



# SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF BIS(3-AMINO-2-CHLOROPYRIDINE)DIBROMIDOCOPPER(II)

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The synthesis, X-ray crystal structure, and variable temperature magnetic properties of [(3-NH<sub>2</sub>-2-Clpy)<sub>2</sub>CuBr<sub>2</sub>] (3-NH<sub>2</sub>-2-Clpy = 3-chloro-2-aminopyridine) (**1**) are presented. The compound was characterized using 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 *P*2<sub>1</sub>/*n*. Inversion related molecules form a dimeric unit via short Cu...Br contacts. The dimers are linked into a step-like chain via short Br...Br contacts. Surprisingly, magnetic susceptibility measurements (1.8-325 K), which indicate weak antiferromagnetic interactions, are best fit by a uniform chain model suggesting that the exchange within and between dimers is nearly identical. Fitting the data with the *S* = ½ uniform chain model gave *J* = -3.38(2) K with *C* = 0.407(1).

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Scientific. Materials were used as received without further purification. X-Ray powder diffraction was carried out on a Bruker AXS-D8 X-ray Powder Diffractometer.

## INTRODUCTION

The factors controlling the sign and strength of magnetic exchange in transition metal complexes has been a field of study for decades. Discoveries such as single-molecule magnets<sup>1</sup> and spin-crossover materials<sup>2</sup> as well as the recognition of the role played by magnetic interactions in the high temperature superconductor<sup>3</sup> have sparked a surge of interest. Copper(II) complexes have played a significant part in recent studies due to the single unpaired electron, making it a quantum system, and the plasticity of the copper(II) coordination sphere - allowing for a wide variety of structure types. In particular, pyridine and substituted pyridine complexes of Cu(II) halides have been investigated with an interest in understanding magnetostructural correlations in such compounds.<sup>4</sup> We have been particularly interested in the behaviour of such compounds with halogen substituents on the pyridine ring to study the influence of halogen bonding on the crystal packing and its resulting effect on the magnetic interactions in the sample.<sup>5</sup> Halogen bonds have a significant role in both intermolecular and interionic supramolecular structure of such compounds.<sup>6</sup> Superexchange pathways may be generated in these materials via the halide ions in either the bridging mode or via the two-halide pathway and these effects have been studied for many years.<sup>7</sup>

In particular, we have been examining the effects of substituents in the 2-position of the pyridine ring, especially halogen substituents.<sup>8</sup> The formation of supramolecular motifs such as dimers and chains through intermolecular interactions is strongly correlated with the conformation of the coordinated pyridine ligand. As part of this ongoing work, we report here the synthesis, structure and magnetic properties of bis(3-amino-2-chloropyridine)dibromidocopper(II).

## EXPERIMENTAL

Copper (II) bromide was purchased from Sigma Aldrich and 3-amino-2-chloropyridine [3-NH<sub>2</sub>-2-Clpy] from Matrix

## Synthesis

Bis(3-amino-2-chloropyridine)dibromidocopper(II) (**1**): 3-NH<sub>2</sub>-2-Clpy (0.69 g, 5.2 mmol) and copper(II) bromide (0.56 g, 2.5 mmol) were dissolved in 20 mL of 50:50 methanol/water at room temperature. The solution was filtered to remove trace insoluble materials and left at room temperature for slow evaporation. After ~ 3 weeks, small black crystals of **1** were recovered by filtration, washed quickly with cold methanol and allowed to air dry to give 0.54 g (45 %). Elem. anal. for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>Br<sub>2</sub>CuN<sub>4</sub>: found (calc.): C, 24.63(24.99); H, 2.41(2.10); N, 11.48(11.66).

## X-Ray Structure Analysis

Data for **1** were collected at 87(2) K using a Bruker/Siemens SMART APEX instrument (Mo K $\alpha$  radiation,  $\lambda$  = 0.71073 Å) via  $\phi$  by and  $\omega$  scans. Cell parameters were retrieved using SMART<sup>9</sup> software and refined using SAINTPlus<sup>10</sup> on all observed reflections. Absorption corrections were applied using SADABS.<sup>11</sup> The structure was solved and refined using the SHELXS97 program<sup>12</sup> and refined via least-squares analysis via SHELXL-2018.<sup>13</sup> 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. Hydrogen atoms bonded to carbon atoms were placed in geometrically calculated positions and refined using a riding model with fixed isotropic thermal parameters. Data collection and refinement details are presented in Table 1.

## Magnetic Susceptibility Data Collection

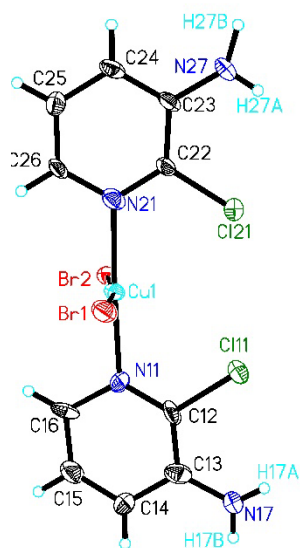
Magnetization data for **1** were collected using a Quantum Design MPMS-XL SQUID magnetometer. Finely ground crystals were packed into a #3 gelatin capsule and placed in a clear plastic straw for data collection. Data were collected as a function of field from 0 to 50 kOe at 1.8 K. As the field was reduced to 0 kOe several data points were recollected to check

for hysteresis effects; no hysteresis was observed. The M(H) response was linear beyond 10 kOe. Magnetization was also measured as a function of temperature from 1.8 to 325 K in a 1 kOe applied field. The data were corrected for the background signal (measured independently), the temperature independent paramagnetism of the Cu(II) ion and the diamagnetic contributions of the constituent atoms, estimated via Pascal's constants.<sup>14</sup> All data were fit using the Hamiltonian  $H = -J\Sigma S_1 \cdot S_2$ . Powder X-ray diffraction data for **1** were compared to the single crystal structure prior to magnetic data collection to ensure that the sample was the same phase as the single crystal structure. No impurities were detected.

## RESULTS

### Crystal Structure Analysis

Reaction of copper(II) bromide with 3-amino-2-chloropyridine in aqueous methanol gave compound **1** which crystallizes in the monoclinic space group  $P2_1/n$ . The molecular unit is shown in Figure 1. Selected bond lengths and angles are provided in Table 2. The Cu(II) ions is coordinated by two symmetry independent bromide ions and two symmetry independent 3-NH<sub>2</sub>-2-Clpy ligands in a nearly square planar geometry (mean trans angle<sup>15</sup> = 173.8°). The mean deviation from the coordination plane is 0.107 Å, with the bromide ions and N atoms displaced to opposite sides as seen in Fig. 1. The 3-NH<sub>2</sub>-2-Clpy ligands are in the *syn*-conformation with the chlorine substituents oriented to the same face of the coordination plane. The pyridine rings are nearly planar [mean deviations of constituent atoms = 0.0057 Å (N11 ring)=0.0066 Å] with the chlorine and amino substituents displaced slightly to opposite faces of the N11 ring and to the same face of the N21 ring. The pyridine rings are nearly perpendicular to the Cu-coordination plane and canted 11.8° to each other.



**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, 1/2-z).

**Table 1.** X-ray data of compound **1**.

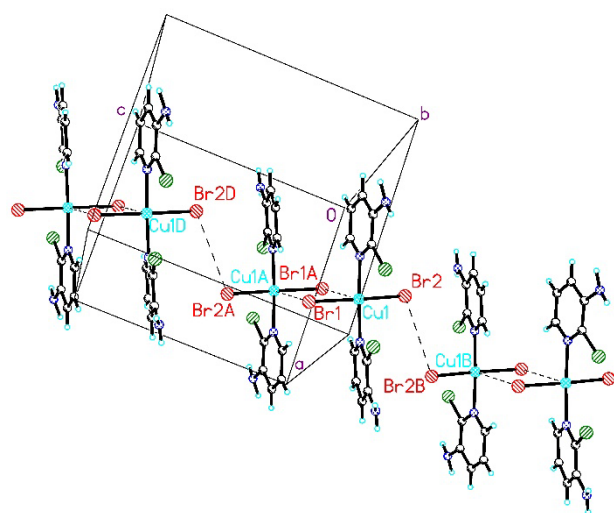
Empirical formula	C <sub>10</sub> H <sub>10</sub> Br <sub>2</sub> Cl <sub>2</sub> CuN <sub>4</sub>
Formula weight	480.48
Temperature	140(2) K
Wavelength	0.71073 Å
Space group	$P2_1/n$
<i>a</i>	8.9724(7) Å
<i>b</i>	15.6059(14) Å
<i>c</i>	10.5491(9) Å
$\alpha$	90°
$\beta$	92.370(6)°
$\gamma$	90°
Volume	1475.8(2) Å <sup>3</sup>
<i>Z</i>	4
Density (calculated)	2.162 Mg m <sup>-3</sup>
Absorption coefficient	7.246 mm <sup>-1</sup>
<i>F</i> (000)	924
Crystal size	0.51 x 0.30 x 0.30 mm <sup>3</sup>
$\theta$ range for data collection	2.610 to 28.376°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -20 ≤ <i>k</i> ≤ 20, -13 ≤ <i>l</i> ≤ 13
Reflections collected	20287
Independent reflections	3626 [ <i>R</i> (int) = 0.1081]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.277 and 0.8372
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	3626 / 3 / 184
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.043
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sup>1</sup> = 0.0618 <i>wR</i> <sub>2</sub> = 0.1431
<i>R</i> indices (all data)	<i>R</i> <sup>1</sup> = 0.1105 <i>wR</i> <sub>2</sub> = 0.1644
Largest diff. peak and hole	1.81 and -0.946 e Å <sup>-1</sup> near Br2

**Table 2.** Selected bond lengths [Å] and angles [°] for **1**.

Bond	Distance	Bond	Distance
Cu1-Br1	2.4147(13)	Cu1-Br2	2.4365(13)
Cu1-N11	2.019(6)	Cu1-N21	2.020(6)
Bond	Angle	Bond	Angle
Br1-Cu1-Br2	170.94(5)	N11-Cu1-N21	176.7(3)
Br1-Cu1-N11	91.05(19)	Br1-Cu1-N21	91.0(2)
Br2-Cu1-N11	88.95(19)	Br2-Cu1-N21	89.42(19)

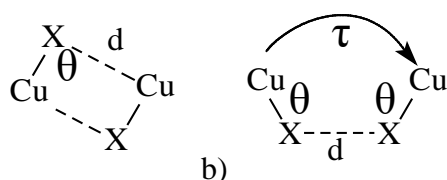
The bond lengths and angles are similar to those observed in similar CuBr<sub>2</sub>L<sub>2</sub> complexes where L is a 2-halopyridine ligand [see the review in Ref. 8a].

As is commonly observed,<sup>8a</sup> the *syn*-conformation of the compound leads to the formation of centrosymmetric dimers via short Cu...Br contacts (see Figure 2 and Table 3). These interactions have the potential to provide a magnetic superexchange pathway. The dimers are further linked into a chain via the two-halide pathway, short Br... Br contacts, as also seen in Figure 2 (parameters in Table 3).



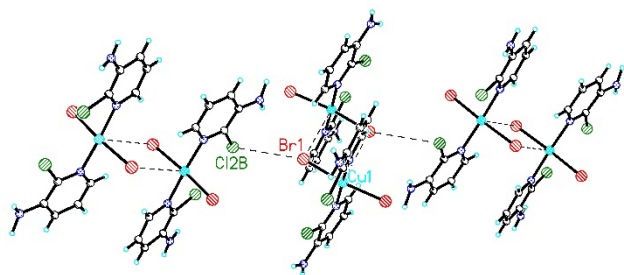
**Figure 2.** Chain formation via short Cu...Br and Br...Br contacts. Dashed lines represent Br...Br contacts and hydrogen bonds.

**Table 3.** Dihalide (a) and two-halide (b) superexchange pathway parameters from Figure 2.



Bond	d (Å)	$\theta$ (°)	$\tau$ (°)
Cu1-Br2... Br2B-Cu1b	4.379	112.5/112.5	180
Cu1-Br1...Cu1A	3.844	99.1	

The lattice is further stabilized via weak halogen bonds between the bromide ions and chloro substituents of the organic moieties ( $d_{\text{Br1}\dots\text{Cl2B}} = 3.821 \text{ \AA}$ ,  $\angle_{\text{Cu1-Br1}\dots\text{Cl2B}} = 159^\circ$ ) linking the dimers together into chains parallel to the *c*-axis.

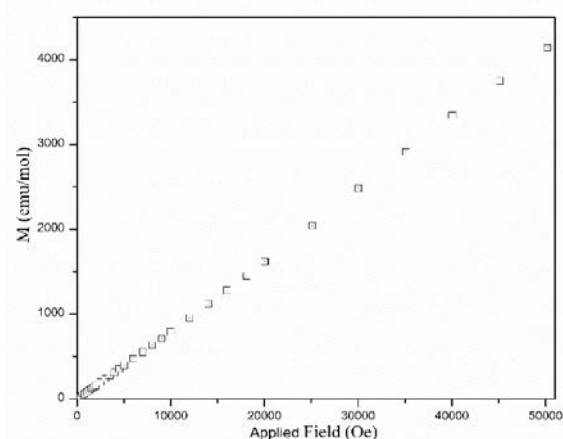


**Figure 3.** Halogen bonds in **1**.

### Magnetic Study

Magnetization data as a function of applied field for **1** (Figure 4) show a linear response through most of the measured region and reach just over 4,000 emu/mol at 50 kOe, slightly below the expected saturation magnetization of  $\sim 5,800 \text{ emu mol}^{-1}$  for a  $S=1/2$  system with *g* slightly greater than 2,

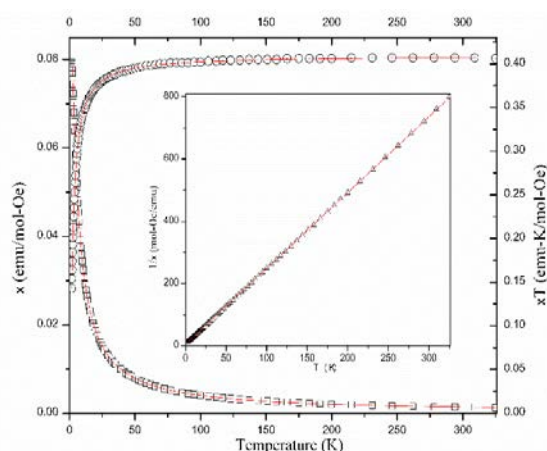
indicating the presence of weak antiferromagnetic interactions in the sample.



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

Magnetic susceptibility as a function of temperature is shown in Figure 5.  $\chi(T)$  shows a monotonic increase with decreasing temperature until below 3 K where a modest turn, but no maximum, is seen.  $\chi T(T)$  is more enlightening. The high temperature region suggests a Curie constant of slightly greater than 0.40. The downturn at low temperatures suggests weak antiferromagnetic interactions, in agreement with  $M(H)$ . The inset to Figure 5 shows the Curie-Weiss plot. The near zero intercept is again in agreement with weak antiferromagnetic interactions. The  $1/\chi(T)$  data above 10 K were fit to the Curie-Weiss model yielding  $C=0.410(2) \text{ emu K mol}^{-1} \text{ Oe}^{-1}$  and a Weiss constant ( $\theta$ ) of  $-1.90(6) \text{ K}$  (solid line in the inset to Figure 5).

A variety of models were used to fit the  $\chi(T)$  and  $\chi T(T)$  data including those for a dimer, a uniform chain and an alternating chain.<sup>16</sup> The best fit to the  $\chi(T)$  data was given by the uniform chain model which yielded a Curie constant of  $0.407(1) [0.409(2)] \text{ emu K mol}^{-1} \text{ Oe}^{-1}$  and an exchange constant, *J*, of  $-3.38(2) [-4.1(2)] \text{ K}$  with a paramagnetic impurity of  $0.7(1)\% [1.9(2)\%]$  (values in brackets were obtained from the fit of the  $\chi T(T)$  data to the uniform chain model).



**Figure 5.** Susceptibility data for **1** plotted as  $\chi(T)$  ( $\square$ , left axis) and  $\chi T(T)$  ( $\circ$ , right axis). The inset shows a plot of  $1/\chi(T)$ . The solid lines represent the best fits to the appropriate models (see text).



## DISCUSSION

Compound **1** crystallizes in the *syn*-conformation with a slight deviation of the Cu(II) coordination sphere from planarity. Although several N-coordinated complexes of 3-NH<sub>2</sub>-2-Clpy with tin and germanium have been reported,<sup>17</sup> only zinc complexes have been reported with first-row +2 transition metals.<sup>18</sup> As is frequently observed for 2-chloro-substituted pyridine ligands,<sup>8c,19</sup> the *syn*-conformation resulted in the formation of dimers via long Cu...X interactions, generating a dihalide superexchange pathway. A second interaction, via the two-halide pathway, was also possible (Figure 2) due to short intermolecular Br...Br contacts. However, attempts to fit the magnetic data to an antiferromagnetic dimer model, even with a Curie-Weiss correction for interdimer interactions via the two-halide pathway were unsuccessful; all attempts showed a maximum in  $\chi(T)$ , which was not observed in the data. This caused us to reexamine the structure and note that although the  $\theta$  angles (112.5°) are not optimal ( $\theta$  approaching 180° are best for exchange<sup>15</sup>), the  $\tau$  angle of 180° is an ideal value and the Br...Br distance is well within range for measurable magnetic interactions. Thus we attempted a fit of the magnetic data to the alternating  $S=1/2$  Heisenberg chain model<sup>16</sup> with fair results [Curie constant = 0.385(10) emu K mol<sup>-1</sup> Oe<sup>-1</sup>,  $J=-3.3$  K and 1.6 % paramagnetic impurity] except that the fitted value of  $\alpha$ , the ratio of the two exchange constants within the chain, was equal to 1.0(2). A value of  $\alpha=1$  would indicate that the chain is indeed a uniform chain and thus we attempted a fit to the uniform  $S=1/2$  Heisenberg chain model. To our surprise, the fit was excellent (Figure 5, main figure). This suggests that although the structural pathways are different (dihalide vs. two-halide) within the chain, the magnitude of the exchange via each pathway is accidentally equivalent within the error, leading to an 'apparent' uniform magnetic chain.

## CONCLUSIONS

We have successfully prepared and characterized the first coordination complex of 3-amino-2-chloropyridine with Cu(II). The compound adopts the *syn*-conformation and form alternating chains in the crystal via a combination of dihalide and two-halide bridges. Surprisingly, the variable temperature magnetic data are best fit by the uniform  $S = 1/2$  chain model, suggesting accidental equivalence of the two magnetic superexchange pathways. Further work on the coordination chemistry of the ligand is in progress.

## ACKNOWLEDGEMENTS

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CCDC 1996066 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](mailto:deposit@ccdc.cam.ac.uk).

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