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Strong Antiferromagnetic Exchange in a Bromide-Bridged Copper Dimer, Bis(μ-bromo)bis[bromobis(tetramethylene sulfoxide)copper(II)]. Structure, Susceptibility, and Magnetostructural Correlations

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Crystals of the compound bis(μ-bromo)bis[bromobis(tetramethylene sulfoxide)copper(II)] belong to the monoclinic space group $P2_1/c$ (C_{2h}^5) with lattice constants a = 9.578 (3) Å, b = 14.896 (6) Å, c = 9.727 (3) Å, β = 94.51 (3)°, Z = 4, and D_{calcd} = 2.04. The structure is isomorphic to the corresponding chloride compound and consists of bis(μ-bromo)-bridged copper dimers and coordinated sulfoxide groups. The geometry at each copper(II) site is distorted tetragonal pyramidal with two trans oxygens and two trans bromines in the basal plane; the axial site is occupied by a bromine from the inversion-related copper. There are significant distortions away from planarity within the monomeric unit, as signified by the trans Br(1)–Cu–Br(2) angle of 139.6°. The copper–bromine–copper bridging geometry is asymmetric with one long bond (2.981 Å) and one short bond (2.461 Å); the bridging angle is 85.5°. The magnetic susceptibilities of powdered samples have been measured over the temperature range 4.2–260 K; the results show the compound is antiferromagnetically coupled (J/k = –24.2 K (J = –16.9 cm^{-1})). Comparison to other bis(μ-halide)-bridged copper dimers of similar structure shows the magnetic interaction strength is strongly correlated to the degree of nonplanarity within the copper basal plane.

Introduction

What determines the strength of magnetic interaction between metal ions in a crystal? This question has received considerable attention since the early study by Hatfield and Hodgson[1] on the dimeric planar bis(μ-hydroxo) complexes $[\text{CuL(OH)}_2]_2$ in which they revealed a linear relationship between the magnetic exchange parameter J and the Cu–O–Cu bridging angle ϕ. The observed dependence was explained by Hay and co-workers[2] in terms of orbital overlap, using molecular orbital theory. A similar dependence for the analogous planar chloride-bridged dimers has also been seen.[3] These results have been extended by numerous workers[4-6] who have studied the effects upon the exchange strength of altering the coordination geometry, the number of coordinating ligands, and the bridging ligands themselves. Among the findings has been the realization that substitution of bromide for chloride ions as the bridging ligands increases the magnitude of the exchange interaction by approximately a factor of 2.[7,8] Most of this work has concentrated on the copper(II) ion since its d^9 configuration involves only one magnetic orbital in the exchange process and since the copper ion can assume a wide variety of coordination geometries.[9]

An analogous but less understood phenomenon is the dependence of magnetic anisotropy upon ligand substitution. In the two-dimensional copper halide salts $(\text{RNH}_3)_2\text{CuX}_4$ (X = Cl, Br), the magnetic anisotropy normally causes the moments to remain in the plane for the chlorides and align normal to the plane in the bromides.[8] The same reversal of anisotropy has been observed in the one-dimensional copper halide chains $(\text{CHA})\text{CuX}_3$ (X = Cl, Br and CHA = cyclohexylammonium).[10-12] The copper(II) ions are basically isotropic (Heisenberg-like) with anisotropy energies that are typically no more than several percent as large as the isotropic exchange interaction. Since the behavior of a magnet in the ordered state is critically dependent on the amount and type (axial, planar) of the anisotropy present, it remains an important question of magnetochemistry to understand the origins and structural dependence of such an effect.

We are currently studying the copper halide–sulfoxide system to investigate the effect of halide substitution upon both the exchange interaction and the magnetic anisotropy. This system has been selected since a number of magnetically interesting compounds are already known to exist within it. $\text{CuCl}_2(\text{Me}_2\text{SO})$ and $\text{CuCl}_2(\text{TMSO})$ (Me_2SO = dimethyl sulfoxide, TMSO = tetramethylene sulfoxide) have been shown[13] to form tribridged polymeric chains with ferromagnetic exchange and weak anisotropies. The analogous bromides have not yet been synthesized. The structure of the bis form of the Me_2SO complex $\text{CuX}_2(\text{Me}_2\text{SO})_2$ consists of a monobridged chain for both the chloride[14] and bromide.[15] Antiferromagnetic interactions are present in both compounds,[16] and significant anisotropy is present.[17,18] There are several other isomers formed from copper bromide and Me_2SO that have not yet been characterized. The bis form of the TMSO chloride $\text{CuCl}_2(\text{TMSO})_2$ consists of discrete dibridged dimeric units[19] with an asymmetric bridging geometry consisting of one long Cu–Cl bond (3.02 Å) and one short bond (2.27 Å) with a bridging angle of 88.5°. The exchange is antiferromagnetic and relatively strong at J/k = –12 K (J = –8.3 cm^{-1}). We report here on the crystal structure and magnetic behavior of the analogous bromide $\text{CuBr}_2(\text{TMSO})_2$, which is also an antiferromagnetic dimer. A preliminary report of the magnetic results has been published elsewhere.[20]

Experimental Section

Sample Preparation. One mole percent of CuBr_2 was dissolved in 10 mL of methanol at room temperature. A slight excess (2.3 mol %) of the TMSO was added in 3 mL of MeOH. The solution was stirred at room temperature for 30 min and then put in a cold room at –5 °C. Dark green microcrystals formed overnight. These were filtered off, and

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Table I. X-ray Data Collection Parameters

compd name	copper(II) bromide bis(tetramethylene sulfoxide)
empirical formula	$C_8H_{16}O_2S_2CuBr_2$
diffractometer syst	Nicolet R3m/E
cryst class	monoclinic
space group	$P2_1/c$
systematic absences	$h0l$, l odd; $0k0$, k odd
lattice constants[a]	$a = 9.578$ (3) Å $b = 14.896$ (6) Å $c = 9.727$ (4) Å $\beta = 94.51$ (3)°
radiation:	Mo Kα with Zr filter
cryst size	$0.2 \times 0.22 \times 0.4$ mm^3
abs coeff	77.4 cm^{-1}
calcd density:	$\rho = 2.04$ g/cm^3 ($Z = 2$)
type of abs cor	empirical ψ scan
max transmission	0.92
min transmission	0.37
data collection technique	ω scan
scan range	2
scan speed	8.37 deg/min (min), 29.30 deg/min (max)
check reflecns[b]	0,2,3; 0,4,0; 2,1,0
total reflecns	1984
2θ (max)	45°
unique reflecns	1766; 1211 with $I > 3\sigma$
R for equiv reflecns	0.0252
structure solution package	Nicolet SHELXTL
structure solution technique	direct methods
R ($= \sum\|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.055
R_w ($= [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$ with $w = 1/[\sigma^2(F) + g(F)^2]$	0.039; $g = 0.000\,01$
goodness of fit	1.61
Δ/σ (mean)	0.015
Δ/σ (max)	0.063
total params refined	130
thermal params	anisotropic on all non-hydrogen atoms
hydrogen atoms	constrained to C–H and N–H = 0.96 Å, thermal parameters fixed at 0.10
largest peak on final difference map	1 e/Å^3 (near Br(1))
extinction cor	none

[a] Based on 25 reflections in the range $29° < 2\theta < 31°$. [b] Monitored every 100 reflections.

the filtrate was placed over KOH at +5 °C. Over a period of several weeks, well-formed dark green prismatic crystals were formed. When the crystals are crushed, the powder is a light yellow-green. The composition was verified by commercial chemical analysis.[21] Anal. Calcd for $C_8H_{16}O_2CuBr_2$: C, 22.26; H, 3.73; O, 7.41; S, 14.85; Cu, 14.72; Br, 37.02. Found: C, 22.08; H, 3.68; O, 7.41; S, 14.90; Cu, 14.85; Br, 36.82. The magnetic study and chemical analysis were conducted on the same batch. The X-ray analysis was conducted on crystals obtained from different batches that are formed from room-temperature evaporation of methanol solutions of stoichiometric mixtures of copper bromide and TMSO. The identity of the magnetic and X-ray batches were confirmed by comparison of powder X-ray patterns.

It has been found that strict 1:2 stoichiometry is not necessary for the production of the bis form of $CuBr_2$/TMSO, provided the solvent is methanol: batches have been prepared with both copper bromide and TMSO as much as 15% in excess, and only the bis phase is obtained. However, use of alcohols other than methanol does lead to the formation of other phases, even when the starting materials are in a strict 1:2 ratio. When ethanol is used, the most stable phase is $CuBr_2 \cdot {}^4/_3$TMSO, which readily grows as black triclinic crystals. Preliminary studies[22] show this black phase to consist of alternating chains of dimers and monomers, held together by long Cu–Br bonds. In addition, a third phase has been obtained as red powder from both ethanol and propanol. Preliminary susceptibility studies in our laboratory of the red phase show the presence of strong ferromagnetic interactions (Curie–Weiss $\Theta = +30$ K).

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$ Å^2)

	x	y	z	U^a
Br(1)	5753 (1)	3803 (1)	662 (1)	40 (1)
Br(2)	8116 (1)	6141 (1)	2912 (1)	55 (1)
Cu	6425 (2)	5349 (1)	1326 (2)	40 (1)
S(1)	4545 (3)	6387 (2)	2988 (3)	40 (1)
S(2)	2045 (3)	3589 (2)	614 (3)	42 (1)
O(1)	4957 (8)	5420 (5)	2609 (7)	40 (3)
O(2)	2306 (7)	4571 (5)	150 (7)	39 (3)
C(11)	4718 (13)	6398 (8)	4861 (11)	45 (5)
C(12)	3232 (14)	6399 (11)	5345 (13)	82 (7)
C(13)	2221 (14)	6019 (12)	4296 (14)	96 (8)
C(14)	2637 (13)	6357 (9)	2926 (12)	56 (6)
C(21)	7677 (12)	6355 (9)	−2468 (11)	60 (6)
C(22)	9101 (12)	6194 (14)	−3003 (13)	128 (10)
C(23)	10174 (14)	6270 (14)	−2057 (13)	123 (10)
C(24)	9862 (11)	6455 (9)	−671 (12)	50 (5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III

(a) Bond Lengths (Å)

Br(1)–Cu	2.461 (2)	Br(1)–Cu(a)	2.981 (2)
Br(2)–Cu	2.429 (2)	Cu–O(1)	1.932 (8)
Cu–Br(1a)	2.981 (2)	Cu–O(2a)	1.940 (7)
S(1)–O(1)	1.544 (8)	S(1)–C(11)	1.816 (11)
S(1)–C(14)	1.786 (12)	S(2)–O(2)	1.556 (8)
S(2)–C(21a)	1.804 (11)	S(2)–C(24a)	1.794 (11)
O(2)–Cu(a)	1.940 (7)	C(11)–C(12)	1.506 (18)
C(12)–C(13)	1.452 (19)	C(13)–C(14)	1.504 (19)
C(21)–C(22)	1.490 (17)	C(21)–S(2a)	1.804 (11)
C(22)–C(23)	1.314 (17)	C(23)–C(24)	1.429 (18)
C(24)–S(2a)	1.794 (11)		

(b) Bond Angles (deg)

Cu–Br(1)–Cu(a)	85.5 (1)	Br(1)–Cu–Br(2)	139.6 (1)
Br(1)–Cu–O(1)	92.3 (2)	Br(2)–Cu–O(1)	91.5 (2)
Br(1)–Cu–Br(1a)	94.5 (1)	Br(2)–Cu–Br(1a)	125.9 (1)
O(1)–Cu–Br(1a)	84.8 (2)	Br(1)–Cu–O(2a)	91.3 (2)
Br(2)–Cu–O(2a)	91.9 (2)	O(1)–Cu–O(2a)	169.9 (3)
O(1)–S(1)–C(11)	104.1 (5)	O(1)–S(1)–C(14)	103.7 (5)
C(11)–S(1)–C(14)	92.6 (6)	O(2)–S(2)–C(21a)	103.4 (5)
O(2)–S(2)–C(24a)	102.9 (5)	Cu–O(1)–S(1)	114.2 (4)
S(2)–O(2)–Cu(a)	113.1 (4)	S(1)–C(11)–C(12)	107.6 (8)
C(11)–C(12)–C(13)	110.4 (11)	C(12)–C(13)–C(14)	107.0 (12)
S(1)–C(14)–C(13)	107.9 (8)	C(22)–C(21)–S(2a)	107.0 (8)
C(21)–C(22)–C(23)	113.6 (12)	C(22)–C(23)–C(24)	118.4 (12)
C(23)–C(24)–S(2a)	107.5 (8)		

Structural Determination. The structure of the title compound has been determined by Professor R. D. Willett of Washington State University using a Nicolet R3m/E automated diffractometer and standard procedures.[23] Data collection details are given in Table I, and heavy-atom positional and isotropic thermal parameters are given in Table II. The important bond distances and angles are listed in Table III. Tables of structural parameters and observed and calculated structure factors have been deposited as supplementary material.

Magnetic Measurements. The magnetic susceptibility of a 228-mg sample of $[CuBr_2(TMSO)_2]_2$ was measured between 4 and 260 K in a PAR Model 155 vibrating-sample magnetometer. The temperatures were determined with a carbon-glass resistance thermometer calibrated against a commercially calibrated diode and magnetic standards.[24] The magnetic field was measured with a Hall probe. The susceptibilities were corrected for diamagnetism (-190×10^{-6} emu/mol) and temperature-independent paramagnetism of the cupric ion ($+60 \times 10^{-6}$ emu/mol). Since the preliminary report[20] the data have been corrected slightly for changes in the temperature scale[24] and for the background signal.

Results

Structural Description. The structure is the same as that found for the analogous chloride,[19] consisting of dimeric [Cu-

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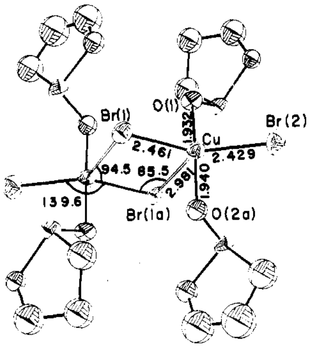

Figure 1. View of the dimeric unit in [$CuBr_2(TMSO)_2$]. Bond distances and angles are given in units of angstroms and degrees, respectively.

$(TMSO)_2Br_2]_2$ units that are essentially isolated from one another. The dimeric unit is shown in Figure 1. The geometry at each copper(II) center is a significantly distorted tetragonal pyramid with the basal plane made up of the two trans-oxygen atoms from the TMSO ligands and two trans-bromide ions; the axial site is occupied by the bromide ion Br(1a), which is basal to the other copper in the dimer. The basal Cu–Br distances are 2.461 and 2.429 Å while the Cu–O distances are 1.932 and 1.940 Å. The two *trans*-$CuBr_2((CH_2)_4SO)_2$ monomeric units are connected by the long Cu–Br(1a) bond of 2.981 Å. The bridging unit lies on an inversion center which requires it to be planar. It is important to note that the basal planes of the two monomeric units are offset from one another and are not coplanar; we shall refer to dimers of this structural type as eclipsed.

As in the chloride,[19] the distortions that exist can be thought of as arising from a distortion away from an ideal tetrahedral $CuBr_2O_2$ ion with trans Br–Cu–Br angles near 130°. As the fifth ligand, Br(1a), is brought near, the O–Cu–O angle opens up to the observed value of 169.9° while the Br–Cu–Br angle is forced to 139.6°. Consequently, the basal unit is nonplanar with the Br(2) ion lying below the plane determined by Br(1) and the two oxygens. The copper ion lies nearly in this plane. Alternatively, the distortion may be thought of as arising from an idealized trigonal-bipyramidal arrangement or a 4 + 1 semicoordinate geometry.

The bond distances and angles about the copper(II) ion are given in Table III for the title compound. Comparison of these parameters with those of the analogous chloride[19] show there are few differences between the two structures. The Cu–Br distances are greater than the corresponding Cu–Cl distances, as expected, except for the Cu–X(1)′ long bond, which is shorter at 2.981 Å for the bromide than 3.02 Å for the chloride. The Cu–X(1)-Cu′ bridging angle is 85.8° for the bromide and 88.5° for the chloride. Consequently, the Cu–Cu′ distance is reduced from 3.737 to 3.714 Å in the bromide in spite of the increased size of the ligand. In addition, the distortions away from ideal tetragonal-pyramidal geometry are greater in the bromide complex as indicated by the increase in the trans X(1)–Cu–X(2) angle from 145.7° in the chloride to 139.6° in the bromide.

It is interesting to note the differences between the structures of the bis forms of the copper halide/Me_2SO and copper halide/TMSO compounds. For either sulfoxide group, the structures remain unchanged by halide substitution, and in all four compounds, the copper geometry consists of a distorted 4 + 1 arrangement. However, the structure of $CuX_2(Me_2SO)_2$ consists of monobridged chains for the chloride[14] and the bromide[15] whereas the structure of $CuX_2(TMSO)_2$ X = Cl, Br) consists of the dibridged dimers described above. The differences between the two structures can thus be attributed to differences between the two sulfoxide groups.

The dimeric structure of the $CuX_2(TMSO)_2$ compounds is to be expected for nonplanar ligands such as TMSO. It has been observed previously[25] that substitution of methyl groups onto pyridine or thiazole ligands has led to systematic changes in the geometry of the inner coördination sphere of the copper ions in CuL_2X_2 compounds. For example, $Cu(py)_2Cl_2$ has a six-coordinate structure consisting of dibridged chains; $Cu(2\text{-pic})_2Cl_2$ has five-coordinate coppers since the methyl groups on the pyridine rings have blocked access to one of the bonding sites of the copper. The structure is dimeric and is similar to that of the title compound. Doubly substituted pyridine or thiazole blocks more bonding sites and leads to four-coordinate copper monomers. In view of this trend the dimeric structure of $CuX_2(TMSO)_2$ is expected and that of the Me_2SO is anomalous; the Me_2SO ligand is similarly nonplanar and would be expected to lead to dimerization.

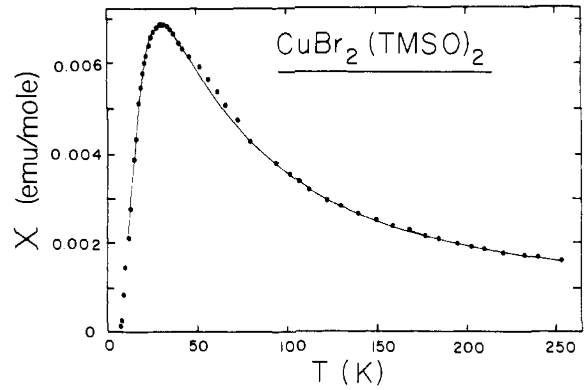

Figure 2. Magnetic susceptibility per mote of copper ions of $CuBr_2(TMSO)_2$ plotted as a function of temperature. The solid line corresponds to the theoretical prediction for the data based on eq 1 of the text with best-fit parameters $J = -16.9\ cm^{-1}$ and $g = 2.10$.

The explanation for the structure of the $(Me_2SO)_2$ phase has been given previously.[15] The methyl groups and halide ions of neighboring chains interlock, fixing their respective positions.[26] The methyl groups are thus held out of the way, and the adjacent copper is able to form a long bond to the bridging halide, forming the chains. Such a monobridged chain structure is rare but has been observed in at least three other compounds.[27] The steric forces are thus more important in determining the copper geometry than the X–O repulsions. Since the interleaving of the chains is not possible for the TMSO ligands, the resulting copper geometry is that more normally observed.

Magnetic Susceptibility. The susceptibility per mole of copper ions is plotted as a function of temperature in Figure 2. The dominant features of the data are a rounded hump near 30 K and a rapid decrease to zero at lower temperatures, indicating antiferromagnetism within a cluster compound. A Curie–Weiss analysis of the data above 100 K yields a Curie–Weiss $\Theta = -24$ K and the Curie constant $C = 0.43$ emu K/mol ($g = 2.14$).

The model of an isolated Heisenberg dimer of $S = {}^1/_2$ ions with interaction Hamiltonian $H = -2JS_1 \cdot S_2$ has been used to analyze the data. The use of the isotropic Heisenberg is justified in terms of the low magnetic anisotropy for the Cu^{2+} discussed previously. The susceptibility of this model has been shown[28] to be

$$\chi_m = \frac{Ng^2\mu_B{}^2}{kT} \frac{e^x}{1 + 3e^x} \qquad (1)$$

where $x = -2J/kT$. This expression predicts the antiferromagnetic exchange constant to be related to the temperature of the maximum susceptibility (T_{max}) as $J/k = -0.801 T_{max}$. Since T_{max} is 30 K for this compound, the exchange constant should be near −24 K ($-16.6\ cm^{-1}$) if this is the appropriate model for the data. The data have been fit to this model with use of a nonlinear least-squares procedure.[29] The data have been weighted so the

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Table IV[a]

no.	compd	geom	Cu-X, Å	Cu-X′, Å	Cu-X-Cu, deg	J, cm^{-1}	ϕ/R'	X-Cu-L, deg	ref
1	$[Cu(4\text{-meox})_2Cl_2]_2$	TP	2.38	2.60	89.46	−1.3	34.4	159.6	36
	$[Cu(4\text{-meox})_2Br_2]_2$	TP	2.556	2.71	87.0	−7.6	32.1	157.1	25
2	$[Cu(2\text{-pic})_2Cl_2]_2$	TP	2.287	3.364	100.6	−3.7	29.9	177.6	7, 31
	$[Cu(2\text{-pic})_2Br_2]_2$	TP	2.426	3.872	100.4	−2.5	25.9	176.2	7, 32
3	$[Cu(dmen)Cl_2]_2$	TP	2.309	2.734	86.13	−1.05	31.5	167.7	33, 34
	$[Cu(dmen)Br_2]_2$	TP	2.463	2.868	83.71	−1.0	29.2	166.2	33, 34
4	$[Cu(DMG)Cl_2]_2$	TP	2.240	2.698	88.0	+3.15, 0.15	32.6	166.7	35–37
	$[Cu(DMG)Br_2]_2$	TP	2.387	2.883	85.6	−1.5	24.7	NA	37, 38
5	$[Cu(tmen)Cl_2]_2$	TP	2.264	3.147	96.8	−2.8	30.8	170.8	39, 40
	$[Cu(tmen)Br_2]_2$	TP	2.42	3.20	95.6	−2.0	29.9	NA	34, 41
6	$[Cu(TMSO)_2Cl_2]_2$	TP	2.28	3.02	88.5	−8.3	29.3	145.7	19
	$[Cu(TMSO)_2Br_2]_2$	TP	2.461	2.981	85.5	−16.9	28.7	139.6	this work
7	$[Cu(4\text{-metz})_2Br_2]_2$	TP	2.49	3.03	94.16	−1.24	31.1	171.8	42
8	$[Cu(MAEP)Br_2]_2$	TBP	2.47	2.80	92.14	−2.1	32.9	DNA	43
9	$[Cu(dien)Br_2]_2(ClO_4)_2$	TP	2.42	2.89	90.63	+1.35	31.4	178.8	44

[a] Abbreviations: TP = tetragonal pyramidal; TBP = trigonal bipyramidal; NA = not available; DNA = does not apply; 4-meox = 4-methyloxazole; 2-pic = 2-picoline (2-methylpyridine); dmen = *N*,*N*-dimethylethylenediamine; DMG = dimethylglyoxime; tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; TMSO = tetramethylene sulfoxide; 4-metz = 4-methylthiazole; MAEP = 2-(2-(methylamino)ethyl)pyridine; dien = diethylenetriamine.

percent difference deviation is minimized. The results of the fit to the data with both the exchange constant and g varied independently are shown as the solid curve in Figure 2. The best-fit parameters are $J/k = -24.4$ (2) K ($J = -16.9$ (2) cm^{-1}) and $g = 2.10$ (1). The predicted curve lies within the experimental scatter of the data between 10 and 300 K but lies somewhat under the data below 10 K. The slight systematic deviation seen between 60 and 90 K is due to a remnant error in the temperature scale. The validity of the parameters was tested by fitting various ranges of the data to the model and looking for systematic changes of the parameters as a function of the lowest temperature (T_{low}) included in the range. The data from 260 K down were included. This test showed the parameters to be independent of the range down to 10 K provided the region of the maxima was included, i.e. $T_{\text{low}} < 30$ K. The standard errors are smallest when $T_{\text{low}} = 18$ K, the parameters there being $J/k = -24.4$ (0.08) K and $g = 2.098$ (3). As T_{low} is reduced below 10 K, the parameters start to change, the standard errors increase, and the fit at high temperatures worsens.

Attempts were made to improve the fit at low temperatures by introducing a Curie–Weiss Θ into the denominator of eq 1. Such a parameter would be required if significant interactions between dimers existed. Such attempts were not successful. The parameter Θ was never well-defined, and the quality of the fit to the data below 12 K was not improved, even though the agreement at temperatures above 100 K was lessened. When $T_{\text{low}} = 18$ K and the other two parameters were fixed at the values cited in the above paragraph, Θ was found to be -0.03 ± 0.08, signifying the irrelevance of this parameter. We conclude the disagreement between the data and model prediction below 10 K is due to residual errors in the background correction for these very small susceptibilities. Nevertheless, the exchange constant is well-determined at $J/k = -24.4$ K ($J = -16.9$ cm^{-1}).

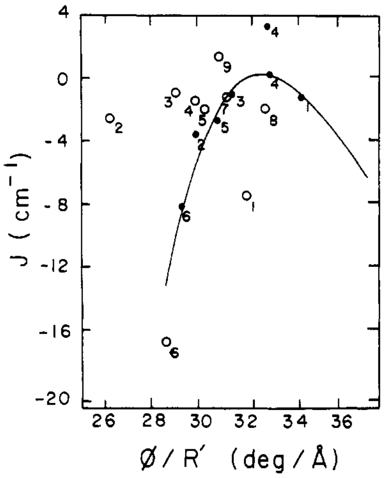

Figure 3. Exchange strengths of the eclipsed-planar dimers listed in Table IV plotted against the ratio ϕ/R', where ϕ is the Cu–X–Cu′ bridging angle and R' is the long Cu–X′ bond distance in the bridging network. The open and closed circles correspond to the bromide and chloride compounds, respectively. The numbers identify the compounds in order of their appearance in Table IV. The solid curve is the correlation for the chloride dimers suggested in ref 4.

Discussion

The magnetostructural and exchange parameters for the title compound and other bis(μ-bromide)-bridged copper dimers that have been structurally and magnetically characterized are listed in Table IV. For ease in comparison to the literature, all exchange constants are reported in units of cm^{-1}. The table also includes those chloride dimers that are isostructural with their bromide analogues. The exchange constant (−16.9 cm^{-1}) of the title compound is the largest yet reported for a bromide member of this class of dimers. Typical values for the exchange in the other

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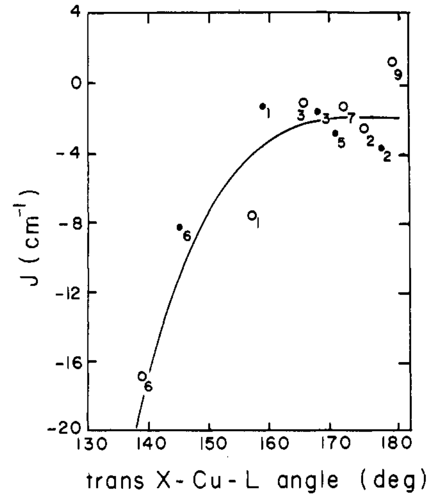

Figure 4. Exchange strengths of the dimers listed in Table IV plotted against the trans X–Cu–L bridging angle. The solid curve is a guide to the eye. The open and closed circles correspond to the bromide and chloride compounds, respectively, and the numbers identify the compounds in terms of Table IV.

bromide dimers are between −1 and −3 cm^{-1} although [Cu(4-Meox)$_2$Br$_2$]$_2$ has an exchange constant of −7.6 cm^{-1}. The largest exchange for the chloride-bridged members of this family also corresponds to the TMSO compound (−8.3 cm^{-1}).

From the data presented in Table IV, it can be seen that there is no simple dependence of exchange strength upon the Cu–X–Cu′ bridging angle ϕ as has been observed previously for the planar series of copper hydroxide-bridged[1] and copper chloride-bridged[3] dimers. This can easily be seen by comparing the three copper chloride dimers in Table IV, [Cu(4-Meox)$_2$Cl$_2$]$_2$, [Cu(DMG)Cl$_2$]$_2$, and [Cu(TMSO)$_2$Cl$_2$]$_2$, all of which have bridging angles between 88 and 89.5° but whose exchange constants range from slightly ferromagnetic for the DMG dimer, to −1.3 cm^{-1} for the 4-Meox dimer and −8.3 cm^{-1} for the TMSO dimer. The typical values for the exchange of the other chloride dimers are between −1 and −3 cm^{-1} even though their bridging angles reach values as large as 100.4°.

Hatfield, Hodgson, and co-workers[4] have shown that eclisped-planar chloride dimers such as listed in Table IV have a structural dependence of exchange energy that depends on both the bridging angle ϕ and the long Cu–Cl′ distance R' within the bridging network. This relationship is evident in Figure 3, where the exchange strengths of the copper halide dimers are plotted vs. the ratio ϕ/R'; all the data points for the chlorides (plotted as solid circles) lie on a smooth curve. It is also seen in this figure that the correlation fails for the bromides (open circles). Most of the exchange energies for the bromide dimers are near −2 cm^{-1}, and there is little variation with the parameter ϕ/R'. In addition, three of the bromide dimers have exchange constants that are significantly different from the average, those being the 4-Meox dimer, the dien dimer, and the title compound, whose exchange constants are −7.6, +1.35 and −16.9 cm^{-1}, respectively.

It is significant that the largest exchange constants determined for the nonplanar dimers of Table IV are for the bromide and chloride TMSO dimers and that these are the dimers with the largest distortions away from ideal tetragonal-pyramidal geometry. The importance of such distortions upon the exchange strength has previously been noted.[25] For the compounds described in Table IV, the d($x^2 - y^2$) orbital lies in the plane determined by the four closest ligands. For the title compound, these include Br(1), Br(2), and the two oxygens from the TMSO groups. Were these atoms to lie in a plane, the magnetic orbital would have little density out of the plane and the amount of overlap onto the Br(1a) ion would be small. Consequently, the superexchange interaction between the two copper ions would be weak. This is observed for most of the compounds in Table IV. However, when the environment about the copper ion becomes distorted, the magnetic orbital becomes more strongly mixed into the bridging ligand and the magnetic interaction becomes stronger. One way of characterizing the amount of distortion present is to examine the trans X–Cu–L angle where X is the tightly bound bridging halide (Br(1) in the present case) and L is the ligand trans to X (Br(2)). This angle, labeled as δ, is 180° for the ideal tetragonal pyramid and decreases as the distortion increases toward trigonal bipyramidal. For the title compound, δ is 139.6°, the smallest value of any dimer listed in Table IV. The exchange strengths are plotted[45] vs. the distortion angle δ in Figure 4, where it is seen that the experimental values for both the chlorides and bromides lie close to a universal curve. For small distortions (values of $\delta > 160°$), the exchange constants for all compounds are approximately −2 cm^{-1} and independent of δ. Only when the distortion causes δ to become less than 160° is a noticeable effect observed on J. Despite earlier observations,[7,8] there does not appear to be any significant difference between the magnitude of the exchange constants for the chloride and bromide eclipsed dimers. It therefore appears that the dominant factor controlling the superexchange strength in eclipsed-planar copper dimers is not related to the bridging angle but instead to the amount of distortion within the copper basal plane.

No information could be obtained about the magnetic anisotropy in CuBr$_2$(TMSO)$_2$ with the magnetic measurements. Anisotropy which is weak compared to the exchange strength only influences the susceptibility at temperatures which are low compared to J/k; the antiferromagnetic nature of that exchange in the title compound caused the susceptibility to decrease exponentially toward zero and prevented the possibility of meaningful single-crystal measurements.

Summary

Discrete dimers have been shown to exist in the 1:2 phase of CuBr$_2$ and TMSO. The coordination geometry about the copper ion corresponds to a significantly distorted tetragonal pyramid with close bonds to two oxygen and two bromine atoms and a long bond to a third bromide atom. The copper atoms within the dimer interact through a pair of asymmetric Cu–Br···Cu bridges, which leads to an antiferromagnetic exchange energy J/k of −24.4 K (J = −16.9 cm). This value is the largest yet seen for this type of copper bromide dimer but can be understood as arising from the distortions present in the coordination sphere.

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates and isotropic thermal parameters (1 page); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(45) The value for the dimer [Cu(MAEP)Br$_2$]$_2$ was not plotted since this dimer is trigonal bipyramidal.