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X-ray Structure and Variable Temperature Magnetic Properties of a Zigzag $(Cu-Cl)_n$ Chain

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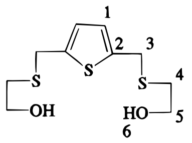
The ligand 2,5-bis(4-hydroxy-2-thiabutyl)thiophene (L) and its polymeric complex $(CuCl_2{\cdot}L)_n$ have been prepared. The complex $(C_{10}H_{16}Cl_2CuO_2S_3)_n$ crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 6.8096(4)$ Å, $b = 9.4542(5)$ Å, $c = 22.899(3)$ Å, $Z = 4$. Each copper atom is six-coordinate with cis chlorines and trans sulfurs. One bond to chlorine and one to oxygen are elongated, and each copper is part of a zigzag $(Cu-Cl)_n$ chain. The chains are cross-linked by the organic ligand, which coordinates through each of its arms to different coppers by using thioether sulfur and hydroxyl oxygen. Electrical neutrality is achieved by the remaining chlorine required by stoichiometry being present as an isolated Cl^- ion in empty spaces in the structure. The complex has been investigated by cyclic voltammetry, IR, and UV/vis spectroscopy, and the polymer structure has been observed to be destroyed upon dissolving. Magnetic susceptibility measurements (5−302 K) have been fitted to a uniform chain model with molecular field and paramagnetic "impurity" corrections. Intrachain ($-2J = 26.4$ cm^{-1}) and interchain ($J' = -8.46$ cm^{-1}) couplings were found to be small and antiferromagnetic.

Introduction

The study of the magnetic properties of chains, layers, and three-dimensional polymers containing metal ions is of current interest to both chemists and physicists engaged in the development of new materials.[1] Chains in particular have been studied in considerable detail for several years,[2,3] and the simpler Heisenberg chains exhibiting intrachain antiferromagnetic coupling are well understood and well documented. For example, chains with single chlorine bridges between coppers, although not particularly common, have $-2J$ values that range from -0.96 to 12.2 cm^{-1} [3] when the magnetic orbitals on adjacent coppers are nearly orthogonal. Chains with double chlorine bridges display values of $-2J$ between -6.30 and 82.6 cm^{-1},[4] while chains of $Cu(C_2O_4){\cdot}{}^1/_3H_2O$ with oxalate bridges between coppers and parallel magnetic orbitals have $-2J = 291$ cm^{-1}, whereas $Cu(C_2O_4)(NH_3)_2{\cdot}H_2O$, in which the magnetic orbitals on copper are perpendicular to the oxalate bridge plane and thus unfavorably oriented to overlap, have $-2J$ reduced to 15.4 cm^{-1}.[5] The production of chains that give bulk samples with overall ferromagnetic character, while having been achieved, is still synthetically uncertain even though greatly desired since much of magnetic materials research is aimed ultimately at the production of molecular-based magnets. One synthetic strategy to achieve ferromagnetic chains might be to design monomer molecules that form polymer chains in which the magnetic orbitals on adjacent monomer units are orthogonal. In this way, the apparently overwhelming tendency for antiferromagnetic coupling between adjacent metals in chains may be avoided and ferromagnetic coupling achieved. Alternatively, using cross-linked polymer chains to build an interwoven structure containing holes that can be filled with species providing sterically oriented, isolated and uncompensated spins could also lead to overall ferromagnetic behavior. In this paper, we describe an attempt at such an approach.

Ligand L, developed for this purpose, is shown below.



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Experimental Section

Commercially available reagents were obtained from the Aldrich Chemical Co. Inc. or from Morton Thiokol Alfa Products Inc. and were used without further purification. Those used for cyclic voltammetry measurements were of spectroscopic grade. 2,5-Bis(chloromethyl)thiophene was prepared by the literature method.[6] Spectroscopic data were obtained by using the following instruments: IR, Mattson Polaris FT; UV/vis, Cary Model 17; NMR, General Electric 300-NB. Magnetic susceptibility data were obtained at room temperature by the Faraday method. Variable temperature magnetic susceptibility data on powder samples were obtained in the range 5−300 K by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. Main solenoid fields of 1.5 and 2.0 T and a gradient field of 10 T·m^{-1} were employed, and the susceptibility data were corrected for diamagnetism by using Pascal constants. A value of 60×10^{-6} cgsu/mol of copper atoms was used as a correction for temperature independent magnetism (TIP) where such a term appears in our calculations.[7] The calibrant was $HgCo(NCS)_4$. Curve fittings were carried out using a locally modified

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Table 1. Crystallographic Data[a]

complex	$\{[CuCl(L)][Cl]\}_n$
empirical formula	$C_{10}H_{16}Cl_2CuO_2S_3$
fw	396.85
space group	$P2_12_12_1$ (No. 19)
T (°C)	22
a (Å)	6.8096(4)
b (Å)	9.4542(5)
c (Å)	22.899(3)
ρ_{calcd} (g cm^{-3})	1.788
V (Å^3)	1474(2)
Z	4
λ (Å)	0.709 30
μ (mm^{-1})	2.25
R^b	0.031
$R_w{}^c$	0.034

[a] Estimated standard deviations for data in this table and elsewhere in this paper refer to the least significant figure and are given in parentheses. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

program for nonlinear weighted least squares as proposed by Wentworth[8] on the basis of work by Deming.[9] Electrochemical measurements were carried out under a nitrogen atmosphere at room temperature by using a Cypress Systems, Inc., CS-1087 computer-controlled potentiostat. Solution concentrations were 10^{-3} mol/L in complex and 0.1 mol/L in supporting electrolyte (tetraethylammonium perchlorate). Voltammograms were recorded in acetonitrile by using a glassy carbon working electrode that was prepolished with 0.3 μm Al_2O_3, a platinum counter electrode, and an aqueous saturated calomel reference electrode checked periodically relative to a 1.0×10^{-3} mol/L solution of ferrocene in acetonitrile containing 0.1 mol/L tetraethylammonium perchlorate for which the ferrocene/ferrocenium reduction potential was 400 mV. The reference electrode was separated from the bulk of the solution by a porous Vycor tube. Junction potential corrections were not used. Analyses were performed by Canadian Microanalytical Service Ltd.

Preparative Details. $C_{10}H_{16}O_2S_3$, Ligand L. Sodium metal (2.3 g, 0.10 mol) was dissolved in commercial absolute ethanol (200 mL) under an atmosphere of nitrogen and heated to reflux. After the addition of 2-mercaptoethanol (7.8 g, 0.10 mol), the solution was refluxed for 10 min and 2,5-bis(chloromethyl)thiophene (9.1 g, 0.050 mol) in benzene (100 mL) was added dropwise over 3 h. The mixture was refluxed for another 1 h, and then the solvent was removed on a rotary evaporator to leave a yellowish-brown oil. The oil was extracted with chloroform (3 × 60 mL), and the extracts were washed with water and dried over $CaCl_2$. Removal of the solvent gave a thick liquid, which crystallized overnight at 0 °C. Recrystallization from benzene/acetone (50:50) gave white crystals of ligand L. Yield: 5.0 g (38%). Mp: 39−40 °C. MS: calcd for $[C_{10}H_{16}O_2S_3]^+$, $m/z = 264.0316$; found, $m/z = 264.0310$. NMR ($CDCl_3$, in ppm from TMS internal standard, position identification, see Introduction): ^1H, 6.73 (s, 2H, H1), 3.87 (s, 4H, H3), 3.66 (q, $J = 6.1$ Hz, 4H, H5), 2.85 (t, $J = 6.0$ Hz, 2H, H6), 2.68 (t, $J = 6.2$ Hz, 4H, H4); ^{13}C (proton decoupled), 141.6 (C2), 125.9 (C1), 60.5 (C5), 34.3 (C4), 30.6 (C3).

$\{[CuCl(L)][Cl]\}_n$. Solutions of $CuCl_2{\cdot}2H_2O$ (170 mg, 1.00 mmol) in ethanol (10 mL) and ligand L (264 mg, 1.00 mmol) in ethanol (10 mL) were mixed. The deep green solution was filtered quickly and left standing in an open beaker until the solution had been reduced to a volume of about 5 mL when a dark brownish-green crystalline solid was deposited. The crystals were separated, washed with a little acetone, and dried in air. Yield: 249 mg (62%). Mp: 113 °C dec. Anal. Calcd for $C_{10}H_{16}Cl_2CuO_2S_3$: C, 30.09; H, 4.04; Cl, 17.78; Cu, 15.93. Found: C, 30.27; H, 4.09; Cl, 17.83; Cu, 15.70.

X-ray Studies. A summary of crystallographic data for $\{[CuCl(L)][Cl]\}_n$ is in Table 1. The diffraction intensities were collected at 295 K using the $\theta/2\theta$ scan technique with profile analysis[10] at a scan speed of 4°/min to a maximum 2θ value of 45.0°. Three standards were measured after every 100 reflections, and no significant crystal decay was detected. The space group was determined by systematic absences. Unit cell parameters (Table 1) were determined by a least squares refinement of the setting angles for 22 reflections in the range $30.00° \le 2\theta \le 37.00°$. Lorentz and polarization factors were applied, but no corrections were made for absorption. The structure was solved by MULTAN[11] plus a difference Fourier map and refined by full matrix least squares with unit weights. H-atom positions were calculated, but their parameters were not refined. All non-hydrogen atoms were refined anisotropically. The final cycle of refinement was based on 926 observed reflections ($I > 3.0\sigma(I)$) and 165 variables. A parallel refinement of the mirror-image structure gave higher residuals than those reported in Table 1. All calculations were performed with the NRCVAX Crystal Structure Programs.[12] Scattering factors were taken from the usual source.[13]

Results and Discussion

The single-crystal X-ray structural study reveals (Figure 1 and Table 3) a distorted octahedral coordination sphere about Cu(II). Jahn−Teller elongation is apparent in the bonds Cu−Cl(1a) (2.772(3) Å) and Cu−O(1′) (2.380(7) Å) when compared to Cu−Cl(1) (2.261(3) Å) and Cu−O(1) (2.045(6) Å) in the same coordination sphere or to bridging chlorine (2.321(3) Å) in $(CuCl_2{\cdot}L)_2$ (L = 2,5,8-trithia[9](2,5)thiophenophane),[14] terminal chlorine (2.272(1) Å) in $CuCl_2{\cdot}L'$ (L′ = 1,6-bis(2-thienyl)-2,5-dithiahexane),[15] or Cu−O bonds in square pyramidal $[Cu_2(bpm)(H_2O)_2(OH)_2(NO_3)_2]{\cdot}4H_2O$[16] (bpm = 2,2′-bipyrimidine) (1.944(3) and 2.310(2) Å) in comparable sites. The Cu−S bonds (2.338(3) and 2.345(3) Å) are similar to those found in other thioether−Cu(II) species such as the five-coordinate complex of 1,9-bis(2-pyridyl)-5-oxa-2,8-dithianonane (2.373(2) and 2.376(3) Å).[17] In addition to Jahn−Teller distortion, angular distortions are also apparent, with the largest appearing at S(1)−Cu−O(1′) (103.41(18)°) and Cl(1a)−Cu−O(1′) (167.22(20)°).

Each copper atom is bridged to two other coppers by cis-related chlorines so that a $(Cu{-}Cl)_n$ chain is created that is kinked sharply (96.05(9)°) at each copper but less so (144.30(12)°) at the chlorines. These chains are cross-linked by the organic ligands with arms from two different ligands attached to any given copper. Each organic ligand bridges to a different $(Cu{-}Cl)_n$ chain. Overall, the structure consists of $(Cu{-}Cl)_n$ and $(Cu{-}L)_n$ chains with Cl^- ions embedded in the three-dimensional network to give electrical neutrality.

The IR spectrum (Nujol mull) of $\{[CuCl(L)][Cl]\}_n$ has a broad band of medium intensity centered at 3160 cm^{-1} that is typical of coordinated hydroxyl. There are also bands of weak to medium intensity at 300 and 238 cm^{-1}. While the former is too weak to be a typical terminal Cu−Cl stretch, the latter is similar to bands seen in spectra of many dinuclear Cu(II) species with chlorine bridges.[14]

The solid state (Nujol mull) electronic spectrum of $\{[CuCl(L)][Cl]\}_n$ has a main band at 450 and a shoulder at 360 nm similar to those of other Cu(II) species with thioether and chlorine ligands in a pseudooctahedral coordination sphere.[14]

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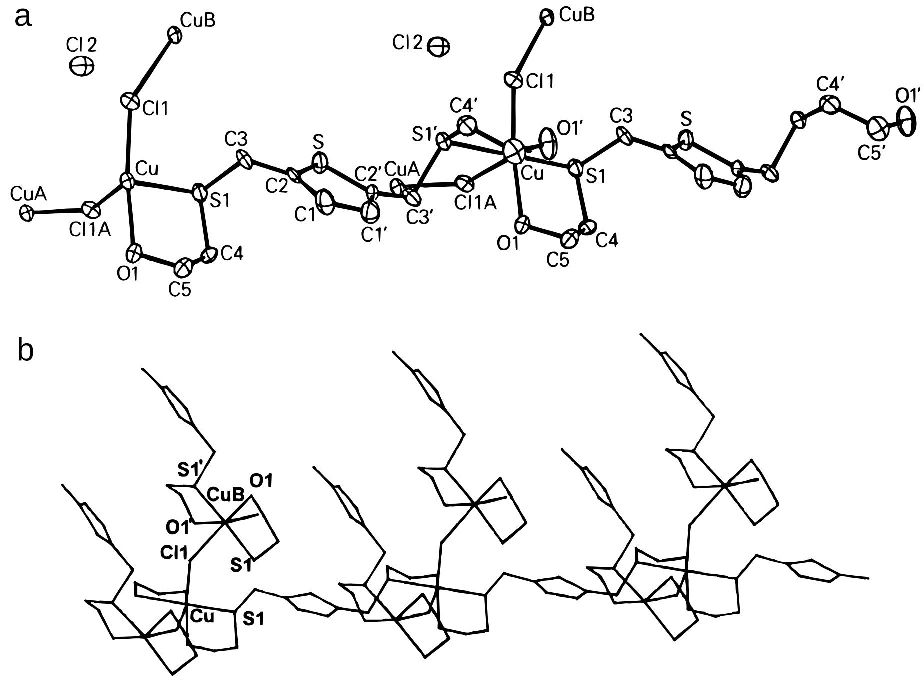

Figure 1. (a) ORTEP diagram of $\{[CuCl(L)][Cl]\}_n$ with 50% probability thermal ellipsoids. (b) Stick drawing of the chains.

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors for $\{[CuCl(L)][Cl]\}_n$

atom	*x*	*y*	*z*	B_{iso}[a]
Cu	0.77293(16)	−0.25617(13)	0.57361(5)	1.92(4)
Cl(1)	0.5454(4)	−0.3313(3)	0.50873(11)	2.59(11)
Cl(2)	0.7340(4)	−0.2245(3)	0.27271(10)	3.34(12)
S	0.2761(3)	0.2411(3)	0.56062(9)	2.30(10)
C(1)	0.3149(16)	0.1668(11)	0.6675(4)	3.0(5)
C(2)	0.3401(14)	0.1147(10)	0.6124(4)	1.8(4)
C(3)	0.4096(14)	−0.0296(11)	0.5973(4)	2.2(4)
S(1)	0.6583(3)	−0.02379(25)	0.56606(11)	2.12(10)
C(4)	0.8035(4)	0.0521(10)	0.6250(5)	2.8(5)
C(5)	0.8616(16)	−0.0593(10)	0.6685(4)	2.8(4)
O(1)	0.9531(10)	−0.1724(7)	0.6361(3)	2.4(3)
C(1′)	0.2542(18)	0.3113(11)	0.6679(4)	3.0(5)
C(2′)	0.2162(14)	0.3659(9)	0.6140(4)	2.0(4)
C(3′)	0.1489(14)	0.5109(11)	0.6008(4)	2.6(4)
S(1′)	−0.1024(3)	0.5127(3)	0.57158(11)	2.13(10)
C(4′)	−0.2449(17)	0.4337(9)	0.6298(5)	2.7(5)
C(5′)	−0.3002(16)	0.5353(12)	0.6786(4)	3.1(5)
O(1′)	−0.3979(12)	0.6537(7)	0.6563(3)	3.7(3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 3. Selected Bond Lengths and Angles in $\{[CuCl(L)][Cl]\}_n$

Distances (Å)			
Cu−Cl(1)	2.261(3)	Cu−S(1)	2.338(3)
Cu−Cl(1a)	2.772(3)	Cu−S(1′)	2.345(3)
Cu−O(1)	2.045(6)	Cu−O(1′)	2.380(7)
Angles (deg)			
Cl(1)−Cu−Cl(1a)	96.05(9)	Cl(1)−Cu−S(1)	91.02(10)
Cl(1)−Cu−S(1′)	86.69(10)	Cl(1)−Cu−O(1)	173.12(20)
Cl(1)−Cu−O(1′)	94.33(21)	Cl(1a)−Cu−S(1)	83.85(9)
Cl(1a)−Cu−S(1′)	91.27(9)	Cl(1a)−Cu−O(1)	87.64(20)
Cl(1a)−Cu−O(1′)	167.22(20)	S(1)−Cu−S(1′)	174.38(10)
S(1)−Cu−O(1)	83.59(19)	S(1)−Cu−O(1′)	103.41(18)
S(1′)−Cu−O(1)	99.05(19)	S(1′)−Cu−O(1′)	81.90(18)
O(1)−Cu−O(1′)	82.8(3)		

In both *N,N′*-dimethylformamide and dimethyl sulfoxide solutions its spectrum consists of a shoulder at 420 and a main peak at 900 nm with $\epsilon = 81$ L mol^{-1} cm^{-1}. In view of the polymeric nature of the solid and the spectral changes between solid and solution, it is probable that the solution structure is not the same as that of the solid. Since similar complexes are known to dissociate both thioether and chloride ligands in these solvents,[15] it is likely that $\{[CuCl(L)][Cl]\}_n$ exists in solution as some form of fragmented solvate. Cyclic voltammetry is consistent with this conclusion.

Cyclic voltammograms of $\{[CuCl(L)][Cl]\}_n$ in acetonitrile are characteristic of quasi-reversible processes with $E_{1/2} = 520$ mV vs SCE and $\Delta E_p = 120$ mV while those in nitromethane are very similar with $E_{1/2} = 560$ mV vs SCE and $\Delta E_p = 100$ mV. These voltammograms for $\{[CuCl(L)][Cl]\}_n$ with its $S_2O_2Cl_2$ coordination sphere are similar to those for Cu(II) species with S_2OCl_2 coordination spheres under comparable conditions.[15] The small differences in $E_{1/2}$ (20−40 mV) can be attributed to the differences in the coordination spheres.[17,18]

The magnetic susceptibility at room temperature (23 °C) when corrected for diamagnetic effects and TIP (60×10^{-6} cgsu/mol) gave a magnetic moment $\mu_{eff} = 1.72\ \mu_B$. Magnetic susceptibility measurements over the temperature range 5−302 K produced the results displayed in Figure 2. The local maximum at about 20 K implies antiferromagnetic coupling, and the low-temperature "tail" is typical of the presence of small amounts of a paramagnetic impurity that can be modeled in dinuclear systems if the impurity is assumed to follow the Curie law and to have the same molar mass and *g*-factor as the main component in the system.[5] The X-ray structure of $\{[CuCl(L)][Cl]\}_n$ shows that its $(Cu{-}Cl)_n$ chains have uniform distances between coppers, which implies a single intrachain value for the coupling constant, *J*, described by the Hamiltonian

$$H = -2J_{ij}\sum \mathbf{S}_i\mathbf{S}_j$$

under the assumption that coupling occurs only between adjacent coppers in the chains.

On the basis of these considerations, an attempt was made to fit the data at $T > 20$ K to the numerical expression developed by Bonner and Fisher[19] and by Hall[20] for an isolated Heisenberg

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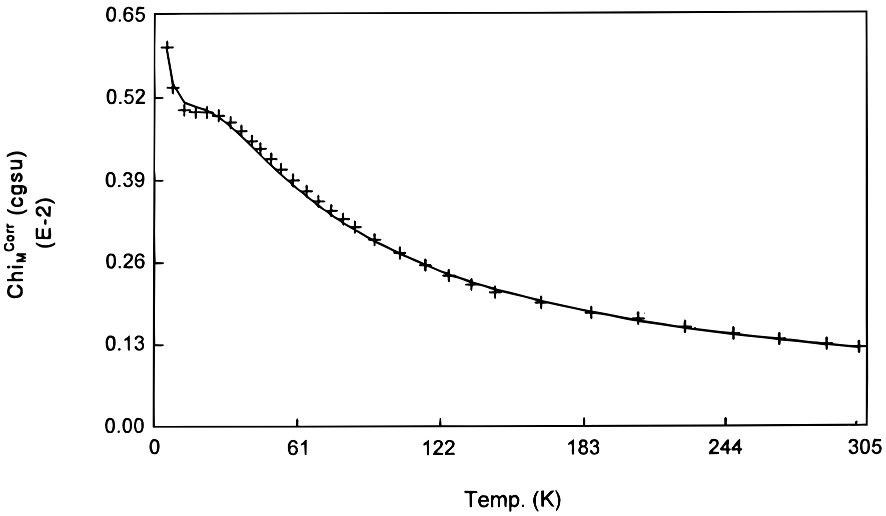

Figure 2. χ_M corrected for diamagnetic effects vs T. Solid line is theoretical curve obtained with $g = 2.06$, $J/k = -19.1$ K ($-2J = 26.4$ cm^{-1}), $J' = -1.68 \times 10^{-15}$ erg (-8.46 cm^{-1}), and $\rho = 0.016$.

chain

$$\chi_{HC} \approx \frac{Ng^2\beta^2}{kT}\,\frac{0.25 + 0.14995X + 0.30094X^2}{1.0 + 1.9862X + 0.68854X^2 + 6.0626X^3}$$

where $X = |J|/kT$. The quality of the fit, however, was poor throughout the entire temperature range, but especially near 20 K, and of course, the calculated curve did not show the impurity "tail" below 20 K. The poor fit suggested the possibility of interchain interactions, and the theoretical equation was therefore modified to take these into account through a molecular field correction[21]

$$\chi = (\chi_{HC})/[1 - (2zJ'\chi_{HC})/(Ng^2\beta^2)]$$

where J' is the interchain exchange in ergs and z (in the present case $z = 4$) is the number of nearest neighbor chains to each chain as determined from the X-ray structure. The fit improved dramatically and correctly predicted the temperature of the maximum near 20 K. Although the molecular field approximation is considered a poor method for dealing with secondary magnetic interactions when these interactions are less than 5 or 10 times the magnitude of the primary interactions,[22] it has the merit that it is relatively easy mathematically to apply compared to the alternative, which is a theoretical approach with both primary and secondary magnetic interactions appearing in the spin Hamiltonian. The Curie "tail" was added to the curve by including a parameter, ρ, to represent the mole fraction of impurity according to[5]

$$\chi' = \chi(1 - \rho) + \frac{N\beta^2g^2}{4kT}\rho + \mathrm{TIP}$$

The final fit is displayed in Figure 2 and was obtained with $g = 2.06$, $J/k = -19.1$ K ($-2J = 26.4$ cm^{-1}), $J' = -1.68 \times 10^{-15}$ ergs (-8.46 cm^{-1}), and $\rho = 0.016$.

The relatively small value of J/k is consistent with the appearance of a local maximum in the χ vs T curve at about 20 K. By using the expression[23] $|-2J|/kT_{max} \approx 8/5$, the value of $|-2J|$ can be estimated as $\approx$22 cm^{-1}, a value close to that obtained from the fitting process. This small value is also consistent with structural features of the chains. In the tetragonally elongated octahedral coordination sphere about copper, the magnetically active orbital is the $d_{x^2-y^2}$ that lies in the plane roughly defined by one Cl, one O, and two S-donors. The remaining Cl, forming the bridge to the adjacent copper, is on the local z axis. Thus, the bridge is essentially orthogonal to the magnetic orbital, leading to poor coupling between adjacent coppers, as observed. The interchain antiferromagnetic interaction is weak but apparently significant since fits of experimental data to a model that does not include it are poor. There are three obvious interchain contacts along which this coupling may be propagated. These are between Cl of one chain and S(1′) of another (3.1620(6) Å), between Cl and S(1) (3.4291(6) Å), and between O(1) and O(1′) (2.9377(7) Å). The sums of the van der Waals radii of the atoms concerned are 3.60, 3.60, and 3.00 Å, respectively.[24] There is no obvious role in the interchain coupling for the ionic chlorides embedded in the structure since each is more than 3.6 Å from any copper atom (sum of van der Waals radii is 3.3 Å).[24] The ionic chlorides do, however, lie close (2.519 Å) to one hydrogen on C3 at a distance that is convincingly less than the sum of the van der Waals radii (2.90 Å).[24] The Curie "tail" impurity of 1.6 mol % seems rather high, but we note that even larger "impurity" levels have been reported in other curve-fitting results for polymeric copper systems.[25] One may speculate that the open or basket-weave structure from the intersecting chains affords interstices into which not only the ionic chlorides but also the "impurities" may fit. In addition, chain ends may contribute to the Curie "tail" noncoupled "impurity".

Conclusions

Use of an acyclic tetradentate organic ligand with a rigid planar spacer in its center plus bridge-forming chloride ligands has resulted in the generation of an interwoven structure of (Cu−Cl)$_n$ and (Cu−L)$_n$ polymer chains with internal void spaces. In the present case, these voids are partially occupied by Cl$^-$ ions. The structure is not stable in the presence of solvents but rather gives rise to solutions most likely containing solvated monomer units or even solvated metal halide and dissociated ligand depending on the nucleophilicity of the solvent used. The

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magnetic properties of the solid as a function of temperature are those of uniform chains with small intrachain and interchain antiferromagnetic couplings plus small amounts of noncoupled paramagnetic material probably located in the voids or arising from chain ends. Although unsuccessful in producing ferromagnetic material, this approach has nonetheless reduced antiferromagnetic couplings to small values. In future experiments, inclusion in the voids of anions other than chloride that have suitable uncompensated moments and that will be preferentially oriented by steric interaction with the walls of the voids will be attempted.

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Supporting Information Available: Details of the structure determination, tables of bond lengths and angles and anisotropic thermal parameters, and a listing of atomic coordinates (8 pages). Ordering information is given on any current masthead page.

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