Synthesis, Crystal Structure, Magnetic Properties, and EPR of Cu(bp3ca)Br_2·H_2O (bp3ca = 2,2′-Bipyridine-3,3′-dicarboxylic Acid). Ferromagnetic Interactions via Unsymmetrical Bromide Bridges

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Cu(bp3ca)Br_2·H_2O crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.622(2)$ Å, $b = 10.832(2)$ Å, $c = 14.684(2)$ Å, $\alpha = 106.13(1)°$, $\beta = 105.91(1)°$, $\gamma = 102.74(1)°$, and $Z = 2$. The asymmetric unit consists of a bis μ-bromo unsymmetrically dibridged dimer which is further linked to its inversion-related partner to form a dimer of dimers. Weak intertetramer contacts are also observed. The magnetic data for this compound were fit to a linear tetramer model to give $J_1 = J_3 = -8.69 \times 10^{-3}$ cm^{-1}, $J_2 = 91.52$ cm^{-1}, and the intertetramer interaction $J' = -1.187$ cm^{-1} with $g = 1.93$. EPR data are consistent with the magnetic data. This system is compared to its previously reported chloro counterpart, which differs markedly in both structure and magnetic properties.

Introduction

Magnetostructural correlations in copper(II) complexes have attracted considerable attention over decades. The flexibility of the coordination sphere around Cu(II), in combination with steric and crystal packing forces, leads to its tremendous structural diversity. Small changes in structure can have far-reaching effects on the magnetic properties of these systems.[1]

While dinuclear systems are fairly well documented,[2] clusters of higher nuclearity provide greater variety in terms of structural and magnetic properties. Several tetranuclear complexes of Cu(II) have been studied in recent times. These include tetrahedral,[3] cubane-type,[4] ladder-type,[5] square,[6] face-to-face dimers,[7] and linear clusters.[8] We report here the structure and magnetic properties of Cu(bp3ca)Br_2·H_2O (**1**) (bp3ca = 2,2′-bipyridine-3,3′-dicarboxylic acid), a bis μ-bromo bridged system forming a steplike dimer of dimers. The chloro analog, Cu(bp3ca)Cl_2·H_2O (**2**), has been reported previously.[9] Although both systems have similar CuN_2X_2 chromophores, the packing in **1** differs greatly from that observed in **2**. The magnetic behavior of these two complexes differs markedly from each other; **1** contains strongly ferromagnetically coupled dimers with weaker antiferromagnetic coupling also observed in the lattice, while **2** shows weak interactions through three different pathways.[9b] The complexes of bp3ca provide an example of significant magnetic changes occurring because of electronic and structural changes caused by the replacement of Cl with Br.

Experimental Section

Synthesis. The ligand bp3ca was synthesized by a reported procedure.[10] $CuBr_2$ (0.301 g, 1.35 mmol) and bp3ca (0.329 g, 1.35 mmol) were dissolved in 0.5 N HBr to give brown crystals of **1** after about two weeks. Yield: 0.412 g, 63.2%. Anal. Calcd for $CuC_{12}H_{10}N_2Br_2O_5$: C, 29.68; H, 2.08; N, 5.77. Found: C, 29.85; H, 1.975; N, 5.696. IR (KBr disc, cm^{-1}): 3422, 3076, 1703, 1581, 1412, 1282, 1093, 758

X-ray Crystallography. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer, using Mo Kα radiation. A single crystal of approximate dimensions 0.30 × 0.25 × 0.15 mm was used. A semiempirical ψ-scan absorption correction was applied. The structure was solved by direct methods using SHELXS86[11a] and refined by least-squares methods using SHELXL93.[11b] All non-hydrogen atoms were refined anisotropically. Some disorder was observed around one of the water molecules, OW2, which was refined with a fractional site occupation factor of 0.79. It was not possible to locate its H atoms or refine them in calculated positions. Bond length constraints were applied to the O−H and H−H distances of the other water molecule, OW1. Ring hydrogens were located at calculated positions and allowed to ride on the atoms to which they are bonded. The refinement converged to $R1 = 0.0369$ and $wR2 = 0.0895$ values for reflections with $I > 2\sigma(I)$. Crystal data are given in Table 1, while atomic coordinates and important bond lengths and angles are listed in Tables 2 and 3, respectively.

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Table 1. Crystallographic Data for **1**

formula	$C_{24}H_{20}Br_4Cu_2N_4O_{10}$
formula weight	971.14
a	10.622(2) Å
b	10.832(2) Å
c	14.684(2) Å
α	106.13(1)°
β	105.91(1)°
γ	102.74(1)°
V	1478.1(5) Å^3
Z	2
space group	$P\bar{1}$ (No. 2)
T	20 °C
λ	0.710 73 Å
ρ(obsd)	2.18 g cm^{-3}
ρ(calcd)	2.174 g cm^{-3}
μ	69.07 cm^{-1}
$R1(F_o^2)$[a]	0.0369
$wR2(F_o^2)$[b]	0.0743

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum(wF_o^4)]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0238P)^2 + 7.43P]$, $P = (F_o^2 + 2F_c^2)/3$.

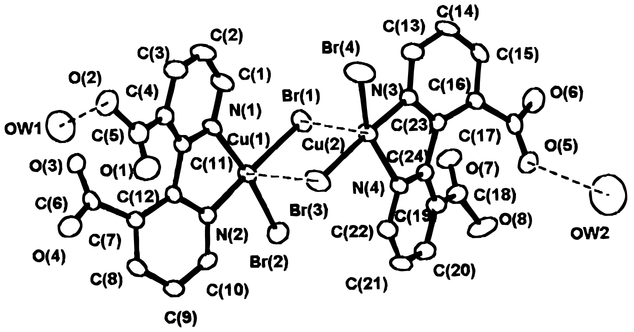

Figure 1. Molecular structure of Cu(bp3ca)Br$_2$·H$_2$O (**1**). Atoms are represented by thermal vibration ellipsoids at 50% probability level.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **1**[a]

atom	x	y	z	U(eq)[b]
Cu(1)	748(1)	594(1)	1436(1)	30(1)
Cu(2)	3487(1)	−41(1)	3441(1)	29(1)
Br(1)	3073(1)	633(1)	1655(1)	39(1)
Br(2)	−64(1)	−1702(1)	275(1)	39(1)
Br(3)	1293(1)	83(1)	3538(1)	46(1)
Br(4)	4663(1)	1974(1)	4913(1)	53(1)
N(1)	1212(4)	2581(4)	2265(3)	27(1)
N(2)	1099(4)	641(4)	1543(3)	27(1)
N(3)	5217(4)	−293(4)	3216(3)	25(1)
N(4)	2809(4)	−2071(4)	2614(3)	25(1)
O(1)	−1407(5)	3856(4)	3846(3)	47(1)
O(2)	−346(5)	5942(4)	3938(3)	47(1)
O(3)	−2026(4)	4331(4)	1730(3)	35(1)
O(4)	−3907(4)	3385(4)	2004(4)	51(1)
O(5)	5696(4)	−4245(4)	2522(3)	40(1)
O(6)	7545(5)	−3320(4)	2198(4)	48(1)
O(7)	4863(4)	−3519(4)	606(3)	36(1)
O(8)	3626(5)	−5597(4)	405(4)	50(1)
C(1)	2500(6)	3452(6)	2700(5)	41(2)
C(2)	2823(6)	4722(6)	3378(5)	46(2)
C(3)	1816(6)	5092(6)	3677(5)	40(2)
C(4)	460(6)	4214(5)	3247(4)	30(1)
C(5)	−552(6)	4626(6)	3696(4)	33(1)
C(6)	−2787(5)	3371(6)	1827(4)	30(1)
C(7)	−2513(5)	2054(5)	1690(4)	25(1)
C(8)	−3680(6)	900(6)	1248(4)	31(1)
C(9)	−3541(6)	−362(5)	975(4)	31(1)
C(10)	−2243(6)	−448(5)	1096(4)	32(1)
C(11)	173(5)	2962(5)	2495(4)	24(1)
C(12)	−1205(5)	1892(5)	1891(4)	22(1)
C(13)	6425(6)	707(6)	3647(5)	35(1)
C(14)	7653(6)	488(6)	3693(5)	37(1)
C(15)	7639(6)	−819(6)	3301(4)	32(1)
C(16)	6388(5)	−1876(5)	2820(4)	25(1)
C(17)	6509(6)	−3256(6)	2486(4)	30(1)
C(18)	3998(6)	−4267(5)	782(4)	31(1)
C(19)	3203(6)	−3761(5)	1412(4)	28(1)
C(20)	1831(6)	−4571(6)	1092(4)	33(1)
C(21)	974(6)	−4116(6)	1549(5)	36(1)
C(22)	1485(6)	−2844(6)	2282(4)	33(1)
C(23)	5156(5)	−1577(5)	2747(4)	22(1)
C(24)	3698(5)	−2530(5)	2219(4)	23(1)
OW1	1977(6)	3171(6)	5234(5)	74(2)
OW2(.79)	5856(12)	4291(11)	4054(9)	135(4)

[a] The site occupation factors of disordered sites are given after the respective atom labels. [b] U(eq) is defined as one third of the trace of the orthogonalized **U***ij* tensor.

Physical Measurements. Variable-temperature magnetic susceptibility measurements were obtained for a powdered sample of **1** on a Quantum Design MPMS SQUID susceptometer in the temperature range 2−300 K. Diamagnetic corrections were applied by using Pascal's constants. Least-squares fittings of the magnetic data were performed by using a program reported recently.[12]

EPR spectra were recorded on polycrystalline and single-crystal samples at 300 and 123 K using a JEOL-FE3X spectrometer operating at X-band frequency. Q-band measurements were carried out on a Varian E-112 spectrometer.

Results and Discussion

Crystal Structure. 1 crystallizes in a triclinic cell with space group $P\bar{1}$. The asymmetric unit consists of an unsymmetrically bis μ-bromo bridged dimer (Figure 1). This dimer is linked to its inversion-related counterpart through a second bis μ-bromo bridge resulting in the tetrameric cluster of the unit cell. Very weak intertetrameric contacts lead to a chainlike arrangement (Figure 2).

The coordination sphere around Cu(1) can be described as a 4 + 2 tetragonally elongated octahedron. The equatorial plane including Cu(1), N(1), N(2), Br(1), and Br(2) is very slightly distorted, the root-mean-square deviation from a least-squares plane containing these atoms being 0.139 Å. The axial coordination involves Br(3), (Cu(1)−Br(3) = 3.207(1) Å) and Br(2)′ (′ = −x, −y, −z; Cu(1)−Br(2)′ = 3.055(1) Å). The in-plane and axial trans angles show some deviation from 180° (171.5(1)° for Br(2)−Cu(1)−N(1), 168.9(1)° for Br(1)−Cu(1)−N(2), and 165.5(3)° for Br(3)−Cu(1)−Br(2)′). The 0.75 tetragonality, T, of Cu(1) can be considered as a measure of the distortion of the complex from regular octahedral geometry.[13]

The geometry around Cu(2), on the other hand, is best described as square pyramidal or 4 + 1. The equatorial plane containing Cu(2), N(3), N(4), Br(3), and Br(4) is distorted, the root-mean-square deviation from a least-square planes containing these atoms being 0.222 Å. Br(1) coordinates weakly to Cu(2) (Cu(2)−Br(1) = 2.859(1) Å) almost perpendicularly to the equatorial plane, with 7.35° deviation to the plane normal. The in-plane trans angles are 174.1(1)° for Br(3)−Cu(2)−N(3) and 156.7(1)° for Br(4)−Cu(2)−N(4). This type of geometry, with one angle closer to 180° than the other one is described as "folded" and is quite commonly observed in 5-coordinate systems.[14] Cu(2) also shows a very weak coordination to Br(4)″ (″ = −x + 1, −y, −z + 1; Cu(2)−Br(4)″ = 4.014(1) Å).

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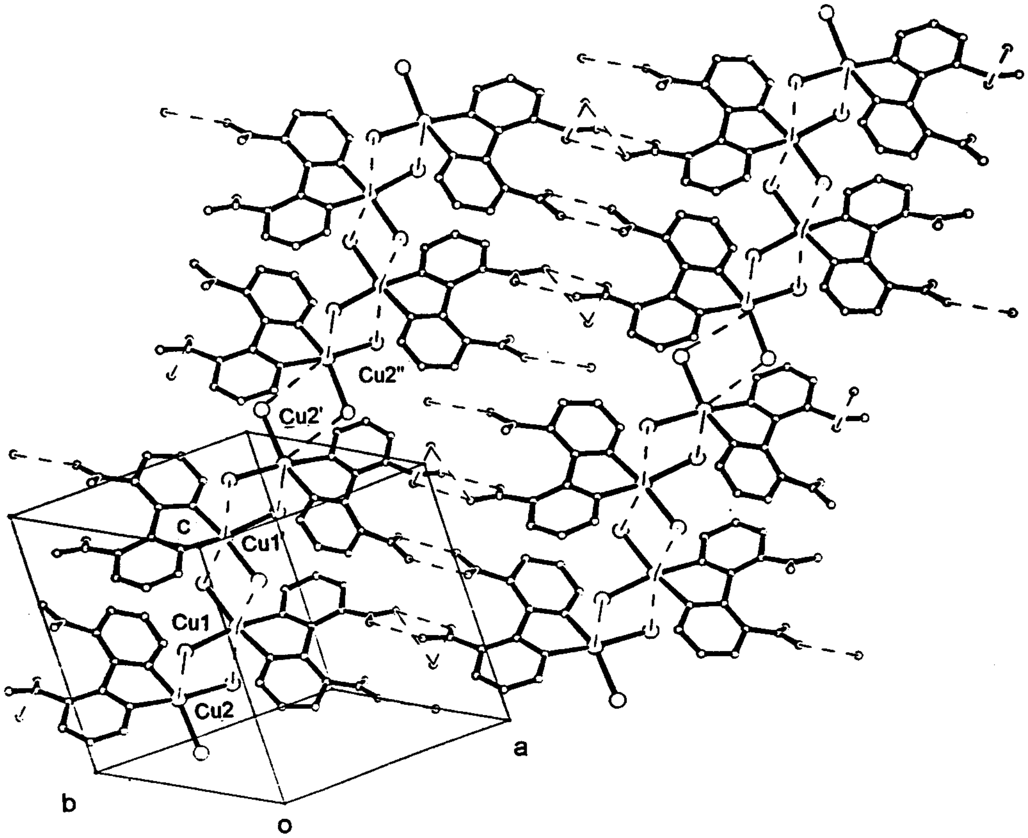

Figure 2. Packing diagram of **1**, showing intermolecular contacts including hydrogen bonding. (′ = −*x*, −*y*, −*z*; ″ = −*x* + 1, −*y*, −*z* + 1).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

	Bond Distances		
Cu(1)−N(2)	2.020(4)	Cu(1)−N(1)	2.026(4)
Cu(1)−Br(1)	2.391(1)	Cu(1)−Br(2)	2.394(1)
Cu(1)−Br(2)#1[a]	3.055(1)	Cu(1)−Br(3)	3.207(1)
Cu(2)−N(3)	2.017(4)	Cu(2)−N(4)	2.041(4)
Cu(2)−Br(4)	2.385(1)	Cu(2)−Br(3)	2.4032(9)
Cu(2)−Br(1)	2.859(1)	Cu(2)−Br(4)#2[a]	4.014(1)
	Bond Angles		
N(2)−Cu(1)−N(1)	79.0(2)	N(2)−Cu(1)−Br(1)	168.9(1)
N(1)−Cu(1)−Br(1)	96.5(1)	N(2)−Cu(1)−Br(2)	96.1(1)
N(1)−Cu(1)−Br(2)	171.5(1)	Br(1)−Cu(1)−Br(2)	89.45(3)
N(2)−Cu(1)−Br(2)#1	87.4(1)	N(1)−Cu(1)−Br(2)#1	80.2(1)
Br(1)−Cu(1)−Br(2)#1	101.97(3)	Br(2)−Cu(1)−Br(2)#1	92.72(3)
N(2)−Cu(1)−Br(3)	83.9(1)	N(1)−Cu(1)−Br(3)	86.8(1)
Br(1)−Cu(1)−Br(3)	85.71(3)	Br(2)−Cu(1)−Br(3)	99.76(3)
Br(2)#1−Cu(1)−Br(3)	165.46(3)	N(3)−Cu(2)−N(4)	79.1(2)
N(3)−Cu(2)−Br(4)	95.2(1)	N(4)−Cu(2)−Br(4)	156.7(1)
N(3)−Cu(2)−Br(3)	174.1(1)	N(4)−Cu(2)−Br(3)	96.0(1)
Br(4)−Cu(2)−Br(3)	90.63(3)	N(3)−Cu(2)−Br(1)	83.1(1)
N(4)−Cu(2)−Br(1)	92.2(1)	Br(4)−Cu(2)−Br(1)	109.73(4)
Br(3)−Cu(2)−Br(1)	93.78(3)	N(3)−Cu(2)−Br(4)#2	65.9(1)
N(4)−Cu(2)−Br(4)#2	70.2(1)	Br(4)−Cu(2)−Br(4)#2	86.77(3)
Br(3)−Cu(2)−Br(4)#2	115.73(3)	Br(1)−Cu(2)−Br(4)#2	146.42(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, −*x*, −*y*, −*z*; #2, −*x* + 1, −*y*, −*z* + 1.

This copper is better described as a 5-coordinate, 4 + 1 center, rather than a 6-coordinate 4 + 1 + 1 system because, apart from the weakness of the sixth contact, the axial trans angle, Br(1)−Cu(2)−Br(4)″ is highly distorted at 146.42(2)°.

Cu(1) and Cu(2) are unsymmetrically bridged by Br(1) and Br(3) with bridging angles of 94.32(4) and 85.76(4)°, respectively. Two inversion-related dimers form a tetramer in which Cu(1) and Cu(1)′ are unsymmetrically bridged through Br(2) and Br(2)′ at an angle of 87.28(4)°. Cu(1) and Cu(2) are 3.863(1) Å apart, while Cu(1) and Cu(1)′ are 3.791(1) Å apart. The weak Cu(2)−Br(4)″ contact links the tetramers together (Cu(2)···Cu(2)″ = 4.784(1) Å) with a bridging angle of 93.24(4)° to form chains in the lattice (Figure 2).

Two uncoordinated lattice water molecules are present in the asymmetric unit. Hydrogen bonding between these water molecules and the carboxylic acid groups stabilizes the structure. The strongest among these is observed between HO2 and OW1 with an O···H distance of 1.57(9) Å, the H-bond angle, O(2)−HO2−OW1, being 168(7)°. Strong H-bonds are also observed between the carboxylic acid groups on adjacent chains in the lattice. H-bonds occur between O(7) and HO8, the distance between them being 1.61(1) Å and the O(8)−HO8−O(7) angle being 174(7)°. O(3) and HO6, at a distance of 1.61(4) Å, the O(6)−HO(6)−O(3) angle being 167(7)°, also form fairly strong H-bonds. These H-bonds, which form hexagonal motifs as observed in acetic acid dimers,[15] link parallel chains into a two-dimensional network (Figure 2).

The chromophore of the chloro analog, **2**,[9] is similar to **1** in that the copper ion is coordinated to two Cl and two N atoms from the ligand. However, **2**, which crystallizes in an orthorhombic cell with space group *Pbca*, packs in a very different fashion. The asymmetric unit contains a single $Cu(bp3ca)Cl_2$ unit, the geometry around Cu being 4 + 2. Units related by the inversion center are linked into dimers by a bis μ-chloro bridge corresponding to the fifth position of the "octahedron", the sixth position being occupied by an oxygen atom from a neighboring carboxylic acid group.

Magnetic Susceptibility. Variable-temperature magnetic susceptibility measurements were carried out on a polycrystalline sample of **1**. While the magnetic susceptibility (χ) increases with decreasing temperature, μ_{eff} (or χT) increases from 300 to ~60 K and then decreases to 2 K (Figure 3). This indicates that ferromagnetic exchanges dominate the magnetic behavior

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[15] Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991; p 96.

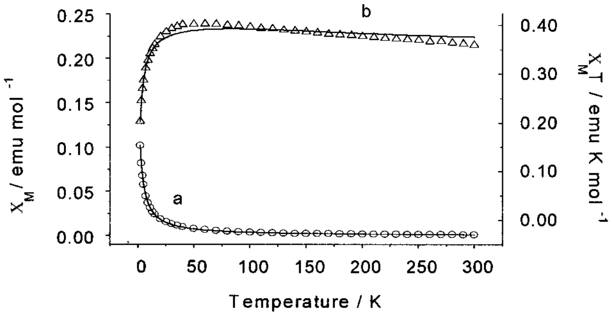

Figure 3. Variation of (a) molar magnetic susceptibility χ_M and (b) $\chi_M T$ with temperature for **1**. The theoretical curves are calculated based on the Hamiltonian given in the text.

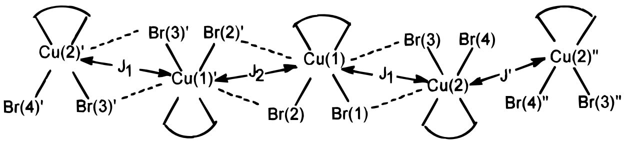

Figure 4. Schematic representation of the magnetic coupling model in **1**. Relevant bridging distances (Å) and angles (deg): Cu(1)−Br(2)′ = 3.055(1), Cu(1)−Br(2)−Cu(1)′ = 87.28(4); Cu(1)−Br(3) = 3.207(2), Cu(2)−Br(1) = 2.859(1), Cu(1)−Br(3)−Cu(2) = 85.76(4), Cu(1)−Br(1)−Cu(2) = 94.32(4); Cu(2)−Br(4)″ = 4.014(2), Cu(2)−Br(4)″−Cu(2)″ = 93.24(4) (′ = $-x$, $-y$, $-z$; ″ = $-x + 1$, $-y$, $-z + 1$).

at higher temperatures, while antiferromagnetic interactions seem to dominate at lower temperatures.

The data have been fitted to a dimer model using the Bleany−Bower's equation[16] to give a strongly ferromagnetic J value of 104.2 cm^{-1} and an interdimer antiferromagnetic J of −1.17 cm^{-1}. Although the fit was reasonable with a residual,[12] $R = 5.7 \times 10^{-4}$, the g-value for the fit was 1.829, which is too small for Cu(II) complexes of this type. The data were also fit to a linear tetramer[8,17] model with better results (Figure 3) by employing the following Hamiltonian:

$$H = -2[J_1 S_1 \cdot S_2 + J_2 S_2 \cdot S_3 + J_3 S_3 \cdot S_4]$$

Because of the inversion symmetry within the tetramer, $J_1 = J_3$ (Figure 4). The best fit ($R = 6.5 \times 10^{-5}$) gave a strongly ferromagnetic J_2 value (91.52 cm^{-1}), while J_1 was almost negligible (-8.69×10^{-3} cm^{-1}). Intertetrameric interactions were included in the mean field approximation,[18] affording $J' = -1.187$ cm^{-1}. The g-value (1.93) resulting from this fit was once again abnormally low, but g-values of this magnitude have been reported for some systems.[19] The low g-value and the poorness of the fit at higher temperatures (Figure 3b) result probably from the use of a single g-value for two structurally dissimilar copper ions. The g-value was strongly correlated to J_2. Fixing the g at 1.97 afforded $J_2 \approx 47$ cm^{-1}, while a g of 1.98 afforded $J_2 \approx 35$ cm^{-1}, both with reasonably good least-squares fits ($R \approx 3 \times 10^{-4}$). Thus the magnitude of J_2 is suspect, although one can be certain of its ferromagnetic nature. Such correlations between parameters have been previously observed for some Cu(II) complexes.[8b]

The magnetic behavior of Cu(II) complexes as a function of various structural parameters has drawn the attention of several workers.[1,20,21] Hay *et al.*[22] have carried out theoretical calculations on the singlet−triplet gap for various systems as a function of the Cu−X−Cu bridging angle, ϕ. They have observed that angles close to 90° or less favor minimum overlap, leading to ferromagnetic interactions. It has been suggested that a more reliable parameter for unsymmetrically bridged systems, as the present one, is the ratio ϕ/R, R being the distance of Cu to the bridging halide.[21] For the Cu(1)−Cu(1)′ interaction, the small bridging angle of 87.28(4)° is expected to lead to ferromagnetic interactions owing to "accidental orthogonality" of the orbitals.[23] The ϕ/R ratio of 28.56° Å^{-1} is at a maximum for a J versus ϕ/R curve constructed using experimental data points from bromide bridged dimers.[1] However, there is no experimental point at the curve maximum. Generally, weak interactions have been observed for unsymmetrically bridged complexes, with very few examples of ferromagnetism among them.[24] In this respect, the strong ferromagnetic J_2 interaction is unexpected. A factor of probable significance is the 85° angle made by the plane of the bridging Cu(1)−Br$_2$−Cu(1)′ unit with the plane containing the Cu(1) chromophore, which precludes the possibility of overlap between these centers. Yet another variable which may influence the magnetic interaction is the value of R for a given value of ϕ/R. It has been observed[1] that, among a group of sulfur bridged Cu(II) compounds, Cu(dedtc)$_2$ (dedtc = *N*,*N*-diethyldithiocarbamate) having the shortest Cu···S distance shows ferromagnetic coupling with a J of 12 cm^{-1}. The Cu(1)−Br bridge has the shortest length in the present system. Coming to the Cu(2)−Cu(2)″ interaction, it is expected to be weakly antiferromagnetic, both because the magnitude of the bridging angle is greater than 90° (93.24(4)°) and because $\phi/R = 23.23°$ Å^{-1}. The Cu(1)−Cu(2) interactions has two bridging contributions, with angles of 85.76(4) and 94.32(4)°, respectively. It is possible to decompose the Cu(1)−Cu(2) coupling into its contributions arising from each bridge.[25] The ϕ/R ratio for the larger angle is 32.98° Å^{-1}, which is expected to lead to weakly antiferromagnetic interaction, while the ratio for the smaller bridging angle is 26.75° Å^{-1}, which could lead to weakly ferromagnetic interaction. We propose that a near cancellation of the interactions between Cu(1) and Cu(2) occurs leading to the negligibly small calculated J value.

Many linear tetramers adopt a Bleany−Bower kind of behavior with interdimer coupling, to a first approximation.[8c] Chains of $S = 2$ tetramers with antiferromagnetic coupling between them have also been observed.[8b,d] The importance of further neighbor interactions has also been considered for one system.[8e] In our case, although chains are present, some of the links in these chains (Cu(1)···Cu(2) interactions) are very weak.

The chloro analog,[9] in contrast to **1**, has three types of interactions. The first, through a bis μ-chloro unsymmetric bridge with a ϕ/R ratio of 30.1° Å^{-1} is weakly antiferromagnetic, as expected ($J = -1.25$ cm^{-1}). A 5-atom bridge via a bridging carboxylic acid group gave a $|J|$ value of 0.0006(2) cm^{-1}, while

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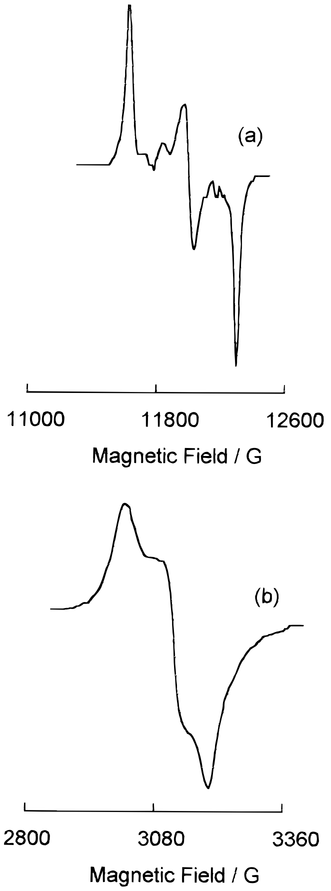

Figure 5. Polycrystalline EPR spectra of **1** at (a) Q-band and (b) X-band.

a 13-atom bridge through an uncoordinated lattice water led to a $|J|$ value of 0.056 cm^{-1} (from EPR).

EPR. The EPR of tetranuclear copper(II) complexes has recently attracted a great deal of attention,[26] although much information is not available for linear tetramers. Powder EPR for this system is not very informative, giving a three-line pattern at both X and Q bands (Figure 5). The *g*-values ($g_1 = 2.175$, $g_2 = 2.107$, $g_3 = 2.056$) do not correspond to a typically rhombic pattern commonly observed for Cu(II) complexes with elongated rhombic geometry.[13] The Q-band spectrum shows additional weak resonances, but the spectrum is not a superposition of signals from the two chemically inequivalent Cu(II) centers present in equal concentration in the crystal. These observations, taken together with the magnetic data discussed above, indicate that the EPR has to be discussed in terms of a mixture of spin states. Single-crystal EPR, as can be expected for such a system, is quite complex. A poorly resolved multiline pattern, which is orientation dependent, is observed in three orthogonal planes. At low temperatures, a significant increase in intensity is observed (Figure 6). From the magnetic and structural data, we can expect the coexistence of a triplet state (state 1) due to Cu(1)···Cu(1)′ ferromagnetic interactions and a weakly antiferromagnetically coupled state (state 2) due to Cu(2)···Cu(2)″ interactions. While exchange between these two states is negligible, dipolar interactions are likely to occur. Three main lines are expected, two from state 1 ($S = 1$) and one from state 2, which is very close to a doublet. The singlet−triplet gap is very small for state 2, leading to a significant triplet state population at all temperatures. A Boltzman distribution analysis shows that the ratio of the population of the singlet state to the triplet state would be 1:3. Only at ~4 K would the singlet−triplet population be comparable for state 2. Therefore, at the temperatures of the EPR measurements, state 1 would be three times as likely to have a triplet state neighbor as a singlet state one. This results in triplet−triplet dipolar interactions causing a near loss of the triplet state hyperfine structure although some splitting is seen for some orientations at 123 K. The absence of half-field lines and the small spread of the spectra (~275 G) point to the small magnitude of the *D* value for this system. The poor resolution of the spectra prevents a more detailed analysis of the zero-field splitting. Thus, although EPR is not very conclusive for this system, it is consistent with the magnetic and structural data.

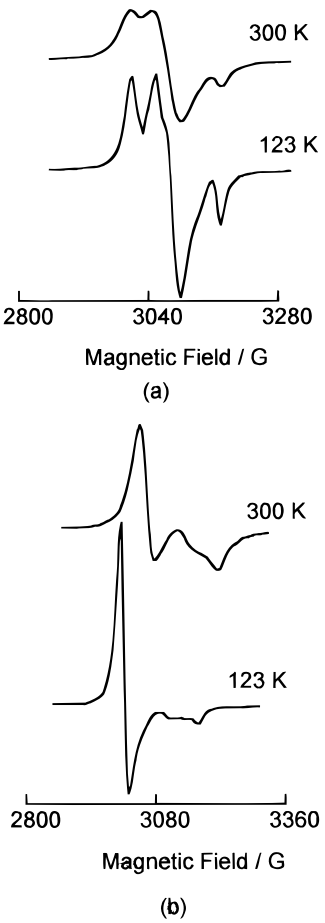

Figure 6. Single-crystal X-band EPR spectra of **1** at two temperatures, with the magnetic field oriented at (a) 0 and (b) 55 °C in an arbitrary crystal plane.

Conclusions

(i) Examples of bromo and chloro analogs of the same metal−ligand complex abound in the literature.[27] These analogs generally adopt the same structure and packing with only minor changes in bond lengths. In this context, the remarkable difference in packing between Cu(bp3ca)Cl_2·H_2O and Cu(bp3ca)Br_2·H_2O is worth examining. Both systems have CuN_2X_2 chromophores which form halo bridged dimers. However, while in the chloro complex, the sixth position around copper is occupied by a carboxylic acid oxygen from a neighboring molecule, in the bromo complex weak bromide bridges are observed. In the latter case, the carboxylic acid groups are involved in strong H-bonding with each other. Probably, these H-bonds have a strong bearing on the final structure and packing of this system. (ii) Bromo and chloro complexes show similar magnetic behavior, with the bromo

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complexes generally being more antiferromagnetic.[27] In the present case, the change in structure results in significant magnetic changes. It must also be pointed out that the ferromagnetic interaction J_2 is surprisingly large for an unsymmetrically bridged system. While a completely satisfactory explanation is not presently available, it is suggested that J depends on both ϕ and R and not just their ratio. More examples are needed to explore the resulting surface. (iii) EPR corresponds to a mixture of an $S = 1$ state with an $S = {}^1/_2$ state. However, dipolar interactions lead to poor resolution of the spectra.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic thermal displacement parameters, bond lengths and angles, and least-squares planes (9 pages). Ordering information is given on any current masthead page.

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