



LOW TEMPERATURE CRYSTAL STRUCTURE AND MAGNETIC BEHAVIOR OF BIS(2-AMINO-4-METHYLPYRIDINIUM) TETRACHLORIDOCUPRATE

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(4-MAPH)₂[CuCl₄] (4MAP = 2-amino-4-methylpyridine) (**1**) has been synthesized and characterized by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group *C2/c*. The tetrachloridocuprate(II)(2-) ions pack in layers parallel to the *ab*-face of the crystal which are well separated by double layers of the 2-amino-4-methylpyridinium cations. The anions generate a square layer via short Cl...Cl interactions due to the C-centering. Variable temperature magnetic susceptibility measurements indicate the presence of weak antiferromagnetic interactions within the layers (*J* ~ -1 K).

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X-ray crystal structure and temperature dependent magnetic study reported here.

Experimental

Copper(II) chloride dihydrate (dehydrated by storing in an oven at 130 C for 24 hours) and 2-amino-4-methylpyridine (4MAP) were 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.

Introduction

Methyl-substituted 2-amino-pyridine molecules have been used as ligands, and their protonated forms as counterions, for a myriad of first-row transition metal halide complexes. 2-Amino-3-methylpyridine (3-MAP) complexes of the form ML₂X₂ are known for CoCl₂ and CoBr₂.¹ The corresponding salts, (3-MAPH)_nMX_m have been reported for Fe(III),² Co(II),³ Cu(II),⁴ and Zn(II)⁵ as well. (3-MAPH)CuCl₃, which forms a bichloride-bridged chain, has been extensively studied for its magnetic properties.⁶ 2-Amino-5-methylpyridine (5-MAP) has been similarly studied. The neutral ML₂X₂ complexes have been described for cobalt(II) and zinc(II) chloride,⁷ while the (5MAPH)_nMX_m salts are reported for Co(II),^{3a,8} Cu(II),^{3b,9} and Zn(II).¹⁰ In the case of 2-amino-6-methylpyridine, (6MAP), the neutral compounds M(6MAP)_nX₂ (*n* = 2,3) for Co, Ni, Cu, and Zn were prepared.¹¹ The related known (6MAPH)_nMX_m salts of first row transition metals include compounds of Co,^{3b,12} Cu^{11,13} and Zn.^{11,14} Here also, similar to the 3MAP compound, detailed studies of the magnetic properties of (6-MAPH)CuCl₃ have been reported.^{6a,15}

The corresponding 4-methyl substituted pyridine moiety, 2-amino-4-methylpyridine (4MAP), has received similar attention. Co(4MAP)₂Cl₂ has been reported^{1a,3b} as have the corresponding copper(II)¹⁶ and zinc(II) compounds.¹⁷ The tetrachloridozincate salt¹⁸ is known as well. We were particularly interested in the (4MAPH)₂CuCl₄ complex. From the room temperature crystal structure,¹⁹ it appeared that the compound could present a well isolated, two-dimensional magnetic lattice, but no magnetic data were reported. Thus, we undertook the synthesis, low-temperature

Synthesis

Bis(2-amino-4-methylpyridinium) tetrachloridocuprate (**1**).

4MAP hydrochloride (2.892 g, 20.0 mmol) was dissolved in 20 mL of isopropyl alcohol. Solid anhydrous CuCl₂ (1.345 g, 10.0 mmol) was added to the solution and stirred for 2 hours to form a light green precipitate (ppt. began to form within 10 minutes). The powder was isolated by vacuum filtration and recrystallized from 95 % ethanol to give yellow-green crystals of **1** (1.78 g, 42 %).

X-Ray structure analysis

Data for **1** were collected at 120(2) K using a Bruker/Siemens SMART APEX instrument (MoK α radiation, $\lambda=0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using phi and omega scans; a full sphere of data was collected. Cell parameters were retrieved using SMART²⁰ software and refined using SAINTPlus²¹ on all observed reflections. Data reduction and correction for *L_p* and decay were performed using SAINTPlus software. Absorption corrections were applied using SADABS.²²

The structure was solved and refined using the SHELXS-97 program²³ and refined via least-squares analysis via SHELXL-2016.²⁴ 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.

Table 1. X-ray data of compound 1.

Empirical formula	C₁₂H₁₈N₄Cl₄Cu
Formula weight	423.64
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal class	monoclinic
Space group	C2/c
<i>a</i>	11.2306(8) Å
<i>b</i>	12.3083(9) Å
<i>c</i>	13.8772(10) Å
β	111.805(2)°
Volume	1781.0(2) Å ³
<i>Z</i>	4
Density (calculated)	1.580 Mg m ⁻³
Absorption coefficient	1.824 mm ⁻¹
<i>F</i> (000)	860
Crystal size	0.28 x 0.28 x 0.50 mm ³
θ range for data collection	2.56 to 33.706°
Index ranges	-16 ≤ <i>h</i> ≤ 13 -18 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 21
Reflections collected	9819
Independent reflections	3259 [<i>R</i> (int) = 0.0543]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.8038
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3259 / 0 / 106
Goodness-of-fit on <i>F</i> ²	1.056
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ¹ = 0.0256, <i>wR</i> ₂ = 0.0715
<i>R</i> indices (all data)	<i>R</i> ¹ = 0.0272 <i>wR</i> ₂ = 0.0725
Largest diff. peak and hole	0.575 and -0.702 e Å ⁻¹

Magnetic susceptibility data collection

A Quantum Design MPMS-XL SQUID magnetometer was used to collect magnetization data for **1**. Powdered crystals were packed into a #3 gelatin capsule and mounted for data collection. Data were collected initially as a function of field from 0 to 50 kOe at 1.8 K. As the field returned to 0 kOe, several data points were recollected to check for hysteresis; none was observed. Magnetization was measured in a constant field of 1 kOe as a function of temperature from 1.8 to 310 K. The data collected were corrected for the background signal of the sample mount (measured independently), the temperature independent paramagnetism of the Cu(II) ion and for diamagnetic contributions of the constituent atoms which were estimated via Pascal's constants.²⁵ Data were fit using the $H = -J\sum S_1 S_2$ Hamiltonian. Sample of **1** used for magnetic data collection was analyzed by powder X-ray diffraction and compared to the predicted

powder pattern based on the single crystal structure. 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. The asymmetric unit comprises one half of the CuCl₄²⁻ and one 4MAPH cation. The Cu(II) ions sits on a two-fold rotation axis. The structure has been reported previously (293 K),¹⁹ selected bond lengths and angles for the two structures are shown in Table 2. A significant Jahn-Teller distortion results in a highly flattened tetrachloridocuprate ion with a mean trans angle²⁶ of 148.374(11)°. Comparison of the bond lengths and angles between 120(2) and 293 K shows only very slight changes.

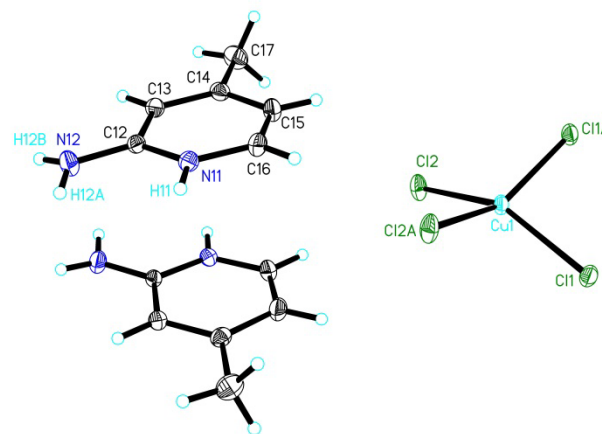


Figure 1. Thermal ellipsoid plot (50% probability) of the molecular unit of **1**. The asymmetric unit, copper coordination sphere and those H-atoms whose positions were refined are labelled. Symmetry operation for Cl1A and Cl2A (-*x*, *y*, 1/2-*z*).

Table 2. Selected bond lengths [Å] and angles [°] for **1** at 87 K (this work) and 295 K.¹⁹

Bond	Distance (120 K)	Distance (295 K)
Cu1-Cl1	2.2756(3)	2.261(2)
Cu1-Cl2	2.2705(3)	2.270(2)
Bond	Angle (120 K)	Angle (295 K)
Cl1-Cu1-Cl1A	94.183(15)	94.34(10)
Cl1-Cu1-Cl2	148.374(11)	146.17(8)
Cl1-Cu1-Cl2A	94.276(11)	95.14(7)
Cl2-Cu1-Cl2A	94.298(16)	94.80(10)

Symmetry operation for Cl1A and Cl2A (-*x*, *y*, 1/2-*z*)

Although there is some deviation from planarity of the NH₂ group, the sum of the angles is only 355.9(1)°, the short N12-C12 distance (1.3473(14) Å) indicates significant sp² character for the nitrogen atom due to conjugation with the pyridine ring. The amino substituent acts as an electron donating group, reducing its basicity while raising the basicity of the pyridine nitrogen atom. The pyridine is highly planar (mean deviation of constituent atoms = 0.0054 Å) and N12 lies only 0.0034 Å out of that plane.

The CuCl_4^{2-} ions pack into layers parallel to the ab -plane via short $\text{Cl}\dots\text{Cl}$ contacts (Figure 2). Adjacent ions are related via the C -centering operation. Parameters for the two-halide magnetic superexchange pathway are given in Table 3.

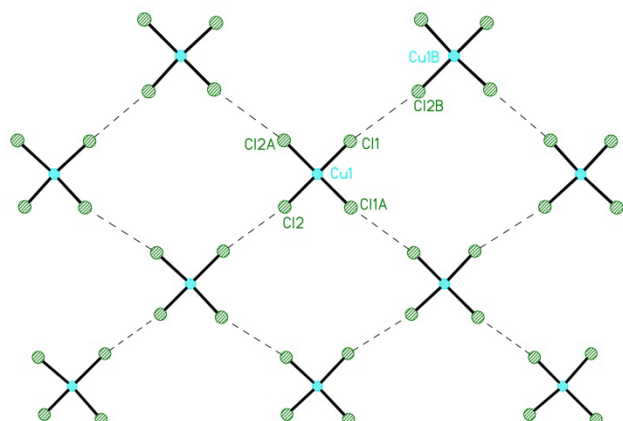
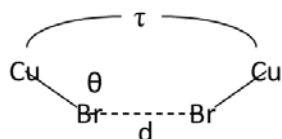


Figure 2. Layer formation in **1** via short $\text{Cl}\dots\text{Cl}$ contacts. The short $\text{Cl}\dots\text{Cl}$ contacts are represented as dashed lines.

Table 3. Two-halide superexchange pathway parameters for **1** at 120 K (this work) and 293 K (Ref. 20).



Bond	d (Å)	$\theta(^{\circ})^a$	$\tau(^{\circ})$
Cu1-Cl1... Cl2B-Cu1B	4.206	166.5/ 137.1	151.6
293 K	4.300	165.8/ 133.8	155.1

Layers of CuCl_4^{2-} anions are separated by double layers of 4MAPH cations as seen in Figure 3. This motif is common in several $(\text{BH})_2\text{CuX}_4$ complexes, where B is an organic base, such as the 5-methyl, 5-bromo and 5-chloro 2-aminopyridine compounds^{9b,d} as well as other compounds in the $C2/c$ space group such as (N-methyl-2-phenylethylammonium) tetrabromocuprate.²⁷ In all of those examples, the aromatic rings are \sim perpendicular to the ab -face of the crystals while in **1** the pyridine rings are nearly parallel to that plane. However, as the rings occur in a double layer (Fig. 3), the interlayer separation is still significant. The rings are nearly parallel (interplanar angle = 5.2°) and exhibit π -stacking with an average interring separation of ~ 3.45 Å, a distance between the ring centroids of 3.586 Å and a slip angle of 13.9° . The closest $\text{Cl}\dots\text{Cl}$ contacts between layers are greater than 5.2 Å.

Table 4. Hydrogen bonding parameters for **1**.

	D-H(Å)	H...A(Å)	D...A(Å)	D-H...A($^{\circ}$)
N11-H11...Cl1	0.88(2)	2.653(19)	3.334(1)	136(1)
N11-H11...Cl2	0.88(2)	2.647(19)	3.412(1)	147(1)
N12-H12D...Cl1	0.86(2)	2.495(19)	3.348(1)	172(2)
N12-H12A...Cl2	0.82(2)	2.52(2)	3.293(1)	158(2)

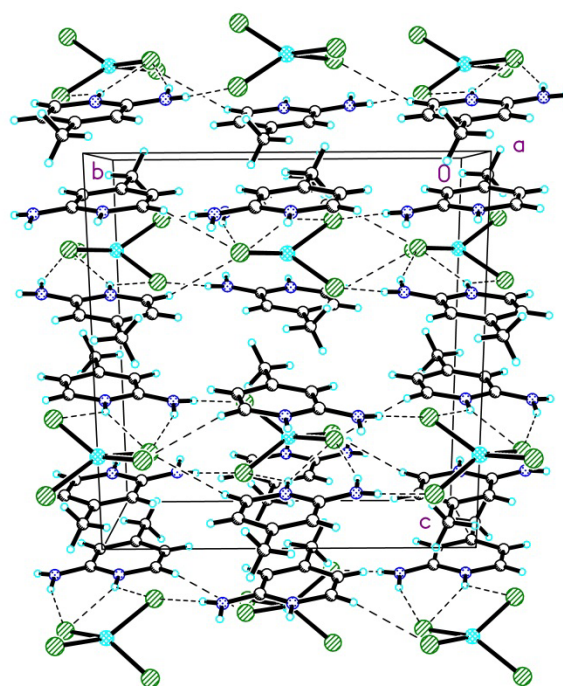


Figure 3. Packing of **1** viewed parallel to the a -axis showing the alternating layer structure.

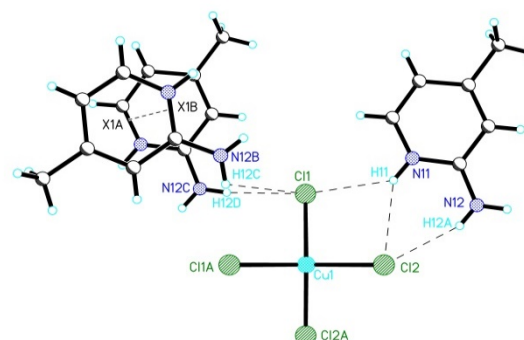


Figure 4. Hydrogen bonding observed in **1**.

The lattice is further stabilized through hydrogen bonds to both the amino and pyridinium hydrogen atoms as shown in Fig. 4. The hydrogen bonding parameters are given in Table 4.

Magnetic study

Magnetization data as a function of applied field show a linear response to ~ 20 kOe and then slight downward curvature to a maximum of ~ 5400 emu/mol at 50 kOe. This is in good agreement with the expected saturation magnetization of $\sim 5,800$ emu/mol for a $S = 1/2$ system with g near 2, indicating the presence of weak antiferromagnetic interactions, and suggest that saturation would be achieved at a slightly higher applied field.

Susceptibility data for **1** were collected as a function of temperature in a 1 kOe applied field from 1.8 K to 310 K. No maximum is visible in the susceptibility of **1** down to 1.8 K. However, a clear decrease in the χT product is seen at low temperatures (Figure 5). Based upon the crystal structure, the

data were fit to the $S=1/2$ uniform Heisenberg square layer model.²⁸ This resulted in a Curie constant (CC) of 0.4345(3) emu-K mol⁻¹ Oe⁻¹ and $J = -1.02(6)$ K with a 7(4) % paramagnetic impurity. The $\chi(T)$ data were also fit to this model resulting in CC = 0.4359(1) emu-K mol⁻¹ Oe⁻¹ and $J = -0.96(5)$ K with a 2(4) % paramagnetic impurity. The $\chi(T)$ fit emphasizes low temperature data, while the $\chi T(T)$ fit emphasizes high temperature data; the strong agreement between the two fits indicates the quality of the data. Attempts to fit the data to the 2D-square layer model with Curie-Weiss correction to account for interlayer interactions yielded θ values of zero within the error, indicating the good isolation of the layers.

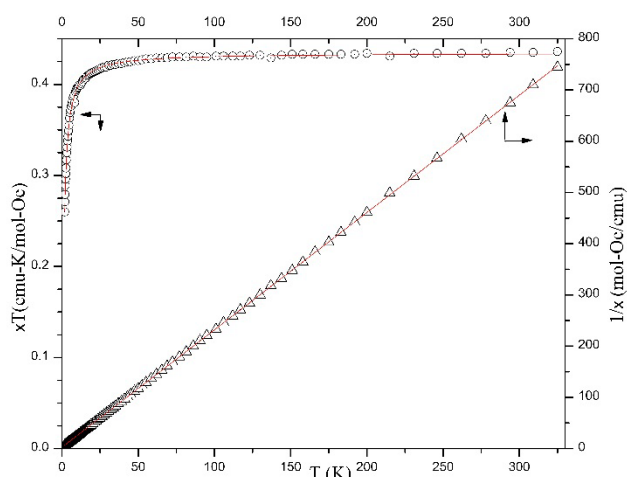


Figure 5. $\chi T(T)$ (o) and $1/\chi(T)$ (Δ) for **1**. The solid lines represent the best fits to the $S = 1/2$ uniform Heisenberg square layer model and the Curie-Weiss law, respectively.

Finally, the data above 5 K were fit to the Curie-Weiss law (Figure 5) resulting in $CC = 0.4365(2)$ emu-K mol⁻¹ Oe⁻¹ and $\theta = -1.19(6)$ K in good agreement with the 2D-Heisenberg model. All are in agreement with very weak antiferromagnetic interactions in the compound.

Discussion

Compound **1** crystallizes as a well isolated 2D-layer which may be mapped onto the 2D-Heisenberg square. Although the Cu(II) ions actually form rhombi (the short and long axes are 11.23 Å and 12.31 Å), the Cl...Cl distances across the rhombi are all greater than 7.5 Å, much too great to propagate magnetic exchange. Similarly, although the interplanar Cl...Cl distance is much shorter (~5.2 Å) it is still greater than the range at which magnetic exchange is observed. Assuming that the exchange parameters for the two-halide pathway are similar to those reported between bromide ions,^{27a} we can analyse the proposed exchange within the layers. The exchange coupling becomes stronger as the Cl...Cl distance shortens, as the θ angles approach 180° and at the τ torsion angle approaches either 0° or 180°. The Cl...Cl distance is within the range where weak antiferromagnetic interactions are typically observed.^{3,4,10,27} However, only one of the θ angles is close to 180° and the torsion angle, while closer to 180° than 90°, is not particularly favourable. Thus, the weak exchange observed may be rationalized in terms of the two-halide superexchange pathway. Although the layers are indeed very well isolated,

as suggested by the room temperature crystal structure, the magnetic exchange within the layers is too weak to warrant more detailed study.

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Supplementary data

CCDC 1917325 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/con-fts/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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