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

WAYNE E. MARSH, TAMARA L. BOWMAN, WILLIAM E. HATFIELD and DEREK J. HODGSON*

Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514, U.S.A.

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The crystal and molecular structure of the copper(II) complex bis[dibromobis(4-methyloxazole)-copper(II)], $[CuBr_2(C_4H_5NO)_2]_2$, *has been determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic space group* $P2_1/n$ *with two dimeric formula units in a cell of dimensions* $a = 8.546(4)$, $b = 13.062(5)$, $c = 11.049(6)$ Å, *and* $\beta = 96.88(4)°$. *The observed and calculated densities are 2.07 and 2.113 g* cm^{-3}, *respectively. The structure has been refined by least-squares methods to a final value of the weighted* R*-factor (on* F*) of 0.037 based on 1579 independent data with* $I \geqslant 3\sigma(I)$. *The complex is dimeric, with severely distorted tetragonal pyramidal geometry at each copper center. The four ligands in the base plane are two* trans *nitrogen atoms from the 4-methyloxazole 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 2.710(1) Å and the Cu–Cu distance is 3.626(1) Å, leading to a bridging Cu–Br–Cu angle of 87.00(3)°. The geometric distortion in the complex is evidenced by the in-plane Br(1)–Cu–Br(2) angle of only 157.15(4)°. The magnetic susceptibility of the complex has been measured as a function of temperature, and the data have been fitted to both the Van Vleck expression and (equally well) to a magnetization expression yielding* $g = 2.087$ *and a singlet-triplet separation of approximately 15.15* cm^{-1} *with the singlet as the ground state. This relatively large singlet-triplet splitting is discussed in the light of the observed structure.*

Introduction

The structural, spectroscopic, and magnetic properties of copper(II) complexes of the general formulation CuA_2X_2 [where A is a neutral unidentate donor and X is a halide] or $CuLX_2$ [where L is a bidentate neutral donor] have been the subjects of intense recent research activity. Much of the interest has arisen because of the observation of a bewildering array of structural types for these complexes, including symmetric six-coordinate chains [1–4], unsymmetric six-coordinate chains [5, 6], five-coordinate chains [7, 8], dimers with square planar [9], tetrahedral [10, 11] trigonal bipyramidal [12–15], and tetragonal pyramidal [16] geometry at copper, tetramers [17], complex polymeric aggregates [18], and simple monomers [19–22]. Consequently, it has proved difficult to predict even gross structural features in these complexes in the absence of crystallographic data.

There are some simple and valuable indicators to probable structure, however. The parent complex in the pyridine series, $Cu(py)_2X_2$, is six-coordinate [1], methyl substitution at the α-carbon atom to give $Cu(2\text{-Mepy})_2X_2$ leads to five coordination [23–25], and further substitution to give $Cu(2,3\text{-Me}_2\text{py})_2X_2$ yields four-coordinate species [19]; entirely analogous results have recently been obtained in our laboratories for the thiazole series, with six-coordinate $Cu(tz)_2X_2$ [3], five-coordinate $Cu(4\text{-Metz})_2X_2$ [16], and four-coordinate $Cu(2,4\text{-Me}_2\ tz)_2X_2$ [22].

We have been particularly focussing our attention on the dimeric species, with the aim of establishing a structure-magnetism correlation for these complexes. In view of the relative paucity of structural data for the trigonal bipyramidal species [12–15] we have concentrated on the tetragonal pyramidal systems. Our recent observation [16] that the 4-methylthiazole complex $Cu(4\text{-Metz})_2Br_2$ is a dimer of this type encouraged us to investigate the 4-methyloxazole analog, $Cu(4\text{-Meox})_2Br_2$. The synthesis, structure, and magnetic properties of this complex are described here.

Experimental

Synthesis

The ligand 4-methyloxazole (C_4H_5NO, 4-Meox), obtained from Aldrich Chemical Company, Inc., was used without further purification. Reagent grade

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*Author to whom correspondence should be addressed.

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copper(II) bromide, from J. T. Baker Chemical Co., was used directly.

The complex was prepared by the addition of 2.490 g (0.03 mol) of the ligand in 25 ml of freshly distilled methanol to a methanolic solution (30 ml) containing 2.234 g (0.01 mol) of anhydrous $CuBr_2$. The resultant dark green solution was warmed with constant stirring for 20 min, and subsequently filtered before being cooled at RT for a few minutes. The filtrate was then placed in the freezer compartment of a refrigerator, and after approximately 24 hours, dark green crystals were removed from the solution by filtration. From these, an appropriate crystal (0.25 mm X 0.31 mm X 0.13 mm) was chosen for the X-ray diffraction study.

Collection of the X-ray Data

The crystal was mounted on an Enraf-Nonius Automated X-ray Diffractometer and preliminary analysis indicated that the crystals belonged to the monoclinic system; on the basis of the observed systematic absences of $0k0$, $k = (2n + 1)$ and $h0l$, $h + k = (2n + 1)$, the crystals were assigned to the space group $P2_1/n$, a non-standard setting of $P2_1/c$ (No. 14). On the basis of a least-squares fit of the diffractometer settings of twenty-five reflections, the cell constants were determined as follows: $a = 8.546(4)$ Å, $b = 13.062(5)$ Å, $c = 11.049(6)$ Å, $\beta = 96.88(4)$; the observations were made using MoKα radiation with an assumed wavelength of 0.7093 Å. The observed density of 2.07(2) g cm^{-3}, obtained by flotation in a mixture of chloroform and bromoform, agreed with the calculated density of 2.113 g cm^{-3} for four monomeric formula units in the cell. Consequently, dimeric species in the cell are constrained to lie on a crystallographic inversion center.

Diffraction data were collected from a prismatic crystal on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and using MoKα radiation. Peaks were scanned in an ω–θ mode. A unique data set having 2θ(Mo) $\leqslant 55°$ was collected. A total of 2927 reflections was recorded; the intensities and centering of three standard reflections were monitored periodically, and the crystal was automatically re-centered 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 MoKα radiation is 87.5 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 0.73, with an average correction of 0.86. Of the 2927 data, 1579 had $I \geqslant 3\sigma(I)$; only these data were used in the subsequent refinement of the structure.

TABLE I. Positional Parameters in $[Cu(4\text{-}Meox)_2Br_2]_2$.

Atom	X	Y	Z
Br1	0.29631(9)	0.06084(6)	–0.00247(7)
Br2	0.38196(10)	–0.30167(6)	–0.08401(7)
Cu	0.3978(1)	–0.11945(7)	–0.03805(8)
O1	0.4425(6)	–0.1851(4)	0.3291(4)
O1′	0.4555(9)	–0.0671(5)	–0.3958(5)
N3	0.3831(6)	–0.1508(4)	0.1349(5)
N3′	0.3830(8)	–0.0894(4)	–0.2142(5)
C2	0.4923(9)	–0.1583(6)	0.2249(6)
C4	0.2445(9)	–0.1744(5)	0.1832(6)
C5	0.2829(10)	–0.1940(6)	0.3004(7)
C6	0.0902(9)	–0.1754(6)	0.1088(7)
C2′	0.4974(12)	–0.0833(6)	–0.2790(7)
C4′	0.2481(12)	–0.0760(6)	–0.2960(7)
C5′	0.2973(15)	–0.0614(7)	–0.4044(8)
C6′	0.0936(13)	–0.0784(7)	–0.2612(8)
H2	0.6028	–0.1453	0.2160
H5	0.2091	–0.2124	0.3573
H6A	0.0064	–0.1927	0.1558
H6B	0.0644	–0.1086	0.0726
H6C	0.0866	–0.2233	0.0423
H2′	0.6111	–0.0906	–0.2450
H5′	0.2276	–0.0469	–0.4800
H6′A	0.0078	–0.0683	–0.3273
H6′B	0.0654	–0.1442	–0.2234
H6′C	0.0731	–0.0271	–0.1995

Solution and Refinement

The solution of the structure was effected by the use of a three-dimensional Patterson function to determine the positions of the copper and two bromine atoms. Isotropic least-squares refinement of these positions yielded values of the usual agreement factors $R_1 = \Sigma \| Fo - Fc \| / \Sigma |Fo|$ and $R_2 = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w(Fo)^2]^{1/2}$ of 0.196 and 0.262, respectively. All least-squares analyses in this work were carried out on F, the function minimized being $\Sigma w(|Fo|-|Fc|)^2$. The weights, w, were initially given the value of unity, but were later replaced by a weighting scheme of the type [26] $w = 4Fo^2/\sigma^2(Fo^2)$, where $\sigma(Fo^2)$ is given by $\sigma(Fo^2) = [\sigma^2(I) + p^2I^2]^{1/2}$ and p is assigned the value 0.01.

The positions of the carbon, nitrogen, and oxygen atoms were determined from a subsequent difference Fourier synthesis, and isotropic least-squares refinement yielded $R_1 = 0.109$ and $R_2 = 0.121$; anisotropic refinement reduced R_1 to 0.080 and R_2 to 0.087. After application of the absorption correction, several of the hydrogen atoms were located in a difference Fourier map and the positions of the other hydrogen atoms were calculated based on trigonal or tetrahedral geometry as appropriate, with the C–H distances assigned as 0.95 Å. The hydrogen atoms were assigned fixed isotropic thermal parameters of 5.0 Å^2, and their parameters were included in sub-

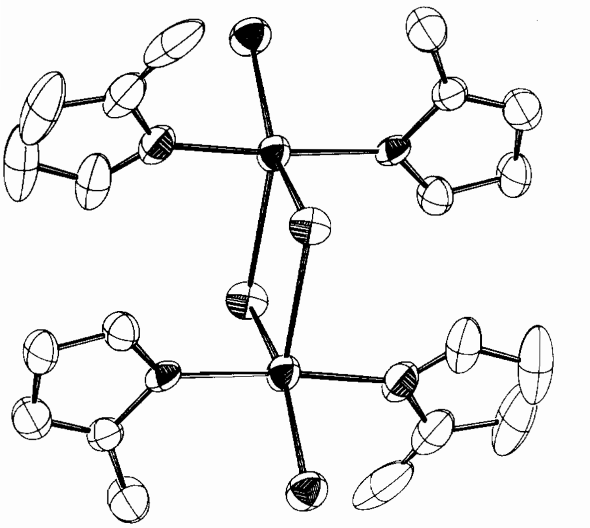

Fig. 1. View of one dimeric unit in $[Cu(4\text{-}Meox)_2Br_2]_2$. Thermal ellipsoids in this and the subsequent figure are drawn at the 40% probability level, but hydrogen atoms are omitted for clarity.

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

Atoms^a	Distance (A)	Atoms	Distance (A)
Cu–Br(1)	2.556(1)	Cu–Br(2)	2.434(1)
Cu–Br(1)″	2.710(1)	Cu–Cu″	3.626(1)
Cu–N(3)	1.973(4)	Cu–N(3)′	1.974(5)
O(1)–C(2)	1.321(6)	O(1)′–C(2)′	1.315(8)
C(2)–N(3)	1.283(7)	C(2)′–N(3)′	1.282(8)
N(3)–C(4)	1.391(7)	N(3)′–C(4)′	1.388(8)
C(4)–C(5)	1.322(8)	C(4)′–C(5)′	1.330(10)
C(5)–O(1)	1.368(7)	C(5)′–O(1)′	1.346(11)
C(4)–C(6)	1.468(8)	C(4)′–C(6)′	1.420(10)

^{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.

sequent least-squares calculations but were not refined. In the final cycle of least-squares refinement, there were 1579 observations and 136 variables, and the values of R_1 and R_2 were 0.043 and 0.037, respectively. The final difference Fourier included several peaks in the vicinity of the bromine atoms, which presumably are indicative of some minor error in our absorption correction; there were no other meaningful features in this map. The positional parameters derived from the last cycle are presented in Table I. A compilation of anisotropic thermal parameters and of observed and calculated structure amplitudes is available as supplementary material [27].

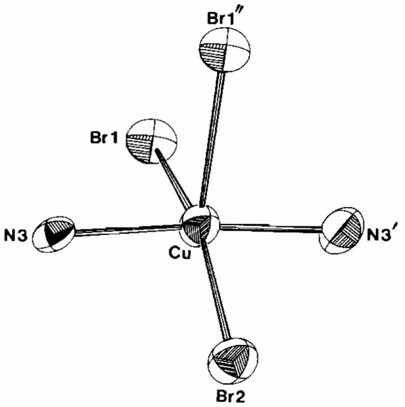

Fig. 2. View of the coordination around a single copper center in $[Cu(4\text{-}Meox)_2Br_2]_2$.

Collection of Magnetic Data

Magnetic susceptibility data 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 GaAs diode by observing the voltage on Fluke 8502 A 6.5-place digital multimeter; further details of the apparatus and temperature measurement have been given elsewhere [28]. A finely ground polycrystalline sample of approximately 200 mg was packed in a precision milled Lucite sample holder. The data were corrected for the diamagnetism of the Lucite holder and for the underlying diamagnetism of the constituent atoms using Pascal's constants [29]. A value of 60×10^{-6} cgsu was assumed for the temperature-independent paramagnetism (TIP) of copper [28].

Description of the Structure

The complex consists of dimeric $[Cu(4\text{-}Meox)_2Br_2]_2$ units which are well separated from each other. A view of the dimeric unit is given in Fig. 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 Fig. 2, and from an examination of Tables II and III, the geometry at each copper(II) center is a severely distorted tetragonal pyramid, the four basal ligands being two *trans*-nitrogen atoms from the 4-Meox 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. As in all distorted five-coordinate complexes,

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

Atoms	Angle (°)	Atoms	Angle (°)
Br(1)–Cu–Br(2)	157.15(4)	Br(1)–Cu–Br(1)″	93.00(3)
Br(1)–Cu–N(3)	88.9(1)	Br(1)–Cu–N(3)′	89.2(1)
Br(2)–Cu–N(3)	89.4(1)	Br(2)–Cu–N(3)′	89.6(1)
Br(2)–Cu–Br(1)″	109.85(3)	N(3)–Cu–N(3)′	172.7(2)
Br(1)″–Cu–N(3)	94.1(1)	Br(1)″–Cu–N(3)′	93.0(2)
Cu–N(3)–C(2)	129.9(4)	Cu–N(3)′–C(2)′	126.9(5)
Cu–N(3)–C(4)	125.0(4)	Cu–N(3)′–C(4)′	128.1(5)
C(2)–N(3)–C(4)	105.1(5)	C(2)′–N(3)′–C(4)′	104.9(6)
C(2)–O(1)–C(5)	103.7(5)	C(2)′–O(1)′–C(5)′	103.4(6)
O(1)–C(2)–N(3)	114.5(5)	O(1)′–C(2)′–N(3)′	115.0(7)
N(3)–C(4)–C(5)	107.2(5)	N(3)′–C(4)′–C(5)′	106.1(8)
N(3)–C(4)–C(6)	122.5(5)	N(3)′–C(4)′–C(6)′	123.2(6)
C(5)–C(4)–C(6)	130.4(6)	C(5)′–C(4)′–C(6)′	130.7(8)
O(1)–C(5)–C(4)	109.6(5)	O(1)′–C(5)′–C(4)′	110.6(7)
Cu–Br(1)–Cu″	87.00(3)		

the present structure could alternatively be viewed as a distorted trigonal bipyramid; in this model, the nitrogen atoms are axial and the three bromide ligands equatorial. This trigonal bipyramidal model, however, requires far greater distortion; for example, the dihedral angle between the planes formed by Cu, N(3), N(3)′, Br(1) and by Cu, N(3), N(3)′, Br(2), which would be 60° in an idealized trigonal bipyramid, is only 19.1° in this structure. The distortions from tetragonal pyramidal geometry are considerable, but are less severe than these. Thus, the *trans* Br(1)–Cu–Br(2) angle is 157.15(4)° rather than the expected value of greater than 170°. Alternatively, the four basal ligands deviate markedly from coplanarity, with Br(1) and Br(2) 0.180(1) and 0.188(1) Å, respectively, below the plane while N(3) and N(3)′ are 0.185(6) and 0.184(7) Å, respectively, above it. As is usual in tetragonal pyramidal complexes [16], the copper atom lies above this plane [in this case by 0.309(1) Å] in the direction of the apical atom, Br(1)″. This highly distorted geometry is in contrast to that of the thiazole analog [16], $[Cu(4\text{-}Metz)_2Br_2]_2$, in which the geometry is very close to that of an idealized tetragonal pyramid.

The Cu–N distances of 1.973(4) and 1.974(5) Å are comparable to the values of 1.978(5) and 1.989(5) Å in the 4-methylthiazole analog and to values reported for related complexes. The basal Cu–Br distances are 2.434(1) and 2.556(1) Å with the distance to the bridging atom [Br(1)] appreciably the longer. The terminal Cu–Br(2) distance of 2.434(1) Å is evidently slightly longer than the values of 2.372(1)–2.420(1) Å found for other bromo-bridged dimers of this type [14, 16, 24, 30–32] but is unremarkable. Similarly, the basal Cu–Br(1) distance of 2.556(1) Å is larger than the range of 2.422(5)–2.492(1) Å in these complexes.

The geometry of the bridging unit is compared with that of all other related dimers in Table IV. The axial Cu–Br(1)″ bond length of 2.710(1) Å is significantly shorter than those in other tetragonal pyramidal dimers, which range from 2.868(2) to 3.872(5) Å, and is also shorter than the bridging Cu–Br bond length of 2.802(4) Å in the only reported trigonal bipyramidal dimer known to us [14]. The bridging Cu–Br(1)–Cu′ angle of 87.00(3)° is, however, within the range previously observed, as is the Cu–Cu′ separation of 3.626(1) Å.

The two independent oxazole rings in the structure are planar, with no atom deviating from the five-atom least-squares plane by more than 0.005(8) Å in one ring and 0.007(9) Å in the other. In both cases, the copper atom is displaced from the plane by approximately 0.07 Å while the methyl carbon atoms are only approximately 0.02 Å out of the plane. The two oxazole planes are inclined at an angle of 10.7° to each other. The bond lengths and angles within the oxazole ligands appear to be normal, the C(2)–N(3) and C(4)–C(5) distances being consistent with their formal double bond character.

Magnetic Properties

The magnetic susceptibility of a powdered sample of the complex is plotted as a function of temper-

TABLE IV. Structural and Magnetic Properties of Dibromobridged Copper(II) Dimers.

Complex[a]	Geometry[a] at Cu	Cu–Br′ (A) out-of-plane (R)	Cu–Cu′ (A)	Cu–Br′–Cu (°) (ϕ)	ϕ/R	J (cm^{-1})	Ref.
$[Cu(DMG)Br_2]_2$	TP	2.883(1)	3.599(1)	85.59(4)	29.7	−1.5	32, 33
$[Cu(tmen)Br_2]_2$	TP	3.20	4.20	95.6(5)	29.9	−2.0	30, 34
$[Cu(dmen)Br_2]_2$	TP	2.868(2)	3.570(3)	83.71(5)	29.2	−1.0	31, 34
$[Cu(2\text{-pic})_2Br_2]_2$	TP	3.872(5)	4.926(6)	100.4(1)	25.9	−2.5	24, 34
$[Cu(4\text{-Metz})_2Br_2]_2$	TP	3.033(1)	4.063(2)	94.16(3)	31.0	−1.2	16
$[Cu(4\text{-Meox})_2Br_2]_2$	Distorted TP	2.710(1)	3.626(1)	87.00(3)	32.1	−7.6	This work
$[Cu(MAEP)Br_2]_2$	TBP	2.802(4)	3.803(4)	92.14(9)	32.9	−2.1	14

[a] Abbreviations: DMG = dimethylglyoxime; tmen = N,N,N′,N′-tetramethylethylenediamine; dmen = N,N,-dimethylethylenediamine; 2-pic = 2-methylpyridine; 4-Metz = 4-methylthiazole; 4-Meox = 4-methyloxazole; MAEP = 2-(2-methylaminoethyl)pyridine; TP = tetragonal pyramid; TBP = trigonal bipyramid.

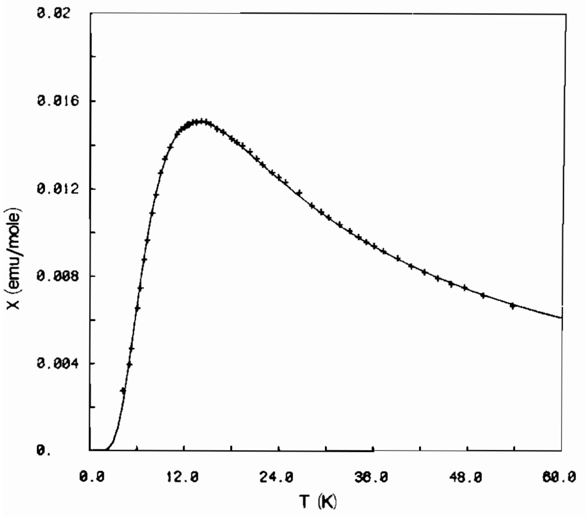

Fig. 3. The temperature dependence of the magnetic susceptibility of $[Cu(4\text{-Meox})_2Br_2]_2$. The solid line represents the best fit to the Van Vleck expression (see text) with g = 2.086 and 2J = −15.12 cm^{-1}.

ature in Fig. 3. As can be seen in the Figure, the susceptibility data exhibit a broad maximum near 14 K which is indicative of antiferromagnetic coupling between the two copper(II) centers in the dimeric unit. The susceptibility data were fitted to the Van Vleck expression for exchange-coupled S = ½ dimers

$$\chi m = \frac{Ng^2\mu_B{}^2}{3kT}\,[1 + 1/3\exp(-2J/kT)]^{-1} \qquad (1)$$

with the parameters g and J as variables using a SIMPLEX fitting routine described elsewhere [28]. The result of this fit, which is displayed as the solid line in Fig. 3, yields values of g = 2.086 and 2J = −15.12 cm^{-1}. In order to check the validity of these results, the data were also fitted to the magnetization expression [35]

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

where the exchange Hamiltonian is

$$Hex = -2J\hat{S}_1\cdot\hat{S}_2 + g\mu_BH\hat{S} \qquad (3)$$

and $\hat{S}$ is the total spin (*i.e.* $\hat{S} = \hat{S}_1 + \hat{S}_2$). The susceptibility data were fitted to the expression (2) using the relationship

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

where H is 10,000 G in all cases (*vide supra*), with g and J again varied in the SIMPLEX procedure. The results in this case were g = 2.087 and 2J = −15.17 cm^{-1}, which are in remarkable agreement with the values obtained from expression (1). Hence, it is apparent that in this complex the first triplet state lies approximately 15.15 cm^{-1} higher in energy than the ground state singlet.

An examination of Table IV, in which the magnetic properties of all known dimers of this kind are tabulated, reveals that |J| in the present complex is far greater than in the other dimers. The cause of this distinction undoubtedly lies in the structural distortions present in the complex. In an idealized tetragonal pyramidal dimer, the unpaired spin is localized in $dx^2 - y^2$ orbitals which overlap extremely weakly with bridge orbitals, while a distortion towards trigonal bipyramidal geometry leads to enhanced interaction with the orbitals on the bridging bromide. It should be noted that further distortion of the type observed here leads eventually to a trigonal bipyramidal structure in which the bridging framework is in the equatorial planes of both copper centers. This is entirely different from the axial-equatorial structure of the trigonal bipyramidal complex listed in Table IV, but is reminiscent of the structure [15] of the dichloro-bridged benzotriazole complex $[Cu(BTAH)_2Cl_2]_2 \cdot H_2O$. In the case of four-coordinate in-plane halogen-bridged dimers, Willett and coworkers [9] have also observed much larger values of |J| than those listed in Table IV.

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