
Cl(6)	−0.2589 (2)	0.3578 (2)	0.5528 (4)	494 (8)
O	0.3213 (6)	−0.1857 (5)	0.7355 (10)	56 (3)
C(1)	0.2945 (9)	−0.2435 (9)	0.9324 (16)	58 (4)
N(1)	−0.4178 (5)	−0.0320 (5)	0.3570 (10)	33 (2)
C(3)	−0.4123 (7)	−0.0616 (8)	0.5792 (13)	41 (3)
N(2)	−0.0234 (6)	−0.0277 (6)	0.3028 (10)	35 (2)
N(3)	0.5962 (5)	0.55500 (6)	0.4004 (11)	36 (2)
C(6)	0.0046 (7)	0.4986 (8)	−0.2822 (13)	48 (3)
N(4)	0.0850 (6)	0.4418 (6)	−0.4072 (12)	43 (3)
C(8)	−0.0976 (7)	0.0379 (7)	0.4175 (13)	37 (3)
C(9)	0.4663 (7)	−0.0261 (8)	0.3045 (13)	44 (3)
C(10)	−0.0354 (7)	0.1058 (7)	−0.4397 (13)	40 (3)
C(11)	0.4518 (7)	0.4024 (7)	−0.5850 (13)	38 (3)
C(12)	0.0400 (8)	0.4049 (7)	−0.5906 (14)	47 (3)
C(13)	0.5136 (7)	0.5011 (8)	−0.7194 (13)	44 (3)

in Table I. The structure amplitudes were obtained after the usual Lorentz and polarization corrections; absorption corrections were deemed unnecessary. Both structures were solved by the heavy-atom technique and refined by full-matrix least-squares methods using anisotropic thermal parameters; hydrogen atoms, placed at the calculated positions, were introduced in the last refinement cycle [as fixed contributors in $(1\text{-MepipzH}_2)_2CuCl_6$]: the final atomic coordinates are quoted in Tables II and III. The atomic scattering factors used, corrected for anomalous dispersion, were taken from ref 18; all the calculations were performed using a Gould 32/77 computer at the Centro di Studio per la Strutturistica Diffractometrica del CNR dell'Università di Parma with SHELX76,[19] ORTEP,[20] and PARST[21] programs. Pertinent bond distances and angles are reported in Tables IV and V.

Table IV. Bond Distances (Å) and Angles (deg) for $(1\text{-MepipzH}_2)_2CuCl_6$

Cu–Cl(1)	2.259 (1)	Cu–Cl(2)	2.252 (2)
N(1)–C(1)	1.499 (5)	N(1)–C(3)	1.495 (5)
N(1)–C(5)	1.496 (6)	N(2)–C(2)	1.508 (5)
N(2)–C(4)	1.484 (6)	C(1)–C(2)	1.513 (6)
C(3)–C(4)	1.503 (6)		

Cl(1)–Cu–Cl(2)	95.86 (6)	N(1)–C(1)–C(2)	109.7 (3)
C(3)–N(1)–C(5)	112.1 (3)	N(2)–C(2)–C(1)	110.7 (3)
C(1)–N(1)–C(5)	112.0 (3)	N(1)–C(3)–C(4)	110.4 (3)
C(1)–N(1)–C(3)	109.2 (3)	N(2)–C(4)–C(3)	111.5 (4)
C(2)–N(2)–C(4)	111.2 (3)	Cl(1)–Cu–Cl(1′a)	147.8 (1)
		Cl(2)–Cu–Cl(2a)	142.7 (1)

Table V. Bond Distances (Å) and Angles (deg) for $(pipzH_2)_2CuCl_6\cdot MeOH$[a]

Cu–Cl(2)	2.328 (2)	Cu–Cl(3)	2.335 (2)
Cu–Cl(4)	2.285 (3)	Cu–Cl(1)	2.305 (3)
Cu–Cl(5)	2.641 (3)	O–C(1)	1.415 (11)
N(1)–C(2)	1.506 (11)	N(1)–C(3)	1.475 (10)
N(2)–C(4)	1.470 (11)	N(2)–C(5)	1.483 (11)
N(3)–C(6)	1.472 (11)	N(3)–C(7)	1.484 (12)
N(4)–C(8)	1.496 (12)	N(4)–C(9)	1.455 (12)
C(2)–C(3a)	1.522 (13)	C(4)–C(5b)	1.514 (12)
C(6)–C(7c)	1.533 (12)	C(8)–C(9d)	1.503 (13)

Cl(1)–Cu–Cl(5)	95.5 (1)	Cl(4)–Cu–Cl(5)	97.7 (1)
Cl(4)–Cu–Cl(1)	166.8 (1)	Cl(3)–Cu–Cl(5)	92.1 (1)
Cl(3)–Cu–Cl(1)	88.8 (1)	Cl(3)–Cu–Cl(4)	90.5 (1)
Cl(2)–Cu–Cl(5)	89.5 (1)	Cl(2)–Cu–Cl(1)	90.2 (1)
Cl(2)–Cu–Cl(4)	90.1 (1)	Cl(2)–Cu–Cl(3)	178.2 (1)
C(2)–N(1)–C(3)	110.0 (6)	C(4)–N(2)–C(5)	112.3 (6)
C(6)–N(3)–C(7)	112.1 (7)	C(8)–N(4)–C(9)	111.7 (7)
N(1)–C(2)–C(3a)	110.3 (7)	N(1)–C(3)–C(2a)	109.8 (7)
N(2)–C(4)–C(5b)	109.8 (7)	N(2)–C(5)–C(4b)	109.1 (7)
N(3)–C(6)–C(7c)	109.0 (7)	N(3)–C(7)–C(6c)	109.5 (7)
N(4)–C(8)–C(9d)	110.8 (7)	N(4)–C(9)–C(8d)	111.5 (8)

[a] Key: $a = -x - 1, -y, 1 - z$; $b = -x, -y, 1 - z$; $c = 1 - x, 1 - y, 1 - z$; $d = -x, 1 - y, -1 - z$.

Thermal studies were carried out on samples of $(pipzH_2)_2CuCl_6\cdot MeOH$ over the temperature range 40–260 °C, with a scanning rate of 5 °C/min. A small anomaly, characteristic of a structural phase transition, was observed with an onset of 97 °C (peak at 102 °C) with a heat of transition of 1700 J/mol. Further anomalies, characteristic of decomposition, occurred at 140 and 245 °C.

Results

Structure Descriptions. Despite the similar stoichiometries, the crystal structures of the two compounds show distinctly different structural characteristics, with neither salt containing a $CuCl_6^{4-}$ anion, as might be implied by the simple stoichiometric formula. The differences between the two structures are attributable to the difference in hydrogen-bonding capabilities of the two cations, as well as to differences in packing energies.

The salt of the 1-methyl derivative contains discrete dications, $CuCl_4^{2-}$ anions, and Cl^- anions, as seen in Figure 1. The $CuCl_4^{2-}$ anions are located on sites of C_2 symmetry, with the symmetry axis parallel to the c axis, and have a compressed tetrahedral geometry: Cu–Cl(1) = 2.259 (1) Å, Cu–Cl(2) = 2.252 (1) Å, Cl(1)–Cu–Cl(1) = 147.8 (1)°, Cl(2)–Cu–Cl(2) = 142.7 (1)°. The trans Cl–Cu–Cl angles cited are at the upper end of the range normally observed for compressed $CuCl_4^{2-}$ tetrahedral systems.[1] It should be noted that the thermal parameters for the chloride ions are anomalously large, generally larger than those

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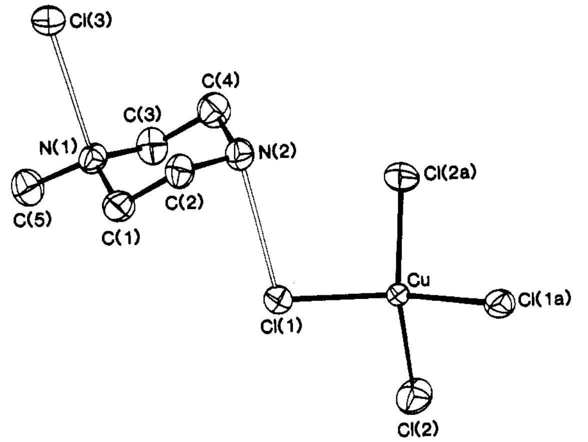

Figure 1. Illustration of the structural unit in (1-MepipzH$_2$)$_2$CuCl$_6$. Hydrogen-bonding interactions are denoted by open bonds.

of the cation. Large thermal parameters for the halide ions in CuCl$_4^{2-}$ anions have been associated with the presence of disorder and/or large librational motions.[1]

The cations and anions are hydrogen-bonded together into a three-dimensional network with the following hydrogen-bonding contacts: N(2)–Cl(1) = 3.174 (4) Å, H(7)–Cl(1) = 2.06 (5) Å; N(1)–Cl(3) = 3.054 (4) Å, H(1)–Cl(3) = 1.98 (5) Å; N(2)–Cl(3) = 3.130 (4) Å, H(6)–Cl(3) = 2.25 (6) Å. Thus, Cl(2) is not involved in the hydrogen bonding, while the isolated chloride ion, Cl(3), has two short N–H···Cl interactions.

The structure of (piperazinium)$_2$CuCl$_6$·MeOH is much more interesting. It contains two independent dications, pentacoordinate CuCl$_5^{3-}$ anions, and Cl$^-$ anions. The CuCl$_5^{3-}$ anions can be described as having essentially a square pyramidal type coordination geometry. The basal Cu–Cl distances average 2.314 Å (range: 2.285 (3)–2.335 (3) Å), while the apical distance is 2.641 (3) Å. A small but significant C_{2v} distortion exists which is apparent in the trans Cl–Cu–Cl angles and the distances in the basal plane. The Cl(1)–Cu–Cl(4) angle is 166.8 (1)°, with the Cu–Cl distance averaging 2.295 Å, while the Cl(2)–Cu–Cl(3) angle is nearly linear, 178.2 (1)°, with longer Cu–Cl distances, 2.332 Å.

The striking feature of the structure is the chains of CuCl$_5^{3-}$ anions formed parallel to the *c* axis. The square pyramids are arranged such that the apical chloride ion occupies the antiapical site beneath the base of the adjacent square pyramid at a distance of 3.936 Å (Figure 2). While this distance is too long to be considered a coordinate or even semicoordinate interaction, it may provide a pathway for a (weak) magnetic superexchange mechanism, as discussed later. The stacks of chains form a distorted square lattice, as seen in Figure 3. One set of short Cl···Cl contacts (dotted lines in Figure 3) exist between pairs of CuCl$_5^{3-}$ anions. In addition, multiple N–H···Cl and O–H···Cl hydrogen bonds (see next paragraph) provide stability to this structure and provide possible magnetic exchange pathways perpendicular to the chain direction.

The structure is tied together through a series of hydrogen bonds between the dications, the methanol molecule, and the CuCl$_5^{3-}$ and Cl$^-$ anions. Again, the lattice chloride, Cl(6), is involved most extensively in hydrogen bonding: Cl(6)–O = 3.024 (7) Å; Cl(6)–N(3) = 3.163 (7) Å, Cl(6)–H(13) = 2.084 Å; Cl(6)–N(2) = 3.152 (7) Å, Cl(6)–H(20) = 2.077 Å. The hydrogen bonding to the basal chloride ions in the CuCl$_5^{3-}$ anions is considerably weaker, and no significant hydrogen bonding to the apical chloride occurs. A short N–H···O contact between one of the dications and the methanol molecule also exists: O–N(1) = 2.780 (9) Å.

Electronic Structure. The electronic absorption spectrum of the (1-MepipzH$_2$) salt has previously been reported by Marcotrigiano et al.[17] The d–d portion of the spectrum consisted of a broad band centered at 10 420 cm^{-1}. Visual inspection of the reported spectrum would indicate the presence of several absorption bands between 9000 and 12 000 cm^{-1}. This agrees well with the calculated transition energies for this geometry,[1] where transitions occurring at 8600, 9000, and 11 400 cm^{-1} are predicted.

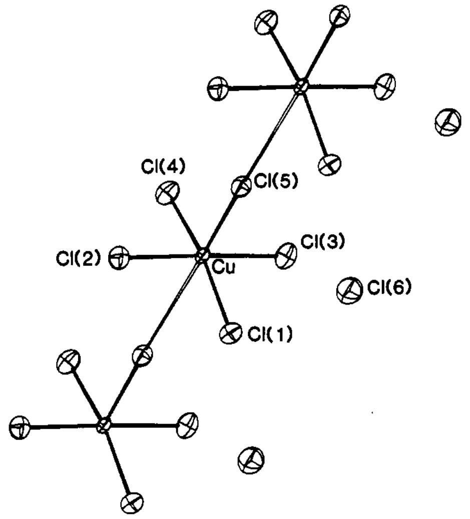

Figure 2. Illustration of the CuCl$_5^{3-}$ anions in (pipzH$_2$)$_2$CuCl$_6$·MeOH, showing the stacking parallel to *c*. The open bonds indicate the long interspecies Cu···Cl interaction.

The powder EPR spectrum at room temperature of (1-MepipzHz)$_2$CuCl$_6$ consists of a single broad, asymmetric line which can be interpreted in terms of an axial **g** tensor with components $g_\perp \sim 2.07$ and $g_\parallel \sim 2.25$. No sharpening of the spectrum is observed at 78 K, but some structure is evident, probably due to unresolved hyperfine lines.

Structurally, the pseudo-S_4 axes of the compressed tetrahedral coordination sphere of the CuCl$_4^{2-}$ anions are all parallel to the crystallographic *c* axis. Thus, the crystal $g_\parallel$ and $g_\perp$ values should be directly identifiable with the molecular $g_\parallel$ and $g_\perp$ values. However, compressed tetrahedral CuCl$_4^{2-}$ anions with trans angles near 145° are found to have values of $g_\parallel \sim 2.30$–2.32, as shown in Table VI.[22-27] To account for this discrepancy, it must be assumed that the local pseudo-S_4 axes are not parallel to the tetragonal *c* axis. Rather, the anions must be disordered in a manner so as to yield the observed average structure.

The electronic absorption spectrum for the pipzH$_2^{2+}$ salt has been reported to consist of a single, relatively sharp band at 11 490 cm^{-1} in the d–d region.[3] Above the phase transition at 97 °C, the spectrum changes abruptly, now exhibiting peaks at 6760 and 10 640 cm^{-1}.[3] This is attributed to the formation of a distorted tetrahedral CuCl$_4^{2-}$ species. Remeasurement in our laboratories of the room-temperature spectrum of a thin film melted between glass plates revealed the presence of several weaker shoulders at approximately 10 500 and 9000 cm^{-1}. The room-temperature spectrum agrees well with the reflection spectra[28] obtained at 5 K for Co(NH$_3$)$_6$CuCl$_5$ and [*N*-(2amet)pipzH$_3$]CuCl$_5$·2H$_2$O. The former shows a series of (four) transitions between 8000 and 11 300 cm^{-1}, while in the latter three transitions are discernible between 8200 and 11 500 cm^{-1}.

For the (pipzH$_2$)$_2$CuCl$_6$·MeOH salt, the powder EPR spectrum is clearly axial in nature with $g_\perp = 2.067$ and $g_\parallel = 2.307$. Virtually

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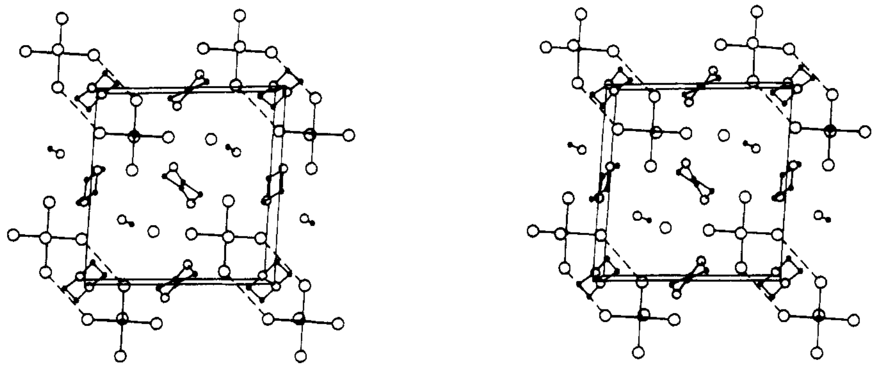

Figure 3. Packing diagram for the $(pipzH_2)_2CuCl_6{\cdot}MeOH$ structure as viewed from the *c* direction. Cl atoms are designated as large open circles; N and O atoms, as smaller open circles.

Table VI. EPR Parameters for $CuCl_4^{2-}$ Anions

cation[a]	trans Cl–Cu–Cl angle, deg	mol *g* values	ref
Cs	129.2	2.384, 2.105, 2.083[c]	22
PCP	132.6	2.363, 2.068[b,d]	23
$4AP{\cdot}H_2O$	134.6	2.315, 2.081[d] 2.372, 2.069[b,d]	24
5MAP	140.0	2.329, 2.064[d]	24
cinc	142.1, 148.0	2.292, 2.051[c]	25
$1\text{-}MepipzH_2$	142.0, 147.8	2.25, 2.07[d]	this work
nmpH	180	2.221, 2.040[d]	26
abtH	180	2.21, 2.05[c]	27

[a] PCP = 1-(1-phenylcyclohexyl)piperidinium, $4AP{\cdot}H_2O$ = 4-aminopyridinium hydrate, 5MAP = 5-methyl-2-aminopyridinium, cinc = cinchonium, nmpH = *N*-methylphenethylammonium, abtH = 2-aminobenzothiazolium. [b] Liquid N_2 measurements. [c] Molecular *g* values calculated from crystal *g* values. [d] Crystal *g* values are identical with molecular *g* values.

no change occurs when the sample is cooled from room temperature to 78 K. The $g_\parallel$ value is somewhat larger than that observed for $[N\text{-}(2amet)pipzH_3]CuCl_5{\cdot}2H_2O$ ($g_\parallel = 2.295$) and the low-temperature form of $Co(NH_3)_6CuCl_5$ ($g_\parallel = 2.28$),[28] indicating a somewhat greater axial elongation in the $(pipzH_2)_2CuCl_6{\cdot}CH_3OH$ salt, in agreement with the structural results.[18]

Magnetic Properties. Figure 4 shows a plot of $\chi_m T$ vs T for the compound $(pipzH_2)_2CuCl_6{\cdot}MeOH$. The downward curvature as T is lowered is clearly indicative of antiferromagnetic exchange coupling. As indicated in the structure description section, two limiting cases for exchange pathways would be anticipated: 1D coupling along the stacks of $CuCl_5^{3-}$ anions and 2D coupling through H-bonding and Cl···Cl contacts perpendicular to the stacks. (It would be anticipated, however, that any coupling along the stacks would be ferromagnetic, since the magnetic $d_{x^2-y^2}$ type orbitals lie perpendicular to the chains with exchange mediated by the apical Cl ion. Thus the overlap integral between adjacent species will be zero by symmetry, which leads to ferromagnetic behavior.) Consequently, the data were fit to the expressions for both the 1D and 2d antiferromagnetic systems,[29,30] although it is known that susceptibility data cannot distinguish between the two. The results are shown in Figure 4 for the 1D model with $J/k = -1.80$ K and $g = 2.10$. The corresponding parameters for the fit to the model for a 2D square lattice (indistinguishable from the 1D fit) are $J/k = -1.0$ K and $g = 2.10$.

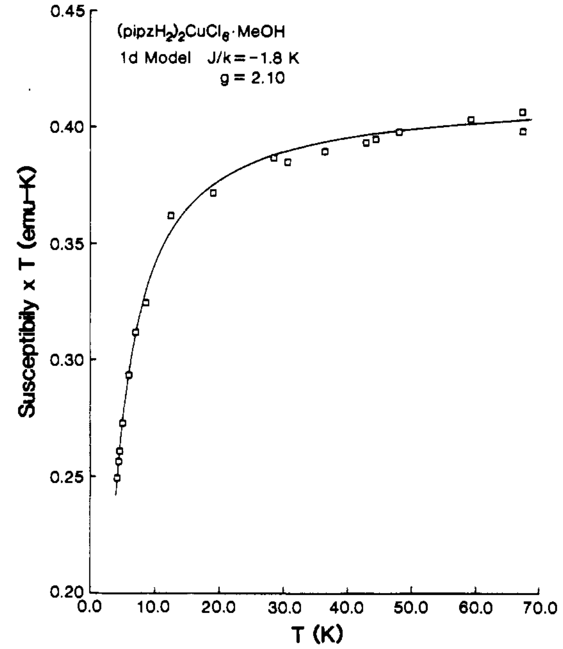

Figure 4. Plot of $\chi_m T$ vs T for $(pipzH_2)_2CuCl_6{\cdot}MeOH$. The solid line is the fit to the spin $^1/_2$ Heisenberg linear chain model with $J/k = -1.8$ K and $g = 2.10$. The 2D spin $^1/_2$ Heisenberg model gives an identical fit with $J/k = -1.0$ K and $g = 2.10$.

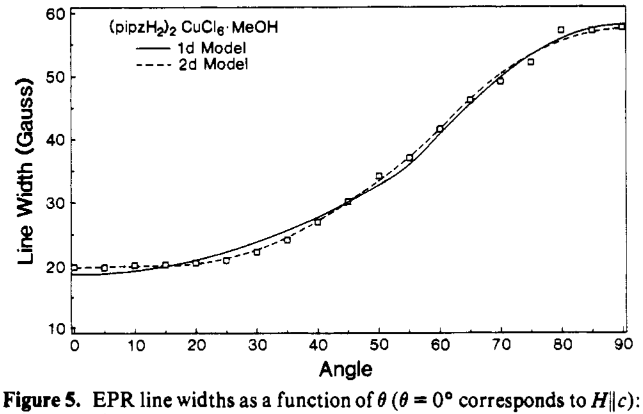

Figure 5. EPR line widths as a function of θ ($\theta = 0°$ corresponds to $H \parallel c$): solid line, fit to 1D spin-diffusion model; dashed line, fit to 2D spin-diffusion model. See text for parameters.

To further characterize the low-dimensional nature of this system, the single-crystal EPR spectra were recorded at room temperature. The resonance fields and line widths exhibit axial symmetry about the chain axis, with $g_\parallel = 2.299$, $g_\perp = 2.063$, $\Delta H_\parallel = 58$ G, and $\Delta H_\perp = 19.5$ G. In addition, the line widths show an angular dependence indicative of spin-diffusion processes associated with low-dimensional magnetic behavior. This contribution to the relaxation processes exhibits a minimum in ΔH when the magnetic field makes an angle of 55° with the chain axis. Figure 5 shows a plot of ΔH vs θ (θ = angle between the

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(29) Baker, G. A., Jr.; Rushbrooke, G. S.; Gilbert, H. E. *Phys. Rev.* **1964**, *135*, 1272.

(30) Baker, G. A., Jr.; Gilbert, H. E.; Eve, J.; Rushbrooke, G. S. *Phys. Lett.* **1967**, *25A*, 207.

Table VII. Coordination Geometry of Representative $CuCl_5^{3-}$ Species

cation	$\delta r_{1,3}$, Å	$\delta r_{2,4}$, Å	δr_5, Å	$\delta\phi_{2,4}$, deg	$\delta\phi_{1,3}$, deg	ref
amet[a]	0.02	−0.076	0.18	±22.4	±7.4	3
$amet_4$[b]	0.014	−0.070	0.329	±21.0	±0.4	36
pipz[c]	0.005	−0.058	0.251	±23.4	±0.9	this work
$Co(NH_3)_6^{3+}$	0	0	0	0	0	34

[a] amet = *N*-(2-ammonioethyl)piperazinium trication. [b] In the salt $(amet)_4Cu_5Cl_{22}$. [c] pipz = the piperazinium dication.

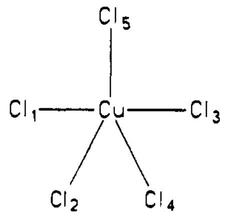
field direction and the chain axis) with a fit to the expression

$$\Delta H(\theta) = A + B\cos^2\theta + C|3\cos^2\theta - 1|^n$$

where the A and B terms arise from spin anisotropies[31] and the C term represents the contribution from spin-diffusion processes[32] with $n = {}^4/_3$ for 1D behavior and $n = 2$ for 2D magnetic systems. The data in Figure 5 were fit to models which included contributions from either 1D (solid line) or 2D (dashed line) spin-diffusion processes with parameter values $A = 14$, $B = 30$, and $C = 5.6$ G for the 1D model and $A = 15.9$, $B = 25.4$, and $C = 2.8$ G for the 2D model. The fit obtained by assuming a 2D type spin-diffusion process is clearly superior. The relaxation processes, as sampled by the EPR experiment, are consistent with the two-dimensional magnetic nature of this system.

Discussion

The $(pipzH_2)_2CuCl_6{\cdot}MeOH$ salt provides a further example of a rather rare species, an isolated five-coordinate CuX_5^{3-} anion, and gives further insight into the distortion pathways for such species. Reinen and Atanasov have examined the idealized $D_{3h} \leftrightarrow C_{4v}$ pathway[33] based the time-averaged trigonal bipyramidal $CuCl_5^{3-}$ anion in $Co(NH_3)_6CuCl_5$[34,35] and the nearly perfect square pyramidal $CuCl_5^{3-}$ anion in $(amet)CuCl_5{\cdot}H_2O$.[3] Starting with the hypothetical D_{3h} species, I, the distortions may be characterized by changes in the Cu–Cl_i distances, δr_i, and in the Cl_5–Cl_i bond angles, $\delta\phi_i$. These parameters, for several species, are given in Table VII. For the idealized $D_{3h} \leftrightarrow C_{4v}$ pathway, the relation $\sum\delta r_i = 0$ holds. This is the case for the species in $(amet)CuCl_5{\cdot}H_2O$ but does not hold for the species in $(pipzH_2)_2CuCl_6{\cdot}MeOH$ nor for the quasi-isolated $CuCl_5^{3-}$ anions in $(amet)_4Cu_5Cl_{22}$.[36] This is in accord with a survey of the structural characteristics of a large number of $CuCl_3L_2$ species where it was shown that only a few species had geometries lying on the $D_{3h} \leftrightarrow C_{4v}$ pathway.[37] Most exhibited a so-called 4+1 geometry, characterized by $\delta\phi_1 = \delta\phi_3 < 5°$, $-20° < \delta\phi_2 = \delta\phi_4 < 10°$, and $\delta r_5 > 0.3$ Å. Thus it would appear the low-energy pathway for the $D_{3h} \leftrightarrow C_{4v}$ interconversion is really the route depicted in II.



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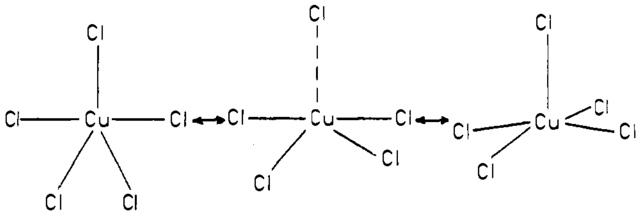

II

Acknowledgment. This research was supported by NSF Grants DMR-8803382 and DMR-9011072. The X-ray diffraction facility at Washington State University was established through funds from the NSF (Grant CHE-8408407) and The Boeing Co.

Note Added in Proof. A preliminary report of the magnetic properties of $(pipzH_2)_2CuCl_6{\cdot}MeOH$ has been given: Grigereit, T. E.; Liu, Y.; Zhou, P.; Drumheller, J. E.; Bonamaratini-Corradi, A.; Bond, M. R.; Place, H.; Willett, R. D. *J. Magn. Magn. Mater.* **1991**, *104–107*, 831.

Supplementary Material Available: Tables of hydrogen atom positions and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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