LOW TEMPERATURE CRYSTAL STRUCTURE AND MAGNETIC BEHAVIOR OF BIS(N-METHYL-2-PHENYLETHYLAMININIUM) TETRABROMIDOCUPRATE

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The low-temperature X-ray structure, and magnetic properties of (MePhenetNH$_2$)$_2$[CuBr$_4$] (MePhenetNH$_2$=N-methyl-2-phenylethylammonium) (**1**) are reported. The compound was characterized using IR, combustion analysis, X-ray powder diffraction, single crystal X-ray diffraction, and temperature-dependent magnetic susceptibility measurements. Compound **1** crystallizes in the monoclinic space group C2/c. In the structure, the tetrabromidocuprate ions are packed into zig-zag chains parallel to the *c*-axis which are stabilized by hydrogen bonds between the ammonium cations and bromide anions. Magnetic measurements (1.8-310 K) indicate weak antiferromagnetic interactions propagated via the two-halide exchange pathway through short Br…Br contacts. Fitting the data with the $S = ½$ uniform chain model gave $J = -7.7(1)$ K with $C = 0.403(1)$.

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INTRODUCTION

The recognition of halogen bonds as a significant factor in intermolecular and interionic interactions, in both biological and laboratory circumstances, has provided a significant impetus for study.[1] At the same time, magnetic exchange through halide ions, both bridging and through halogen bonds,[2] has been of significant interest for decades and the recognition of halogen bonds has provided a uniform framework for presenting such observations.[3] In particular, there has been extensive study of magnetic interactions via the two-halide pathway (a potential halogen bond) for decades.[4]

The vast majority of magnetic interactions reported via the two-halide pathway are antiferromagnetic, ranging from values of J near zero^{Hiba! A könyvjelző nem létezik.},a to very significant exchange ($J = -234$ K).[5] The correlation between the X…X distance as well as Cu-X…X contact angle and Cu-X…X-Cu torsion angle has been established,^{Hiba! A könyvjelző nem létezik.},6 but as yet insufficient data is available to provide any quantitative magnetostructural correlations and hence we have continuing interest in the study of such compounds.

The packing of the tetrabromidocuprate anions and hence, the superexchange parameters via the two-halide pathway, are strongly influenced by the nature of the corresponding cation, including its size, charge and hydrogen or halogen bonding capacity. N-Methyl-2-phenylethylammonium (NMPH) is one such counterion that has been employed to good effect previously. Prior work with NMPH has produced a number of complexes with the tetrachloridocuprate anion, including a chloride-bridged tricopper(II) system (Grigereit

et al.[7]) , a chloride-bridge dicopper(II) complex (Harlow et al.[8]) and polymorphs of the monomeric (NMPH)$_2$CuCl$_4$ compound.[9] We are particularly interested in the corresponding bromide compound, (NMPH)$_2$CuBr$_4$, reported by Place and Willett[10] due to the potential for magnetic interactions between the tetrabromidocuprate anions via the two-halide pathway. Preliminary work by Willett and Drumheller et al. showed the presence of antiferromagnetic interactions in the sample.[11] In an effort to more closely examine the relationship between the structure and its magnetic properties, we have repeated the synthesis of the compound and present here its low-temperature crystal structure and variable temperature magnetic susceptibility (1.8-310 K).

EXPERIMENTAL

Copper(II) bromide and N-methyl-2-phenylethylamine purchased from Sigma Aldrich. Materials were used as received without further purification. IR spectra were recorded via ATR on a Perkin-Elmer Spectrum 100 spectrometer. X-Ray powder diffraction was carried out on a Bruker AXS-D8 X-ray Powder Diffractometer. Bis(N-methyl(2-phenylethyl)ammonium tetrabromidocuprate (**1**) was prepared according to the literature.^{Hiba! A könyvjelző nem létezik.} IR (ν, cm^{-1}): 3024s, 2958s, 2786s, 1561m, 1456s, 1414s, 1374m, 1160m, 1070m, 1011m, 940m, 750vs, 703vs.

X-Ray structure analysis

Data for **1** were collected at 87(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 10 seconds, and a full sphere of data was collected. A total of 2450 frames were collected. Cell parameters were retrieved using SMART[12] software and refined using SAINTPlus[13] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINTPlus software. Absorption corrections were applied using SADABS.[14]

The structure was solved using the SHELXS97 program[15] and refined via least-squares analysis via SHELXL-2016.[16] Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms bonded to nitrogen atoms were located in the difference Fourier maps and their positions refined using fixed isotropic thermal parameters. The remaining hydrogen atoms were placed in geometrically calculated positions and refined using a riding model and fixed isotropic thermal parameters. Crystallographic information and details of the data collection can be found in Table 1.

Magnetic Susceptibility Data Collection

Magnetization data for **1** were collected using a Quantum Design MPMS-XL SQUID magnetometer. Finely ground crystals were packed into a #3 gelatin capsule and placed in a clear plastic straw for data collection. Data were first collected as a function of field from 0 to 50 kOe at 1.8 K. Several data points were recollected as the field returned to 0 kOe to check for hysteresis effects; none were observed. Magnetization was then measured as a function of temperature from 1.8 to 310 K in a 1 kOe applied field. The data collected were corrected for the background signal of the gelatin capsule and straw (measured independently), the temperature independent paramagnetism of the Cu(II) ion and for diamagnetic contributions of the constituent atoms, estimated via Pascal's constants.[17] All data were fit using the Hamiltonian $H = -J\sum S_1 \cdot S_2$. The composition of **1** was analyzed by powder X-ray diffraction and compared to the single crystal structure prior to data collection. No impurities were observed.

RESULTS

Crystal structure analysis

Compound **1** crystallizes in the monoclinic space group *C2/c*. The molecular unit is shown in Figure 1.
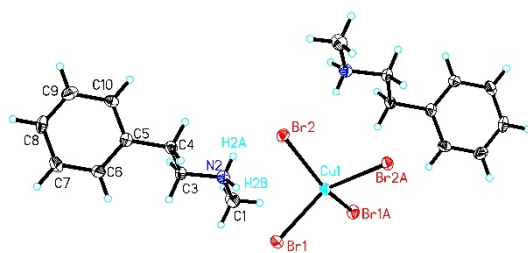

Figure 1. Thermal ellipsoid plot of the molecular unit of **1** showing 50% probability ellipsoids. Only the asymmetric unit, copper coordination sphere and those H-atoms whose positions were refined are labelled. Symmetry operation for Br1A and Br2A (1-*x*, *y*, ½-*z*).

The Cu1 ion is located along a two-fold symmetry axis bonded to two independent bromide ions (See Table 2 for selected bonds and angles). A significant Jahn-Teller distortion results in a highly flattened tetrabromidocuprate ion with a mean trans angle[Hiba! A könyvjelző nem létezik.] of 141.9°. Comparison of the bond lengths and angles between 87 and 295 K shows only very slight changes.

Table 1. X-ray data of compound 1.

Empirical formula	$C_{18}H_{28}N_2CuBr_4$
Formula weight	655.60
Temperature	87(2) K
Wavelength	0.71073 Å
Space group	C2/c
a	23.854(2) Å
b	9.2120(9) Å
c	10.8726(11) Å
α	90°
β	106.787(2)°
γ	90°
Volume	2287.4(4) Å^3
Z	4
Density (calculated)	1.904 Mg m^{-3}
Absorption coefficient	7.947 mm^{-1}
F(000)	1276
Crystal size	0.26 x 0.10 x 0.05 mm^3
□ range for data collection	1.783 to 30.011°
Index ranges	-32 ≤ h ≤ 32,
	-12 ≤ k ≤ 12,
	-15 ≤ l ≤ 15
Reflections collected	16773
Independent reflections	3280 [R(int) = 0.0506]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.671 and 0.224
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3280 / 0 / 121
Goodness-of-fit on F^2	1.075
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0356$, w$R_2 = 0.0710$
R indices (all data)	$R_1 = 0.0475$ w$R_2 = 0.0747$
Largest diff. peak and hole	1.01 and -0.510 e Å^{-1}

Table 2. Selected bond lengths [Å] and angles [°] for **1** at 87 K (this work) and 295 K (Ref. [10]).

Bond	Distance (87 K)	Distance (295 K)
Cu1-Br1	2.3794(4)	2.364
Cu1-Br2	2.3938(4)	2.395
Bond	**Angle (87 K)**	**Angle (295 K)**
Br1-Cu1-Br1A	96.47(2)	97.88
Br1-Cu1-Br2	141.91(1)	142.09
Br1-Cu1-Br2A	96.54(1)	95.77
Br2-Cu1-Br2A	94.89(2)	94.76

Symmetry operation for Br1A and Br2A (1-*x*, *y*, ½-*z*).

The NMPH cation is unremarkable, adopting an antiperiplanar geometry about the C1-N2-C3-C4 and N2-C3-C4-C5 sequences with torsion angles of 179.1(3)° and 174.6(2)°, respectively.

The $CuBr_4^{2-}$ ions form chains parallel to the *c*-axis via short Br…Br contacts between inversion related anions, as shown in Figure 2. Parameters for the two-halide superexchange pathway are given in Table 3. The chains are further stabilized by hydrogen bonds to the ammonium hydrogen atoms.: $d_{N2…Br1C} = 3.439(3)$ Å, $d_{N2…Br2A} = 3.395$ Å. The Br2A…Br2B distance is the shorter contact between the ions, making it an ee$_2$-type interaction.[Hiba! A könyvjelző nem létezik.]
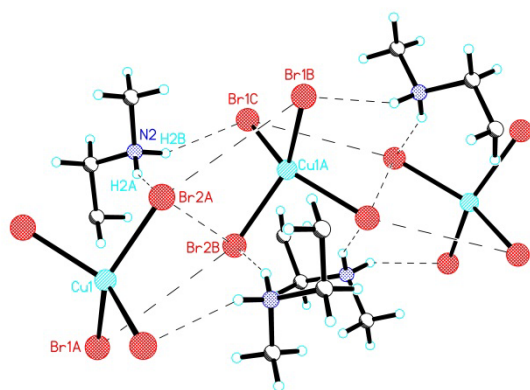
Figure 2. Chain formation via short Br…Br contacts. Dashed lines represent Br…Br contacts and hydrogen bonds. Only the alkyl portions of the NMPH ions are shown for clarity.

Table 3. Two-halide superexchange pathway parameters for 1 at 87 K (this work) and 295 K (Ref. [10]).[a]

Bond	d (Å)	θ(°)[a]	τ (°)
Cu1-Br1A… Br2B-Cu1A			
87 K	4.392	145.60/ 72.4	3.45
295 K	4.404	143.47/ 74.25	4.74
Cu1-Br2A… Br2B-Cu1A			
87 K	3.997	80.75	180
295 K	4.129	79.93	180

[a]For Cu1-Br1A… Br2B-Cu1A, there are two inequivalent interior angles, while for Cu1-Br2A… Br2B-Cu1A, the angles are identical by symmetry. Br2A and Br2B are related by an inversion center which requires $\tau_{Cu1-Br2A… Br2B-Cu1A}$ to be 180° by symmetry.

The tetrabromidocuprate ion chains pack into layers parallel to the *bc*-plane (see Figure 3). The layers are well separated by a double layer of NMPH cations arranged antiparallel to each other. The shortest distance between $CuBr_4^{2-}$ ions in adjacent layers is greater than 9 Å. The closest contacts between the phenyl rings of the NMPH ions is greater than 4.2 Å, indicating the absence of significant π-stacking interactions.

Magnetic study

Magnetization data as a function of applied field (Figure 4) show a linear response throughout the measured region and reach a maximum of 1600 emu mol^{-1} at 50 kOe. This is well below the expected saturation magnetization of ~5,800 emu mol^{-1} for a $S = ½$ system with g near 2, indicating the presence of antiferromagnetic interactions in the sample.

Susceptibility data for **1** were collected in a 1 kOe field from 1.8 K to 310 K. The susceptibility of **1** shows rounded maximum near 4 K, again in support of antiferromagnetic interactions in the sample (Figure 5).
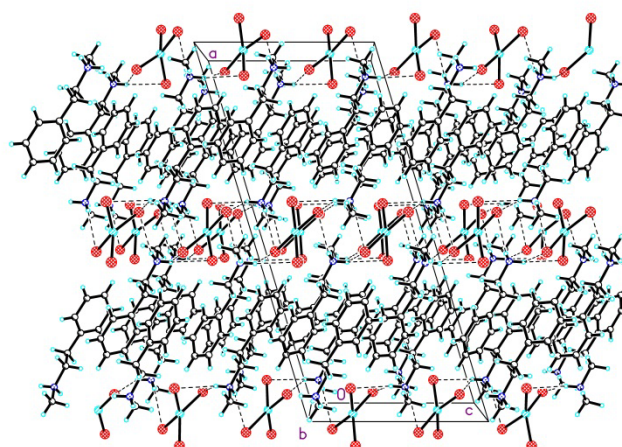

Figure 3. Packing of **1** viewed parallel to the *b*-axis showing the alternating layer structure.
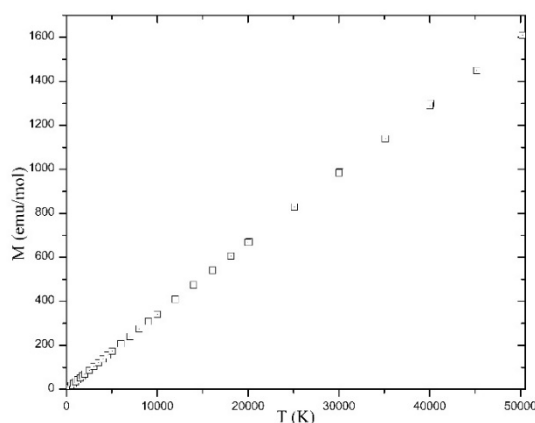

Figure 4. Magnetization as a function of applied field for **1**.

Fitting the data to the $S = ½$ uniform Heisenberg chain model[18] with a Curie-Weiss correction to account for interchain interactions resulted in a Curie constant (*CC*) of 0.403(1) emu-K mol-Oe^{-1}, $J = -7.77(8)$ K and $θ = -0.09(9)$ K, with a 4.0(5) % paramagnetic impurity (seen as the slight increase in χ below 2.5 K).
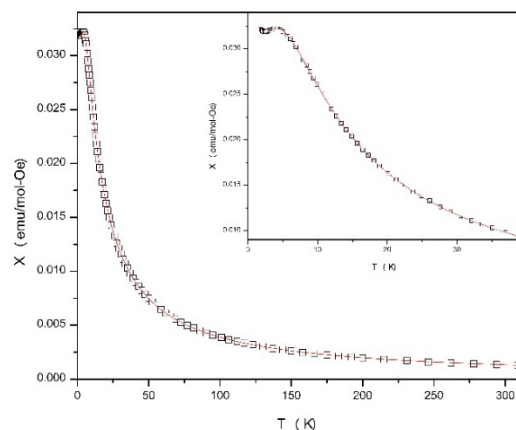

Figure 5. χ(*T*) for **1**. The inset shows an expansion of the region below 40 K. The solid line is the best fit to the $S = ½$ uniform Heisenberg chain model.

Using the same model to fit the $\chi T(T)$ data (Figure 6) gave similar results with $CC = 0.402$ emu-K mol-Oe^{-1}, $J = -7.68(11)$ K and $\theta = -0.11(7)$ K with a 4.2(4) % paramagnetic impurity. A fit of the data above 30 K to the Curie-Weiss law yielded $CC = .397(1)$ emu-K mol-Oe^{-1} and $\theta = -3.05(14)$ K. [*Note*: The value of θ from the Curie-Weiss fit is proportional to S and J. It is not the same as the value obtained from fits of $\chi(T)$ and $\chi T(T)$ where it represents the interchain interactions.] All are in agreement with modest antiferromagnetic interactions in the compound.
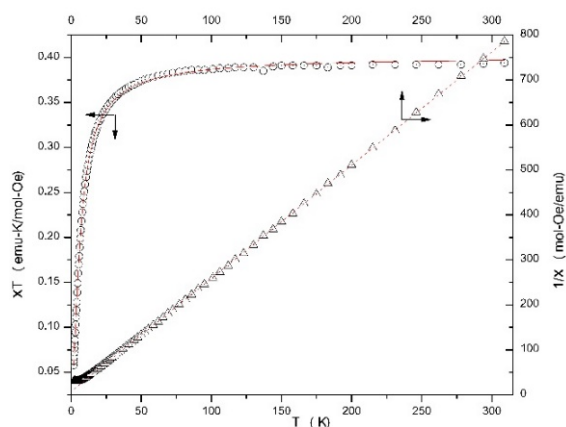

Figure 6. $\chi T(T)$ (o) and $1/\chi(T)$ (Δ) for **1**. The solid lines represent the best fits to the $S = \frac{1}{2}$ uniform Heisenberg chain model and the Curie-Weiss law, respectively.

DISCUSSION

The low-temperature crystal structure of **1** is in good agreement with the room temperature structure of Place and Willett.$^{\text{Hiba! A könyvjelző nem létezik.}}$ Bond lengths and angles within the NMPH$^+$ and CuBr$_4^{-2}$ moieties show negligible changes over the temperature range. The two-halide exchange pathway parameters (Table 3) show more significant, but non-symmetrical changes. There is only a slight decrease in the Cu1-Br1A…Br2B-Cu1A distance, less than 0.25 %, with commensurately small changes in the corresponding angles. However, the Cu1-Br2A…Br2B-Cu1A distance has decreased by nearly 3 %, suggesting a sliding of the CuBr$_4^{2-}$ units parallel to the *ac*-face (Figure 7). This would affect the two-halide pathway superexchange, but as no quantitative relationships between J and the structure parameters are available as yet, the nature of the change cannot be predicted.

Magnetic data confirm the preliminary report by Drumheller and Willett$^{\text{Hiba! A könyvjelző nem létezik.}}$ of the antiferromagnetic response in the complex where data was collected from 4.2-60 K. The data was reported as $\chi T(T)$ and yielded $J = -8.0$ K, in good agreement with the current value of -7.7(1) K obtained from data fit over the full range of 1.8-310 K. Fits of both $\chi(T)$ and $\chi T(T)$ show negligible interchain interactions as seen by the Curie-Weiss corrections, zero or virtually so in both fits (θ values) within experimental error, making them excellent approximations of the uniform $S = \frac{1}{2}$ Heisenberg chain.
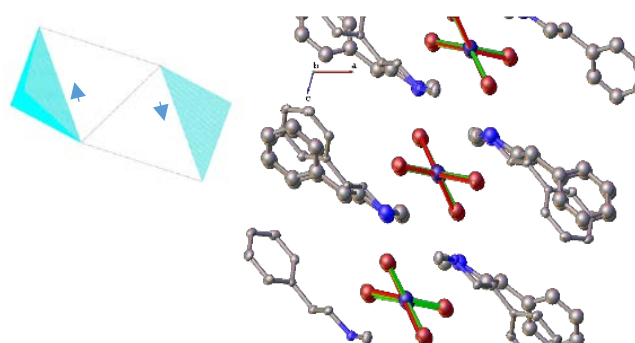

Figure 7. (Left) The relative motion of adjacent CuBr$_4^{-2}$ distorted tetrahedral from 295 K to 87 K viewed perpendicular to the *ac*-plane (right). An view of the overlap of the 87 K (red) and 295 K (green) structures. The N-atoms were used as the anchor point.

In summary, (NMPH)$_2$CuBr$_4$ forms well isolated chains via short Br…Br contacts in the lattice. These contacts support antiferromagnetic exchange through the two-halide exchange pathway and result in modest antiferromagnetic interactions in the compound (-7.7 K) as seen through field and temperature dependent magnetization measurements. Further work is in progress to attempt to quantify the magnetostructural correlations in such materials.

Supplementary data

CCDC 1914519 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/con-ts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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