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Structural Characterization of Dimeric and Monomeric Copper(II) Complexes of 4-Methylthiazole

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The structures of two complexes formed from the reaction of copper(II) chloride with 4-methylthiazole have been determined from three-dimensional X-ray counter data. Crystals of the solvated dinuclear complex $[Cu(C_4H_5NS)_2Cl_2]_2 \cdot 2CH_3OH$ are monoclinic, space group $P2_1/n$, with two dinuclear species in a cell of dimensions a = 7.506 (4) Å, b = 15.987 (6) Å, c = 12.472 (5) Å, and β = 96.24 (4)°. This structure has been refined to R = 0.048 on the basis of 1846 independent data with $I > 3\sigma(I)$. The monomeric complex $[Cu(C_4H_5NS)_3Cl_2]$ crystallizes in the monoclinic space group $P2_1/a$ with four molecules in a cell of dimensions a = 14.147 (6) Å, b = 8.621 (6) Å, c = 16.035 (7) Å, and β = 115.26 (3)°. The final R factor, based on 2416 data, is 0.044. In both complexes the copper(II) centers are five-coordinate, the geometry being distorted from idealized tetragonal pyramidal in both cases. The magnetic properties of the methanol dimer show a weak intradimer antiferromagnetic interaction ($2J = -3.40$ cm^{-1}) with a surprisingly strong interdimer antiferromagnetic interaction ($J' = -1.16$ cm^{-1}). The latter is probably transmitted through nonbonded S···Cl contacts in the crystals.

Introduction

The reaction of copper(II) halides with nitrogen ligands is known to yield monomeric,[2–4] dimeric,[3,5–11] tetrameric,[12,13] or polymeric[14–17] species, depending upon the precise nature of the ligand and the reaction conditions. In a recent communication,[18] we noted that the reaction of copper(II) chloride with 4-methylthiazole (4-Metz), C_4H_5NS, leads to the isolation of complexes of monomeric, dimeric, and tetrameric examples of these structural types, while the analogous reaction[5] with copper(II) bromide apparently yields only a dinuclear species. We have described the synthetic procedures required to obtain each

Table I. Experimental Crystallographic Parameters

complex	$Cu(4\text{-}Metz)_3Cl_2$	$[Cu(4\text{-}Metz)_2Cl_2]_2 \cdot 2CH_3OH$
cryst color and habit	green prism	dark blue lath
a, Å	14.147 (6)	7.506 (4)
b, Å	8.621 (6)	15.987 (6)
c, Å	16.035 (7)	12.472 (5)
α, deg	90	90
β, deg	115.36 (3)	96.24 (4)
γ, deg	90	90
Å^3	1767 (3)	1488 (2)
temp, °C	21	20
space group	$P2_1/a$	$P2_1/n$
μ, cm^{-1}	18.8	19.3
D_{obsd}, g cm^{-3} (flotation)	1.64 (2)	1.63 (2)
Z	4	2
D_{calcd}, g cm^{-3}	1.623	1.628
2θ range, deg	$2 < 2\theta(Mo) < 55$	$2 < 2\theta(Mo) < 55$
data collcd	$\pm h,+k,+l$	$\pm h,+k,+l$
total no. of reflcns	4052	2592
no. of reflcns with $I > 3\sigma(I)$	2416	1846

Table II. Positional Parameters for $Cu(4\text{-}Metz)_3Cl_2$

atom	x	y	z
Cu	−0.091 91 (4)	0.235 05 (7)	0.239 53 (4)
Cl1	0.027 64 (9)	0.0947 (2)	0.191 05 (9)
Cl2	−0.195 30 (9)	0.0434 (2)	0.259 79 (8)
S1A	−0.3911 (1)	0.3627 (2)	−0.0015 (1)
S1B	0.1567 (1)	0.0955 (3)	0.5199 (1)
S1C	0.0921 (1)	0.6707 (2)	0.2628 (1)
N3A	−0.2054 (3)	0.2903 (5)	0.1120 (2)
N3B	0.0074 (3)	0.2042 (5)	0.3774 (3)
N3C	−0.0369 (3)	0.4595 (5)	0.2510 (3)
C2A	−0.3038 (4)	0.2849 (6)	0.0980 (3)
C4A	−0.1985 (4)	0.3582 (6)	0.0360 (3)
C5A	−0.2919 (4)	0.4035 (7)	−0.0312 (3)
C6A	−0.0973 (4)	0.3784 (8)	0.0304 (4)
C2B	0.0944 (4)	0.1294 (8)	0.4050 (4)
C4B	−0.0127 (4)	0.2449 (7)	0.4522 (3)
C5B	0.0612 (5)	0.1928 (8)	0.5327 (4)
C6B	−0.1070 (6)	0.3331 (9)	0.4379 (4)
C2C	0.0580 (4)	0.4821 (7)	0.2642 (4)
C4C	−0.0906 (4)	0.5999 (6)	0.2406 (4)
C5C	−0.0297 (4)	0.7240 (6)	0.2463 (4)
C6C	−0.2031 (4)	0.6065 (7)	0.2212 (4)

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Table III. Positional Parameters for $[Cu(4\text{-}Metz)_2Cl_2{\cdot}CH_3OH]_2$

atom	*x*	*y*	*z*
Cu	0.0366 (1)	0.10734 (5)	0.03011 (6)
Cl1	0.2224 (2)	−0.0104 (1)	0.0612 (1)
Cl2	−0.0693 (2)	0.2426 (1)	0.0262 (1)
S1A	0.1393 (3)	0.1641 (1)	−0.3073 (1)
S1B	−0.2364 (3)	0.0765 (1)	0.3287 (2)
O1	0.2471 (7)	0.3711 (3)	0.0830 (5)
N3A	0.1330 (6)	0.1310 (3)	−0.1101 (4)
N3B	−0.0418 (6)	0.0960 (3)	0.1780 (4)
C2A	0.0285 (9)	0.1293 (4)	−0.2026 (5)
C4A	0.3057 (8)	0.1608 (4)	−0.1195 (5)
C5A	0.3257 (9)	0.1806 (4)	−0.2219 (5)
C6A	0.4366 (9)	0.1711 (4)	−0.0227 (5)
C2B	−0.2015 (9)	0.0712 (4)	0.1968 (5)
C4B	0.0626 (9)	0.1217 (4)	0.2707 (5)
C5B	−0.0254 (10)	0.1140 (4)	0.3597 (5)
C6B	0.2436 (10)	0.1544 (5)	0.2653 (6)
C7	0.1516 (12)	0.4411 (5)	0.1116 (7)

of the species involved and have discussed the characterization of a mixed-valent Cu^ICu^{II} dimer elsewhere;[18] in the present communication we describe the structural characterization of one dimeric and one monomeric complex, while elsewhere we describe the structural and magnetic properties of the dimer formed from the parent $[Cu(4\text{-}Metz)_2Cl_2]_2$ complex by substitution of two 4-Metz ligands by DMF molecules.[19,20]

Experimental Section

X-ray Data Collection and Reduction. The complexes were synthesized as described in ref 18. All data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo radiation [$\lambda(K\alpha_1) = 0.70926$ Å] and a graphite monochromator. Experimental parameters are listed in Table I. In the case of the complex $[Cu(4\text{-}Metz)_2Cl_2]_2$, the crystal decomposed in the X-ray beam; data collection was terminated after decomposition reached 40%, and the data were adjusted by using a linear decomposition program. No corrections for absorption or extinction were applied.

Solution and Refinement of the Structures. For all of the compounds, the least-squares calculations were carried out on *F*, the function minimized being $\sum w(|F_o| - |F_c|)^2$ where the weights, *w*, are assigned as $4F_o^2/\sigma^2(I)$. In the calculation of the structure factors, F_c, the neutral-atom scattering factors were taken from the ref 21. The effects of the anamolous dispersion of all atoms were included. The values of $\Delta f'$ and $\Delta f''$ were also taken from ref 21. All programs used came from the SDP package provided by Enraf-Nonius.

$[Cu(4\text{-}Metz)_3Cl_2]$. The solution of the structure was effected by the use of a Patterson function to locate the copper atom; least-squares refinement in conjunction with difference Fourier maps produced the locations of all non-hydrogen atoms. Isotropic refinement gave values of R_1 and R_2 of 0.092 and 0.090, respectively; anisotropic refinement reduced these values to 0.050 and 0.056, respectively. A difference Fourier map revealed the presence of some of the hydrogen atoms, and the positions of the other hydrogen atoms were calculated on the basis of the appropriate geometry and a C–H distance of 0.95 Å. In the final cycles of least-squares refinement, the hydrogen atoms were given a fixed isotropic thermal parameter of 5.0 $Å^2$ and their positions were not varied, while all other atom positions and anisotropic thermal parameters were refined. The final values of R_1 and R_2 upon convergence were both 0.044. The last difference Fourier map was featureless with no peak higher than 0.28 e $Å^{-3}$. The positional parameters, along with their standard deviations, as estimated from the inverse matrix, are given in Table II. Listings of hydrogen atom positions, anisotropic thermal parameters, and observed and calculated structure amplitudes are available as supplementary material.

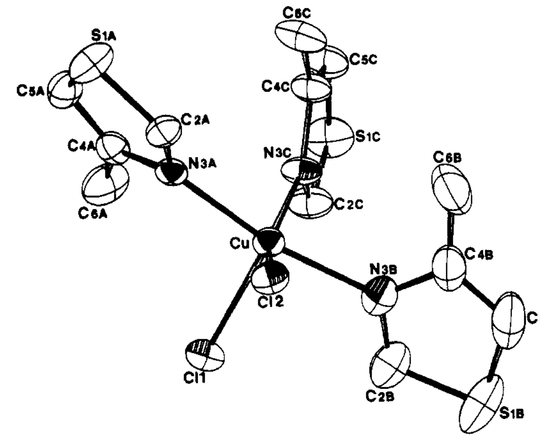

Figure 1. View of a single molecule of the monomeric complex $[Cu(4\text{-}Metz)_3Cl_2]$. Hydrogen atoms are omitted for clarity.

Table IV. Internuclear Separations (Å) in $Cu(4\text{-}Metz)_3Cl_2$

Cu–Cl1	2.461 (1)	S1B–C2B	1.693 (4)
Cu–Cl2	2.319 (1)	C2B–N3B	1.289 (5)
Cu–N3A	2.043 (3)	N3B–C4B	1.392 (5)
Cu–N3B	2.066 (3)	C4B–C5B	1.344 (6)
Cu–N3C	2.064 (3)	C5B–S1B	1.676 (6)
S1A–C2A	1.683 (3)	C4B–C6B	1.466 (6)
C2A–N3A	1.312 (4)	S1C–C2C	1.698 (4)
N3A–C4A	1.393 (4)	C2C–N3C	1.281 (4)
C4A–C5A	1.357 (5)	N3C–C4C	1.401 (4)
C5A–S1A	1.700 (4)	C4C–C5C	1.352 (5)
C4A–C6A	1.483 (5)	C5C–S1C	1.691 (4)
		C4C–C6C	1.486 (5)

Table V. Internuclear Angles (deg) in $Cu(4\text{-}Metz)_3Cl_2$

Cl1–Cu–Cl2	104.71 (4)	Cu–N3B–C2B	122.9 (3)
Cl1–Cu–N3A	98.66 (8)	Cu–N3B–C4B	126.4 (3)
Cl1–Cu–N3B	91.75 (10)	C2B–N3B–C4B	110.4 (4)
Cl1–Cu–N3C	101.85 (8)	N3B–C4B–C5B	112.4 (4)
Cl2–Cu–N3A	91.91 (8)	N3B–C4B–C6B	120.3 (4)
Cl2–Cu–N3B	86.52 (9)	C5B–C4B–C6B	127.3 (4)
Cl2–Cu–N3C	153.03 (9)	C4B–C5B–S1B	112.7 (4)
N3A–Cu–N3B	169.53 (12)	C5B–S1B–C2B	88.6 (2)
N3A–Cu–N3C	88.62 (11)	S1B–C2B–N3B	115.8 (3)
N3B–Cu–N3C	88.12 (12)	Cu–N3C–C2C	119.1 (3)
Cu–N3A–C2A	119.0 (2)	Cu–N3C–C4C	129.4 (2)
Cu–N3A–C4A	130.8 (2)	C2C–N3C–C4C	111.4 (3)
C2A–N3A–C4A	109.4 (3)	N3C–C4C–C5C	112.2 (3)
N3A–C4A–C5A	114.0 (3)	N3C–C4C–C6C	122.4 (3)
N3A–C4A–C6A	122.3 (3)	C5C–C4C–C6C	125.3 (3)
C5A–C4A–C6A	123.8 (3)	C4C–C5C–S1C	111.9 (3)
C4A–C5A–S1A	111.0 (3)	C5C–S1C–C2C	89.2 (2)
C5A–S1A–C2A	89.5 (2)	S1C–C2C–N3C	115.3 (3)
S1A–C2A–N3A	116.2 (3)		

$[Cu(4\text{-}Metz)_2Cl_2]_2{\cdot}2CH_3OH$. The solution of the structure was achieved by the use of a three-dimensional Patterson function to determine the position of the independent copper atom. Least-squares refinement followed by difference Fourier maps produced the locations of the other non-hydrogen atoms. Isotropic least-squares calculations yielded a value for both R_1 and R_2 of 0.100; anisotropic refinement reduced the *R* factors to 0.056 and 0.062, respectively. A difference Fourier map then revealed the positions of all of the hydrogen atoms. In the final cycle of least-squares refinement, the hydrogen atoms were each given a fixed isotropic thermal parameter of 5.0 $Å^2$ and the positions were not varied, while all other atomic positions and thermal parameters were refined. The final values of R_1 and R_2 upon convergence were 0.048 and 0.049, respectively. The last difference Fourier map was featureless with no peak higher than 0.46 e $Å^{-3}$. The positions of the atoms and their estimated standard deviations are given in Table III; the atomic thermal parameters, hydrogen atom parameters, and observed and calculated structure amplitudes are available as supplementary material.

Description of the Structures

$[Cu(4\text{-}Metz)_3Cl_2]$. The complex $Cu(4\text{-}Metz)_3Cl_2$ is a five-coordinate monomer with the molecules well separated from each other; the shortest Cu–Cu distance is 7.078 (1) Å. A view of a single monomer is shown in Figure 1, and the bond lengths and angles for the molecules are given in Tables IV and V. As can

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(19) A preliminary description of some of this material has been presented elsewhere: Hodgson, D. J. Presented at the 1st International Conference on Bioinorganic Chemistry, Florence, Italy, 1983. Hodgson, D. J. *J. Mol. Catal.* **1984**, *23*, 219.

(20) We have also examined the structure of the unsolvated "parent dimer", $[Cu(4\text{-}Metz)_2Cl_2]_2$. Regrettably, the crystals decompose rapidly in the beam, and the structure is poorly determined. The overall features of the structure, however, are similar to those of the solvated dimer.

(21) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

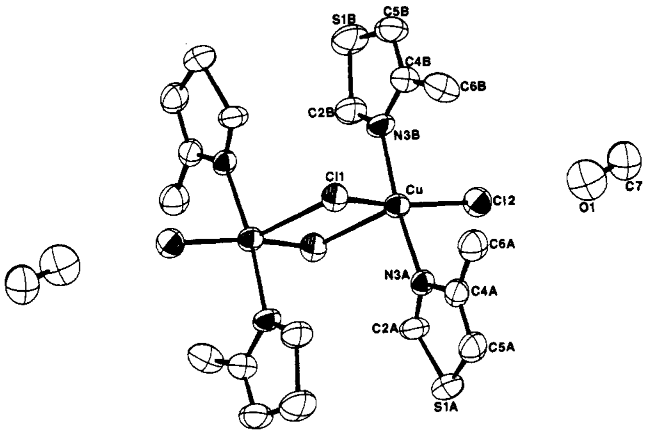

Figure 2. View of the dimeric complex $[Cu(4\text{-}Metz)_2Cl_2]_2 \cdot 2CH_3OH$. The methanol molecules are represented by atoms C7 and O1; hydrogen atoms are omitted for clarity.

be seen in the figure, the coordination sphere about the copper(II) center is made up of three 4-methylthiazole ligands and two chloride ions. The geometry of the molecules can be described as a severely distorted tetragonal pyramid where the basal plane consists of two trans nitrogen atoms from two 4-methylthiazole ligands and a chloride ion that is trans to the nitrogen of a third 4-methylthiazole ligand. The apical site is occupied by the second chloride ion, Cl1. The severe distortions are evidenced by the lack of planarity of the four atoms in the base plane, where N3A, N3B, N3C, and Cl2 deviate from the least-squares plane by 0.16, 0.16, −0.17, and −0.15 Å, respectively. As is common in tetragonal-pyramidal complexes, the copper atom lies above this plane by 0.35 Å in the direction of the apical atom, Cl1. The distortions are also indicated by the two trans angles, N3A–Cu–N3B and N3C–Cu–Cl2, which have values of 153.03 (9) and 169.53 (12)° that are outside the range of 170–180° observed in other complexes (vide infra).

The Cu–N distances of 2.043 (3), 2.066 (3), and 2.064 (3) Å are all somewhat longer than the distances observed in other copper(II) complexes of 4-methylthiazole (v.i.). Presumably, the increase in length is due to the coordination of three bulky 4-methylthiazole groups to the copper(II) center, as opposed to only two in the other complexes. The Cu–Cl distances are 2.461 (1) and 2.319 (1) Å with the distance to the apical chloride Cl1 being appreciably the longer. This result is as expected for a tetragonal-pyramidal geometry, where the bond distance from the metal center to a ligand in the basal plane would be expected to be shorter than the distance to an identical ligand in the axial position.

The three independent thiazole rings in the structure are planar with no atom deviating from the five-atom least-squares plane by more than 0.011 Å in any ring. The exocyclic methyl carbon atom (C6) also lies in the ring plane in rings A and C, but in ring B it is 0.066 Å out of the plane. The bond distances and angles in the ligands are normal.

$[Cu(4\text{-}Metz)_2Cl_2 \cdot CH_3OH]_2$. The complex consists of dimeric $[Cu(4\text{-}Metz)_2Cl_2 \cdot CH_3OH]_2$ units that are well separated from each other. A solvent molecule is present in the cell but is not coordinated to the copper(II) center. A view of the dimeric unit including the methanol molecule is shown in Figure 2. The bridging Cu_2Cl_2 unit is constrained to be planar by the presence of a crystallographic inversion center in the middle of the dimer. The bond distances and angles for the complex are listed in Tables VI and VII.

Table VI. Internuclear Separations (Å) in $[Cu(4\text{-}Metz)_2Cl_2 \cdot CH_3OH]_2$

Cu–Cl1	2.350 (1)	C4A–C5A	1.341 (5)
Cu–Cl1′	2.645 (1)	C4A–C6A	1.480 (5)
Cu–Cl2	2.303 (1)	C5A–S1A	1.685 (4)
Cu–N3A	2.001 (3)	S1B–C2B	1.696 (4)
Cu–N3B	2.004 (3)	C2B–N3B	1.308 (5)
Cu–Cu′	3.543 (1)	N3B–C4B	1.387 (5)
S1A–C2A	1.716 (4)	C4B–C5B	1.358 (5)
C2A–N3A	1.323 (4)	C4B–C6B	1.464 (6)
N3A–C4A	1.397 (4)	C5B–S1B	1.698 (5)
		O1–C7	1.397 (6)

Table VII. Internuclear Angles (deg) in $[Cu(4\text{-}Metz)_2Cl_2 \cdot CH_3OH]$

Cl1–Cu–Cl1′	89.85 (3)	N3A–C4A–C5A	111.2 (4)
Cl1–Cu–Cl2	162.39 (4)	N3A–C4A–C6A	120.6 (4)
Cl1–Cu–N3A	91.82 (9)	C5A–C4A–C6A	128.1 (4)
Cl1–Cu–N3B	90.19 (9)	C4A–C5A–S1A	113.2 (3)
Cl1′–Cu–Cl2	107.75 (4)	C5A–S1A–C2A	90.4 (2)
Cl1′–Cu–N3A	93.09 (9)	S1A–C2A–N3A	111.5 (3)
Cl1′–Cu–N3B	93.86 (10)	Cu–N3B–C2B	124.0 (3)
Cl2–Cu–N3A	87.71 (9)	Cu–N3B–C4B	123.0 (3)
Cl2–Cu–N3B	88.28 (9)	C2B–N3B–C4B	112.7 (3)
N3A–Cu–N3B	172.78 (13)	N3B–C4B–C5B	112.0 (4)
Cu–Cl1–Cu′	90.15 (3)	N3B–C4B–C6B	120.7 (4)
Cu–N3A–C2A	121.4 (3)	C5B–C4B–C6B	127.3 (4)
Cu–N3A–C4A	124.4 (3)	C4B–C5B–S1B	111.8 (3)
C2–N3A–C4A	113.7 (3)	C5B–S1B–C2B	90.0 (2)
		S1B–C2B–N3B	113.6 (3)

As can be seen in Figure 2, each copper(II) center is surrounded by five ligands: two trans nitrogen atoms from the 4-methylthiazole ligands, two trans chloride ions, and a chloride ion that occupies the fifth coordination site. The geometry at each copper(II) center is best described as a distorted tetragonal pyramid, as can be determined by examining the angles subtended at copper (see Table VII). According to this description, the chloride ion in the fifth site is apical to one copper atom but is in the base plane of the other. The atoms forming the base plane, Cl1, Cl2, N3A, and N3B, show distortions away from planarity with the atoms deviating from the least-squares plane by −0.12, −0.13, 0.12, and 0.12 Å, respectively. As is common in tetragonal-pyramidal complexes, the copper atom lies 0.24 Å above this plane in the direction of the apical atom, Cl1′. The angle Cl1–Cu–Cl2 also shows the distortion away from the ideal geometry with a value of 162.38 (4)°, which is outside the range of 170–180° observed in other complexes.

The Cu–N distances observed in this complex of 2.001 (3) and 2.004 (3) Å are consistent with the distances observed in the other copper(II) halide complexes of 4-methylthiazole[5,18] and with distances reported for related complexes. The basal Cu–Cl distances are 2.350 (1) and 2.303 (1) Å with the distance to the bridging atom Cl1 being the longer, as expected. The axial Cu–Cl1′ bond length of 2.645 (1) Å, the Cu–Cl1–Cu′ bridging angle of 90.15 (3)°, and the Cu–Cu′ distance of 3.543 (1) Å are all within the previously observed ranges for bis(μ-chloro) copper(II) complexes.[3,6,11b,19]

The two independent thiazole rings in the structure are planar with no atom deviating from the five-atom least-squares plane by more than 0.002 Å in ring A and 0.004 Å in ring B. In both cases, the methyl carbon atoms are displaced from the five-membered planes by approximately 0.07 Å in A and 0.05 Å in B. The two thiazole planes are inclined at an angle of 17.1° to each other. The bond lengths and angles within the thiazole ligands appear to be comparable to those in other thiazole complexes.[2,5,15,18]

Magnetic Properties

The temperature-dependent magnetic susceptibility of a powdered sample of $[Cu(C_4H_5NS)_2Cl_2 \cdot CH_3OH]_2$ was measured in the range 2.0–298 K, and the lower temperature data are shown in Figure 3. The maximum at about 3 K is indicative of an antiferromagnetic interaction between the $S = {}^1/_2$ ions. Assuming Heisenberg–Dirac–Van Vleck exchange-coupling theory and the Hamiltonian

$$H = -2\hat{S}_1 \cdot \hat{S}_2$$

the following expression results for the magnetization of an exchange-coupled pair of spins:

$$M = \frac{Ng\beta \sinh (g\beta H/kT)}{\exp(-2J/kT) + 2 \cosh (g\beta H/kT) + 1}$$

An unsuccessful attempt was made to fit the data to this expression

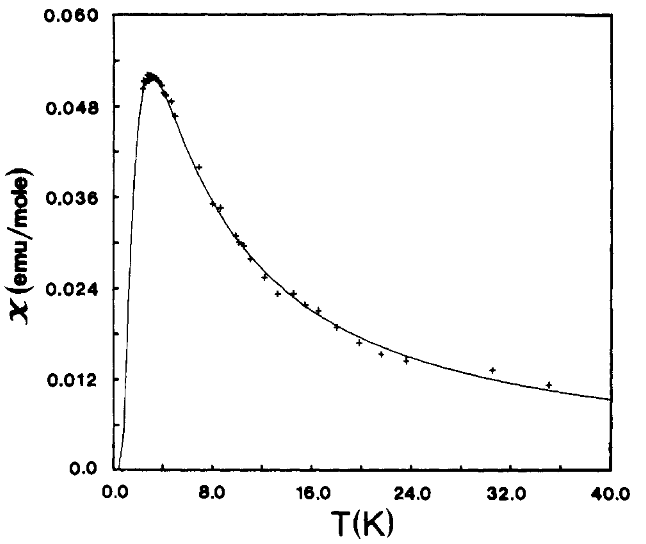

Figure 3. Temperature dependence of the magnetic susceptibility of a powdered sample of $[Cu(4\text{-}Metz)_2Cl_2]_2\cdot2CH_3OH$. The solid line represents the best fit to the data with $J = -1.70$ cm^{-1}, $J' = -1.16$ cm^{-1}, and $g = 2.07$.

by using a Simplex nonlinear least-squares fitting routine with the criterion of best fit being given by

$$F = \sum_i \frac{(\chi_i^{\mathrm{obsd}} - \chi_i^{\mathrm{calcd}})^2}{\chi_i^{\mathrm{obsd}}}$$

The best least-squares fit failed to provide an accurate description of the data in the region of the maximum in the magnetic susceptibility. A molecular field correction was added to the magnetization expression, yielding the equation

$$\chi_{\mathrm{cor}} = \frac{\chi_{\mathrm{iso}}}{1 - (2zJ'\chi_{\mathrm{iso}}/Ng^2\beta^2)}$$

The resulting best fit yielded $J = -1.70$ cm^{-1}, $g = 2.07$, and $J' = -1.16$ cm^{-1}. The number of nearest neighbors, z, is 2. Since J and J' are of the same order of magnitude, additional calculations should be carried out by using the cluster model.[22] We have not done this, since the basic conclusion of the study, that magnetic exchange interactions can be transmitted through long nonbonded contacts, would not be altered.

The value of the exchange-coupling constant J is in the range expected for a bis(μ-chloro)-bridged copper(II) compound with a ϕ/R_0 value of 34.1° Å^{-1}, where ϕ is the Cu–Cl···Cu′ angle and R_0 is the long Cu–Cl bond distance in the Cu_2Cl_2 exchange-coupled unit. J' describes the interdimer exchange interaction.

The most probable superexchange pathway for interdimer exchange involves a S1A···Cl2 interdimer separation of 3.507 Å, where Cl2 is the terminal Cl. The Cu–Cl2 distance is 2.303 Å, and the Cu–Cl2···S1A angle is 128.5°; thus, the Cu···S separation is 5.259 Å. Also, S1A is 4.454 Å from CuA. Exchange coupling over long superexchange pathways is not unknown. For example, $(\text{adeninium})_2CuCl_4$ and $(\text{adeninium})_2CuBr_4$ exhibit linear-chain behavior with exchange-coupling constants of −7.6 and −36.5 cm^{-1}, respectively.[23] In both cases the chain is formed by nonbonded halide–halide contacts yielding nearly linear Cu–X···X–Cu superexchange pathways, and the exchange coupling arises because of substantial unpaired electron density on the ligands.

Exchange coupling through nonbonded contacts involving sulfur atoms has been found in other systems. The sulfur–sulfur contact between molecular units in $[(C_2H_5)_4N][Ni(DDDT)_2]$ (DDDT is 5,6-dihydro-1,4-dithiin-2,3-dithiolate) is 3.98 Å, yet these are exchange-coupled into two-dimensional layers with $J = -8.5$ cm^{-1}. Even though the nickel–nickel interlayer separation is 8.152 Å, $[(C_2H_5)_4N][Ni(DDDT)_2]$ undergoes long-range order near 15 K.[24] EPR evidence and HOMO calculations show that there is substantial delocalization of electron density onto the ligand in $[(C_2H_5)_4N][Ni(DDDT)_2]$.

Nonbonded copper(II)···sulfur contacts between dimeric units in the compounds $[Cu(DTH)Cl_2]_2$ (DTH is 2,5-dithiahexane) and $[Cu(DTD)Cl_2]_2$ (DTD is 4,7-dithiadecane) are more than 5 Å, yet the copper(II) ions are exchange-coupled into alternating chains with exchange-coupling constants and alternation parameters (J, α) being (−10 cm^{-1}, 0.87) and (−20.6 cm^{-1}, 0.35) for $[Cu(DTH)Cl_2]_2$ and $[Cu(DTD)Cl_2]_2$, respectively.[25] The exchange-coupling constants appear to be enormous, especially in view of the long nonbonded distances.

It is shown elsewhere[26] that long, nonbonded sulfur–copper contacts of 3.906 Å in $[Cu(4\text{-}Metz)(DMF)Cl_2]_2$ give rise to ladderlike magnetism. The large mean-field J' found here for $[Cu(C_4H_5NS)_2Cl_2\cdot CH_3OH]_2$ may be understood in terms of similar superexchange pathways involving long nonbonded contacts between dimeric units, and it is likely that the large radial extensions of the sulfur orbitals permit these unexpectedly large interdimer exchange interactions.

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Supplementary Material Available: Tables SI and SII, listing hydrogen positions for the monomer and dimer, respectively, and Tables SIII and SIV, listing thermal parameters for the monomer and dimer, respectively (4 pages); tables of observed and calculated structure amplitudes for both structures (32 pages). Ordering information is given on any current masthead page.

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