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Synthesis and Structural and Magnetic Characterization of the Dimeric Complex Bis[dibromobis(4-methylthiazole)copper(II)]

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The crystal and molecular structure of the copper(II) complex bis[dibromobis(4-methylthiazole)copper(II)], $[CuBr_2(C_4H_5NS)_2]_2$, has been determined from three-dimensional X-ray counter data. The complex crystallizes in the triclinic space group $P\bar{1}$ with one dimeric formula unit in a cell of dimensions $a = 8.669$ (4) Å, $b = 10.985$ (4) Å $c = 7.495$ (3) Å, $\alpha = 97.98$ (3)°, $\beta = 104.65$ (3)°, and $\gamma = 71.55$ (4)°. The observed and calculated densities are 2.10 and 2.141 g cm^{-3}, respectively. The structure has been refined by least-squares methods to a final value of the R factor (on F) of 0.047 based on 1645 independent data with $I \geq 3\sigma(I)$. The complex is dimeric, with tetragonal-pyramidal geometry at each copper center. The four ligands in the base plane are two trans nitrogen atoms from the 4-methylthiazole ligands and two bromide ligands, one of which is apical to the other copper atom, while the apical ligand is a bridging bromide ion. The out-of-plane Cu–Br distance is 3.033 (1) Å and the Cu–Cu distance is 4.063 (2) Å, leading to a bridging Cu–Br–Cu angle of 94.16 (3)°. The magnetic susceptibility of the complex has been measured as a function of temperature, and the data have been fitted to a magnetization expression which yields $g = 2.06$ and a singlet–triplet separation of approximately 2.4 cm^{-1} with the singlet as the ground state.

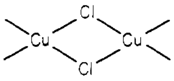
Introduction

There has been intense recent research activity in the magnetochemistry of dimeric copper(II) complexes. For the case of the planar di-μ-hydroxo complexes $[CuL(OH)]_2^{n+}$, where L is a bidentate ligand, it has been possible to demonstrate a correlation between the isotropic magnetic exchange parameter, J, and a single structural variable, ϕ, where ϕ is the bridging Cu–O–Cu angle.[1,2] It should be noted, however, that deviations from square-planar geometry at the metal[3] or from planarity in the bridge[4] lead to systems which violate this simple, linear relationship between J and ϕ. For the planar case, however, we have been able to provide a reasonable basis for the observed dependence of J on ϕ on the basis of qualitative molecular orbital considerations,[1] and Hoffmann and co-workers[5] have provided a more elegant (and more convincing) description using a semi-quantitative extended Hückel molecular orbital treatment.

While these hydroxo-bridged dimers provide an excellent model for binuclear materials bridged by oxygen atoms, the observed structural–magnetic correlation may not be applicable to systems bridged by second-row and third-row atoms. Hence, we and others are also investigating halogen-bridged copper dimers. The magnetic coupling in halogen-bridged complexes of copper(II) is expected to be more complicated than the hydroxo systems because of the presence, in the former, of relatively low-lying ligand d orbitals which can interact with the metal orbitals. A further complication arises from the observation that complexes of the types $CuLX_2$ (where L is a bidentate ligand) or CuA_2X_2 (where A is unidentate) show an amazingly wide variety of geometries. As an example, $Cu(MAEP)Cl_2$ [where MAEP is 2-(2-methylaminoethyl)pyridine] is a chain polymer with single chloride bridges and tetragonal-pyramidal geometry at copper[6] while the analogous bromide is dimeric with two bromide bridges and trigonal-bipyramidal geometry at copper.[7] The parent $Cu(AEP)X_2$ complexes contain both of these interactions, and the copper atoms are six-coordinate,[8,9] while the dimethyl analogue $Cu(DMAEP)Cl_2$ is monomeric and four-coordinate.[10]

The present situation, consequently, is that there are too few data for any given structural type for meaningful structural–magnetic correlations to be made; consequently, we are examining a variety of complexes of these general formulations in order to obtain the necessary data.

For the symmetrical square-planar dimers, I, Willett and co-workers[11] have noted that a linear relationship between J and ϕ apparently obtains, for the same reasons as we had noted for the hydroxo bridged dimers.[1] The tetragonal-pyramidal dimers may be the next easiest class to understand, in part because this geometry is most readily comprehended in the light of our previous molecular orbital schemes, and also because data for these complexes are more prevelant at present, with four dibromo-bridged and five dichloro-bridged fully characterized systems available. In addition to these fully characterized complexes, there are several other dimers of this type whose structures have been determined but which have not been investigated magnetically,[12-14] largely because of difficulties encountered in attempting to obtain pure samples. These tetragonal-pyramidal complexes are, of course, of the out-of-plane type, so in this situation the bridging framework



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is no longer in the *xy* plane of the copper atoms; one bridging ligand is axial to a given copper atom, and the other is equatorial. Since the unpaired spin is in the base planes of the molecule, any exchange interactions are expected to be weak.

Our recent observation[15] that the thiazole complexes $Cu(tz)_2X_2$ are polymeric led us to anticipate that the corresponding 4-methylthiazole complex, $Cu(4\text{-}Metz)_2Br_2$, may well be dimeric and would, therefore, be worthy of structural and magnetic study. We here report, therefore, the synthesis and structural and magnetic properties of this complex.

Experimental Section

Synthesis. The ligand 4-methylthiazole (C_4H_5NS,4-Metz), obtained from Aldrich Chemical Co., Inc., was used in the synthesis without further purification. Reagent grade copper(II) bromide was obtained from J. T. Baker Chemical Co. and used directly.

The complex was prepared by dissolving 2.234 g (0.01 mol) of anhydrous $CuBr_2$ in ~30 mL of freshly distilled methanol followed by the addition of a methanol solution (30 mL) containing 1.983 g (0.02 mol) of the ligand. The resultant dark green solution was warmed with constant stirring for approximately 0.5 h to ensure complete reaction. While still warm, the solution was filtered and then allowed to cool at room temperature for a few minutes; the filtrate was then placed in the freezer compartment of a refrigerator. After approximately 24 h, dark green crystals had formed and were removed from the solution by filtration. These crystals were promptly placed back in the freezer compartment of the refrigerator along with the remaining solution. The crystals were later ground into a powder under a dry N_2 atmosphere, and the powder was used for analysis and for other physical measurements. Anal. Calcd for $Cu(C_8H_{10}N_2S_2)Br_2$: C, 22.79; H, 2.39; N, 6.64. Found: C, 22.64; H, 2.07; N, 6.48. After several days of constant cooling, well-formed dark green crystals began forming in the remaining solution. These were removed, and an appropriate crystal (0.2 mm × 0.13 mm × 0.38 mm) was chosen for the X-ray diffraction study.

Collection of the X-ray Data. The above crystal was mounted and placed upon an Enraf-Nonius Automated X-ray diffractometer, and preliminary analysis indicated that the crystals belong to the triclinic system with the space group being either C_1^1—$P1$ or C_i^1—$P\bar{1}$; the centrosymmetric space group was chosen, and this choice was verified by the successful refinement of the structure. On the basis of a least-squares fit of the diffractometer settings of 25 reflections, the cell constants were determined to be a = 8.669 (4) Å, b = 10.985 (4) Å, c = 7.495 (3) Å, α = 97.98 (3)°, β = 104.65 (3)°, and γ = 71.55 (4)°; the observations were made at 21 °C with the use of Mo $K\alpha_1$ radiation with an assumed wavelength of 0.7093 Å. A calculated density of 2.141 g cm^{-3} for two monomeric formula units in the cell was in agreement with the observed value of 2.10 (2) g cm^{-3} obtained by flotation in a mixture of bromoform and chloroform.

Diffraction data were collected from a prismatic crystal on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and using Mo $K\alpha$ radiation. Peaks were scanned in an ω–2θ mode, with use of variable scan times determined on the basis of a rapid prescan; the maximum scan time used was 70 s. A unique data set having $2\theta(\text{Mo}) \leq 55°$ was gathered. A total of 2994 reflections was recorded; the intensities and centering of three standard reflections were monitored periodically, and the crystal was automatically recentered whenever crystal movement and/or intensity decline was detected. The data were corrected for background counts and assigned standard deviations, $\sigma(I)$, on the basis of counting statistics. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization and for absorption effects. The linear absorption coefficient, μ, for these atoms and Mo $K\alpha$ radiation is 84.9 cm^{-1}, and the application of an empirical absorption correction based on ψ-scan data led to maximum and minimum correction factors (on F) of 1.00 and 0.86, with an average correction of 0.92. Of the 2994 data, 1645 had $I \geq 3\sigma(I)$; only these data were used in the subsequent refinement of the structure.

Solution and Refinement. The positions of the copper and two bromine atoms were determined from a three-dimensional Patterson function, and isotropic least-squares refinement of these positions gave values of the usual agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ of 0.279 and 0.328, respectively. All least-squares analyses in this work were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$. Initially, the weights, w, were assigned as unity, but in the later stages a weighting scheme of the type $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o)$ is given by $\sigma(F_o^2) = [\sigma^2(I) + p^2I^2]^{1/2}$ and the value of p was set to 0.01, was used. This choice of p was confirmed by the absence of any dependence of R_2 on $|F_c|$ in the final refinement cycle (vide infra).

Table I. Positional Parameters for $[Cu(4\text{-}Metz)_2Br_2]_2$

atom	*x*	*y*	*z*
Br1	0.1174 (1)	0.04448 (9)	0.2366 (1)
Br2	−0.3363 (1)	0.35787 (9)	−0.1462 (1)
Cu	−0.1113 (1)	0.1926 (1)	0.0231 (1)
S1	0.2234 (3)	0.2517 (3)	−0.3007 (3)
S1′	−0.4584 (3)	0.0862 (3)	0.2749 (4)
N3	0.0515 (8)	0.2373 (6)	−0.0817 (9)
N3′	−0.2692 (8)	0.1757 (6)	0.1613 (9)
C2	0.076 (1)	0.1989 (8)	−0.249 (1)
C4	0.148 (1)	0.3139 (8)	0.010 (1)
C5	0.251 (1)	0.3298 (8)	−0.089 (1)
C6	0.132 (1)	0.3743 (9)	0.197 (1)
C2′	−0.334 (1)	0.0824 (9)	0.129 (1)
C4′	−0.316 (1)	0.2594 (8)	0.309 (1)
C5′	−0.418 (1)	0.2217 (9)	0.382 (1)
C6′	−0.255 (1)	0.3720 (10)	0.367 (1)
H2	0.0159	0.1453	−0.3348
H5	0.3296	0.3802	−0.0424
H6A	0.2085	0.4248	0.2427
H6B	0.0216	0.4303	0.1941
H6C	0.1558	0.3107	0.2829
H2′	−0.3132	0.0153	0.0324
H5′	−0.4653	0.2689	0.4853
H6′A	−0.2994	0.4220	0.4685
H6′B	−0.1374	0.3506	0.4000
H6′C	−0.2927	0.4305	0.2658

The positions of the carbon, nitrogen, and sulfur atoms were determined from a subsequent difference Fourier synthesis, and isotropic least-squares refinement of the above gave R_1 = 0.108 and R_2 = 0.113. Anisotropic refinement reduced R_1 and R_2 to 0.054 and 0.064, respectively. A difference Fourier map revealed the presence of some of the hydrogen atoms, and the positions of the other hydrogen atoms were calculated based on trigonal or tetrahedral geometry as appropriate, with the C–H distances assigned[16] as 0.95 Å. The hydrogen atoms were assigned fixed isotropic thermal parameters of 1.5 $Å^2$ greater than that of the carbon atom to which they were attached. Hydrogen atom parameters were included in subsequent least-squares calculations but were not refined. In the final cycle of least-squares refinement, there were 1645 observations and 136 variables and no parameter underwent a shift of more than 0.04σ, which is taken as evidence of convergence. The final least-squares yielded an R_1 value of 0.0471 and an R_2 value of 0.0475. A final difference Fourier map was featureless, with no peak higher than 0.6 e $Å^{-3}$. The positional parameters derived from the last cycle of least squares, along with their standard deviations as estimated from the inverse matrix, are presented in Table I. A compilation of observed and calculated structure amplitudes and the atomic thermal parameters are available as supplementary material.

Collection of Magnetic Data. Magnetic susceptibilities were obtained on a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) operating at a field strength of 10 kG. Temperatures at the sample were measured with a calibrated GaAs diode by observing the voltage on a Fluke 8502A 6.5-place digital multimeter; further details of the apparatus and temperature measurement have been given elsewhere.[17] A finely ground polycrystalline sample was packed in a precision milled Lucite sample holder under a dry-N_2 atmosphere. The sample weighed approximately 200 mg. The data were corrected for the diamagnetism of the Lucite holder and for the underlying diamagnetism of the constituent atoms by using Pascal's constants.[18] A value of 60 × 10^{-6} cgsu was assumed for the tem-

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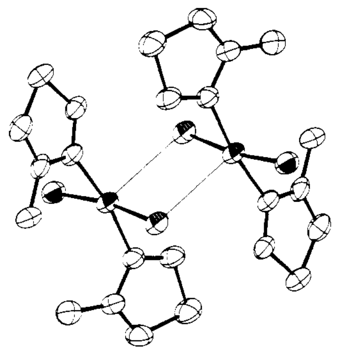

Figure 1. View of one dimeric unit in $[Cu(4\text{-}Metz)_2Br_2]_2$. Thermal ellipsoids in this and the subsequent figure are drawn at the 40% probability level, but hydrogen atoms are omitted for clarity.

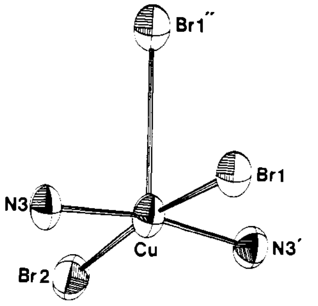

Figure 2. View of the coordination around a single copper center in $[Cu(4\text{-}Metz)_2Br_2]_2$.

Table II. Selected Internuclear Separations in $[Cu(4\text{-}Metz)_2Br_2]_2$

atoms[a]	dist, Å	atoms	dist, Å
Cu-Br(1)	2.492 (1)	Cu-Br(2)	2.420 (1)
Cu-Br(1)″	3.033 (1)	Cu-Cu″	4.063 (2)
Cu-N(3)	1.989 (5)	Cu-N(3)′	1.978 (5)
S(1)-C(2)	1.701 (6)	S(1)′-C(2)′	1.705 (6)
C(2)-N(3)	1.313 (7)	C(2)′-N(3)′	1.286 (8)
N(3)-C(4)	1.372 (7)	N(3)′-C(4)′	1.393 (8)
C(4)-C(5)	1.360 (8)	C(4)′-C(5)′	1.340 (8)
C(5)-S(1)	1.692 (7)	C(5)′-S(1)′	1.684 (7)
C(4)-C(6)	1.483 (9)	C(4)′-C(6)′	1.464 (9)

[a] Atoms designated by a single prime are *not* related by symmetry to unprimed atoms; atoms designated by a double prime are related to unprimed atoms by inversion through the origin.

perature-independent paramagnetism (TIP) of copper.[17]

Description of the Structure

The complex consists of dimeric $[Cu(4\text{-}Metz)_2Br_2]_2$ units which are well separated from each other. A view of the dimeric unit is given in Figure 1. The bridging Cu_2Br_2 unit is constrained to be planar by the presence of the crystallographic inversion center in the middle of the dimer. The bond lengths and angles in the dimer are listed in Tables II and III.

As can be seen in Figure 2, and from an examination of Tables II and III, the geometry at each copper(II) center is tetragonal pyramidal, the four basal ligands being two trans nitrogen atoms from the 4-Metz ligands and two trans bromide ions while the apical site is occupied by a bromide ligand which is basal to the other copper center in the dimer. Thus, the four basal ligands are approximately coplanar with no atom deviating from the least-squares plane by more than 0.01 Å. As is usual in tetragonal-pyramidal compounds,[6] the copper atom lies 0.18 Å above this plane in the direction of the apical atom, Br(1)″.

The Cu–N distances of 1.978 (5) and 1.989 (5) Å are comparable with the value of 1.990 (2) Å reported[15] for the related complex $Cu(tz)_2Cl_2$ and with values reported in a number of other complexes.[19–25] The equatorial Cu–Br distances are 2.420 (1) and 2.492 (1) Å, with the distance to the bridging atom [Br(1)] appreciably the larger of the two as expected. The terminal Cu–Br(2) distance can be compared to the values of 2.372 (1), 2.40, 2.401 (3), and 2.413 (3) Å found in the other bromo-bridged dimers of this geometry,[20–23] that of 2.412 (4) in $Cu_2Br_4(C_5H_5N)_2$,[24] and those of 2.385 (5) and 2.426 (4) Å reported[25] for two related polymeric compounds; and it is evidently normal. The equatorial Cu–Br(1) distance of 2.492 (1) Å is slightly larger than the values of 2.422 (5)–2.468 (2) Å reported in these same compounds but is unremarkable.

Table III. Selected Internuclear Angles in $[Cu(4\text{-}Metz)_2Br_2]_2$

atoms	angle, deg	atoms	angle, deg
Br(1)-Cu-Br(2)	171.85 (5)	Br(1)-Cu-Br(1)″	85.84 (3)
Br(1)-Cu-N(3)	91.6 (1)	Br(1)-Cu-N(3)′	88.3 (1)
Br(2)-Cu-N(3)	90.1 (1)	Br(2)-Cu-N(3)′	88.5 (2)
Br(2)-Cu-Br(1)″	101.98 (3)	N(3)-Cu-N(3)′	169.2 (2)
Br(1)″-Cu-N(3)	94.4 (1)	Br(1)″-Cu-N(3)′	96.4 (1)
Cu-N(3)-C(2)	123.9 (4)	Cu-N(3)′-C(2)′	123.3 (5)
Cu-N(3)-C(4)	124.0 (4)	Cu-N(3)′-C(4)′	124.1 (4)
C(2)-N(3)-C(4)	112.1 (5)	C(2)′-N(3)′-C(4)′	112.6 (6)
C(2)-S(1)-C(5)	90.1 (3)	C(2)′-S(1)′-C(5)′	89.0 (3)
S(1)-C(2)-N(3)	113.5 (5)	S(1)′-C(2)′-N(3)′	114.0 (5)
N(3)-C(4)-C(5)	113.2 (6)	N(3)′-C(4)′-C(5)′	111.3 (6)
N(3)-C(4)-C(6)	121.0 (6)	N(3)′-C(4)′-C(6)′	121.1 (6)
C(5)-C(4)-C(6)	125.8 (6)	C(5)′-C(4)′-C(6)′	127.6 (6)
S(1)-C(5)-C(4)	111.1 (5)	S(1)′-C(5)′-C(4)′	113.0 (5)
Cu-Br(1)-Cu″	94.16 (3)		

The geometry of the bridging unit is compared with that observed[20–23] in the related dimers in Table IV. The out-of-plane Cu–Br(1)′ distance of 3.033 (1) Å is intermediate between the four values previously reported, which range from 2.868 (2) to 3.872 (5) Å. Similarly, the bridging Cu–Br(1)–Cu′ angle of 94.16 (3)° is in the range of 83.71 (5)–100.4 (6)° found in the four related dimers. The consequence of these two features, of course, is that the Cu–Cu′ separation of 4.063 (2) Å is again within the range [3.570 (3)–4.926 (6) Å] observed for the other complexes.

The geometry of the substituted thiazole ligand is comparable to that observed[15,29] in $Cu(tz)_2Cl_2$ and in $Cu(2,4\text{-}Me_2tz)_2Cl_2$. The thiazole rings are planar, with no atom deviating from the least-squares plane by more than 0.008 Å in one case and by 0.001 Å in the other. In the former, the copper atom lies in the plane while the extracyclic atom C(6) appears to be significantly out of the plane, while the reverse situation obtains for the latter. The two thiazole planes are inclined at an angle of 22° to each other and at angles of 76° and 82° to the base plane through the four equatorial atoms. It is apparent that this orientation (see Figure 1) brings the two methyl groups into positions which hinder axial approach to Cu at the potential sixth site and, therefore, prevents the formation of polymeric species. A similar result was seen[23] in the complex $[Cu(2\text{-}pic)_2Br_2]_2$, where 2-pic is 2-methyl-

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Table IV. Structural and Magnetic Properties of Tetragonal-Pyramidal Dibromo-Bridged Copper(II) Dimers

complex[a]	Cu-Br′ out-of-plane (*R*), Å	Cu-Cu′, Å	Cu-Br′-Cu, deg (ϕ)	ϕ/R	*J*, cm^{-1}	ref
$[Cu(DMG)Br_2]_2$	2.883 (1)	3.599 (1)	85.59 (4)	29.7	−1.5	20, 26
$[Cu(tmen)Br_2]_2$	3.20	4.20	95.6 (5)	29.9	−2.0	21, 27
$[Cu(dmen)Br_2]_2$	2.868 (2)	3.570 (3)	83.71 (5)	29.2	−1.0	22, 27
$[Cu(2\text{-pic})_2Br_2]_2$	3.872 (5)	4.926 (6)	100.4 (1)	25.9	−2.5	23, 28
$[Cu(4\text{-Metz})_2Br_2]_2$	3.033 (1)	4.063 (2)	94.16 (3)	31.0	−1.2	this work

[a] Ligand abbreviations: DMG = dimethylglyoxime; tmen = *N,N,N′,N′*-tetramethylethylenediamine; dmen = *N,N*-dimethylethylenediamine; 2-pic = 2-methylpyridine; 4-Metz = 4-methylthiazole.

pyridine, where the pyridine rings are inclined at angles of 81 and 82° to the base plane and 17.2° to each other. In the disubstituted monomer $Cu(2,4\text{-}Me_2tz)_2Cl_2$, these values are[29] similar to those here [85 and 10°], but in the unsubstituted polymeric complex $Cu(tz)_2Cl_2$, the rings are coplanar and are inclined at 60° from the base plane.[15] The bond lengths in the two independent thiazole moieties here are substantially similar to each other and to those in $Cu(tz)_2Cl_2$[15]; regrettably, the disorder encountered[29] in $Cu(2,4\text{-}Me_2tz)_2Cl_2$ renders that structure less useful for such comparisons. Thus, the C(2)–N(3) [1.313 (7) and 1.286 (8) Å] and C(4)–C(5) [1.360 (8) and 1.340 (8) Å] distances are comparable to the values of 1.301 (3) and 1.358 (3) Å in $Cu(tz)_2Cl_2$ and are indicative of double bonds, while the N(3)–C(4) distances [1.372 (7) and 1.393 (8) Å] indicate much less double-bond character in this formally single N–C bond. The S–C bonds are all very similar, with a range of 1.684 (7)–1.705 (6) and an average value of 1.696 (9) Å. As was true in $Cu(tz)_2Cl_2$, the sulfur atom does not participate in coordination to the metal but may be involved in a weak interchain S···S′ interaction with a separation of 3.630 (3) Å. This value, which is comparable to that of 3.619 (1) Å in $Cu(tz)_2Cl_2$, is slightly less than twice the reported value (1.85 Å) of the van der Waals radius of sulfur.[30]

Magnetic Properties

The magnetic susceptibility of a powdered sample of the complex is plotted as a function of temperature in Figure 3. While no maximum in the susceptibility is observed, the data clearly deviate from that predicted by the Curie–Weiss law at low temperatures in a manner which is indicative of antiferromagnetic coupling between the two copper(II) centers in the dimeric unit. It is apparent from Figure 3, however, that $|J|$ is small, and consequently the application of the usual Bleaney-Bowers susceptibility expression[31] is inappropriate since the condition $|J| >> g\mu_BH$ could not be satisfied in this case. Consequently, the data were fitted to the magnetization expression[32] eq 1 where the exchange Hamiltonian is given

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

by eq 2 and $\hat{S}$ is the total spin (i.e., $\hat{S} = \hat{S}_1 + \hat{S}_2$). Additional

$$H_{ex} = -2J\hat{S}_1\cdot\hat{S}_2 + g\mu_BH\hat{S} \quad (2)$$

(interdimer) interactions, which are not included in (2) above, can be estimated from a molecular field approximation of the type

$$H_{eff} = H + \gamma M \quad (3)$$

where H_{eff} is the effective magnetic field, but in the present case attempts to use expression 3 resulted in values for the parameter γ which were insignificantly different from 0.

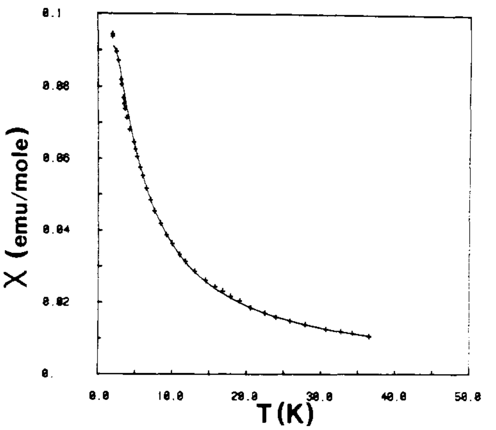

Figure 3. Temperature dependence of the magnetic susceptibility of $[Cu(4\text{-Metz})_2Br_2]_2$. The solid line represents the best fit to the magnetization expression (see text) with $g = 2.058$ and $J = -1.24$ cm^{-1}.

Hence, we conclude that in the present case there are no magnetically significant interdimer interactions.

The observed susceptibility data were fitted to expression 1 with use of the relationship of eq 4 (where χ is the magnetic

$$\chi = M/H \quad (4)$$

susceptibility) with the parameters *g* and *J* as variables with the use of a SIMPLEX fitting routine.[17] The results of this fit, displayed as the solid line in Figure 3, led to values of $g = 2.058$ and $J = -1.24$ cm^{-1}. So that the validity of these results could be tested, the susceptibility data were also fitted to a model in which the calculated susceptibilities were derived directly from the energy levels through the application of the Hellmann–Feynman theorem with use of the local program CAMSFIT.[33] This approach yielded the values $g = 2.032$ (7) and $J = -1.19$ (1) cm^{-1}, which are very similar to those obtained above. Hence, the calculations suggest that in this dimer the singlet ground state lies approximately 2.4 cm^{-1} below the triplet state. The magnetic properties observed for the present dimer are compared wih those of all other known dimers of this structural type in Table IV.

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Supplementary Material Available: Tables of anisotropic thermal parameters (U_{ij}) and observed and calculated structure amplitudes (in electrons × 10) (13 pages). Ordering information is given on any current masthead page.

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