

# Pyridine-based complexes of copper(II) chloride and bromide: ligand conformation effects on crystal structure. Synthesis, structure and magnetic behavior of $\text{Cu}(2\text{-Cl-3-X'py})_2\text{X}_2$ [X, X' = Cl, Br]

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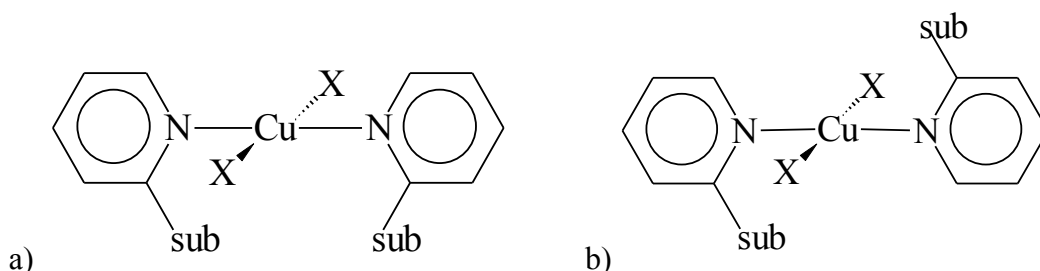
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**Abstract:** Reaction of copper(II) chloride or bromide with 2-chloro-3-bromopyridine (2 or 2,3-dichloropyridine) generates a family of compounds of the general formula  $\text{L}_2\text{CuX}_2$  (**1-4**). X-Ray crystallography shows that the bromide complexes (3-bromo-2-chloropyridine)dibromidocopper(II) (**1**) and (2,3-dichloropyridine)dibromidocopper(II) (**3**) are particularly unusual in that they crystallize with both the syn- and anti-conformation structures in the same crystal. A review of the literature on complexes of the formula (substituted-pyridine) $_2\text{CuX}_2$  suggests that these are the first examples of such complexes. The members of the family show a variety of magnetic behaviors and variable temperature magnetic susceptibility data indicate that **1** is essentially paramagnetic ( $\theta = -0.9(1)$  K) while **3** is weakly ferromagnetic ( $J = 2.9(1)$  K). Compound **2** [(3-bromo-2-chloropyridine)dichloridocopper(II)] is well fit by the uniform one-dimensional antiferromagnetic model ( $J = -19.6(1)$  K), while compound **4** [(2,3-dichloropyridine)dichloridocopper(II)] exhibits weak anti-ferromagnetic interactions ( $J = -3.68(3)$  K).

## INTRODUCTION

Transition metal complexes are very interesting regarding their magnetic properties and offer a wide field of study. Recent work on transition metal complexes in areas such as spin-crossover [1], single-molecule magnetism [2], the magnetocaloric effect [3] and magnetic nanoparticles [4] shows the continuing interest and potential in such materials. One interesting aspect of such complexes arises from their lattice properties such as local geometry and the presence of non-bonding interactions between molecular units such as hydrogen and halogen bonding. One particular family of these complexes is the pyridine-based copper(II) halide complexes [(sub-py) $_2\text{CuX}_2$ ; sub-py = substituted pyridine-based ligand, X = Cl, Br]. The azophilicity of the Cu(II) ion allows for a very wide variety of pyridine-based ligands, in terms of their electron-donating ability and steric requirements, to coordinate to the metal. The resulting compounds adopt two general forms; square planar and tetrahedral. Significant distortion of the tetrahedral geometry is observed in virtually all cases due to the Jahn-Teller effect.

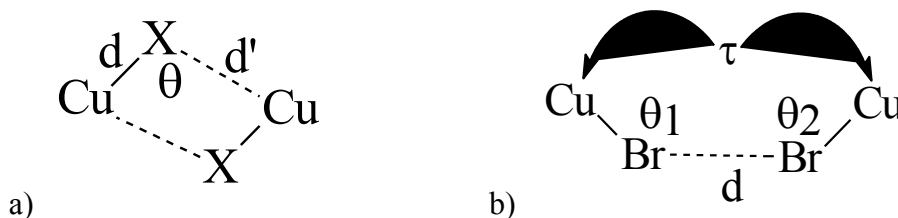
Within each of these coordination geometries, there also exists the possibility of conformational geometric differences with respect to the pyridine-based ligand if the ligand is non-symmetrically substituted. As illustrated in Figure 1, the substituents can adopt a conformation where the proximal substituents lie on the same face of the copper coordination plane (the syn-conformation, Fig. 1a) or on opposite faces of the copper coordination plane (the anti-conformation, Fig. 1b). For square planar complexes, the pyridine ligand is not observed to lie in the copper coordination plane in the absence of chelating ligands.



**Figure 1.** The a) syn- and b) anti-conformations of a (sub-py)<sub>2</sub>CuX<sub>2</sub> complex.

Although a truly tetrahedral complex would not have a ‘coordination plane,’ the Jahn-Teller distortion at Cu(II) is sufficient to make definition of a mean coordination plane unambiguous and thus the terminology is still useful for distorted tetrahedral systems.

We have been interested in this family of complexes for some time for the development of magnetostructural correlations [5]. There are two common superexchange pathways observed in these materials, the bi-halide pathway and the two-halide pathway (see Figure 2). In the bi-halide pathway, a bridge is formed between neighboring Cu(II) ions via a pair of bridging halide ions. The Cu-X distances within a bridge are generally not symmetric, but rather exhibit one traditional Cu-X bond and one semi-coordinate interaction of variable length. The important structural parameters are the Cu-X distances, the Cu-X-Cu angle and the planarity of the system [6]. In the two-halide pathway, magnetic exchange between neighboring Cu(II) ions is achieved via overlap of the van der Waals spheres of the halide ions. Here, the important structural parameters are the inter-halide distance, the Cu-X...X bond angles and the Cu-X...X-Cu torsion angle [7].



**Figure 2.** The a) bi-halide and b) two halide superexchange pathways. In the bi-halide pathway, the distances d and d', the angle (θ) and the planarity of the Cu<sub>2</sub>X<sub>2</sub> ring appear to control the superexchange. In the two-halide pathway, the distance (d), angles (θ<sub>1</sub> and θ<sub>2</sub>) and torsion angle (τ) are the important parameters in the superexchange pathway.

In the course of our studies, we observed that the two distinct conformations demonstrated by (sub-py)<sub>2</sub>CuX<sub>2</sub> complexes exhibited general trends in crystal packing which had a major effect on the likely magnetic superexchange pathways. This prompted an investigation of the known structures of the general formula (sub-py)<sub>2</sub>CuX<sub>2</sub> to see the extent to which the trends we had observed were generally obeyed. What follows is a review of the reported structures of this family of compounds and the relationship between their coordination geometry, ligand conformational geometry and resulting crystal packing. This is followed by a report of the synthesis and magnetic behavior of four new complexes of the general formula (2-Cl-3-X'pyridine)<sub>2</sub>CuX<sub>2</sub>; **(1)** bis(3-bromo-2-chloropyridine)dibromidocopper(II), **(2)** bis(3-bromo-2-chloropyridine)dichloridocopper(II), **(3)** bis(2,3-dichloropyridine)dibromidocopper(II) and **(4)** bis(2,3-dichloropyridine)dichloridocopper(II). To the best of our knowledge, compounds **1** and **3** are unique in the fact that each compound demonstrates two molecular units in the same crystal, one with the pyridine rings in the syn-conformation and the other with the pyridine rings in the anti-conformation.

## EXPERIMENTAL

2,3-Dichloropyridine, 3-bromo-2-chloropyridine, 1-propanol, acetonitrile and methanol were obtained from Aldrich Chemical Company. Copper(II) chloride dihydrate and copper(II) bromide were purchased from J.T. Baker. All materials were used as received. IR spectra were recorded via ATR on a Perkin-Elmer Spectrum 100 spectrophotometer. X-Ray powder diffraction measurements were carried out on a Bruker AXS-D8 X-ray Powder Diffractometer. Elemental analyses were conducted at the Marine Science Institute, University of California, Santa Barbara CA 93106.

### **Bis(3-bromo-2-chloropyridine)dibromidocopper(II) (1).**

Copper(II) bromide (0.120 g, 0.5 mmol) was dissolved in 10.0 ml of methanol resulting in a dark red solution. 3-Bromo-2-chloropyridine (0.195 g, 1.0 mmol) was then dissolved in 5.0 ml of methanol resulting in a colorless solution. The ligand solution was added to the copper(II) bromide solution dropwise with stirring. The resulting solution was left to evaporate slowly on the desktop. Four days later, the solvent had completely evaporated. The resulting mass of black crystals was slurried with methanol and the crystals isolated by vacuum filtration in 43.4 % yield (0.132 g). IR: 3086 w, 1598 m, 1577 m, 1450 w, 1428 s, 1272 m, 1245 m, 1217 s, 1119 m, 1060 , 858 w, 806 s, 720 s, 702 s. CHN for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>Cl<sub>2</sub>Br<sub>4</sub>Cu, found(calc.): C, 19.70(19.73); H, 1.01(0.99); N, 4.56(4.61).

**Bis(3-bromo-2-chloropyridine)dichloridocopper(II) (2).**

3-Bromo-2-chloropyridine (0.191 g, 1.0 mmol) was dissolved in 4.0 ml of 1-propanol. Copper(II) chloride dihydrate (0.089 g, 0.50 mmol) was dissolved in 4.0 ml of 1-propanol to give a light green solution. The copper(II) chloride dihydrate solution was added dropwise to the ligand solution with stirring and the resulting solution was left for slow evaporation. After 16 days, a mixture of green crystals and re-crystallized 3-bromo-2-chloropyridine was observed. The mixture was slurried in a small amount of 1-propanol to dissolve the unreacted ligand and quickly vacuum filtered to give green crystals of **2** in 32% yield (0.084 grams). IR: 3086 w, 1577 s, 1424 w, 1394 s, 1155 m, 1049 s, 803 s, 753 m, 714 s, 678 m. CHN for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>Cl<sub>2</sub>Br<sub>4</sub>Cu, found (calc.): C, 22.67(23.13); H, 1.14(1.16); N, 5.53(5.28).

**Bis (2,3-dichloropyridine)dibromidocopper(II) (3)**

Copper(II) bromide (0.111 g, 0.50 mmol) was dissolved in 10.0 ml of 1-propanol with warming resulting in a dark red solution. 2,3-Dichloropyridine (0.148 g, 1.0 mmol) was then dissolved in 4.0 ml of 1-propanol. The 2,3-dichloropyridine solution was then added to the copper(II) bromide solution. The solution was left on the desktop for slow evaporation. After 14 days, a mass of black thin rectangular crystals were present in a minimal volume of solution. These crystals were isolated by vacuum filtration and washed with a small amount of 1-propanol to give a 62.8 % yield (0.163 g). IR: 3089 w, 3068 w, 1590 w, 1578 m, 1555 w, 1429 w, 1412 m, 1399 s, 1255 w, 1221 m, 1165 s, 1128 w, 1075 s, 1035 w, 985 w, 938 w, 806 s, 792 s, 774 m, 716 s 691 m. CHN for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>OCl<sub>4</sub>Br<sub>2</sub>Cu, found (calc.): C, 22.85(23.13); H, 1.00(1.16); N, 5.20(5.39).

**Bis (2,3-dichloropyridine)dichloridocopper(II) (4).**

2,3-Dichloropyridine (0.248 g, 1.7 mmol) was dissolved in 15.0 ml of acetonitrile with warming. Copper(II) chloride dihydrate (0.153 g, 0.9 g) was added directly, resulting in a brown solution after stirring for ca. 10 minutes. The solution was then allowed to evaporate slowly at room temperature. After eight days a mass of dark black crystals were present in solution which were isolated via vacuum filtration and washed with a small amount of acetonitrile to give a 34.5% yield (0.132 g). IR: 3093 w, 3075 w, 1581 m, 1556 w, 1407 s, 1250 w, 1225 m, 1163 m, 1071 s, 991 w, 948 w, 806 s, 775 w, 718 s, 687 m. CHN for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>Cl<sub>6</sub>Cu, found (calc.): C, 20.83(21.27); H, 1.03(1.03); N, 4.82(4.96).

**Magnetic data**

Magnetic data for compounds **1** - **4** were collected using a Quantum Design MPMP-XL SQUID magnetometer. Powdered crystalline samples were loaded in a gelatin capsule which was then placed in a straw and mounted in the instrument. Magnetic moments were measured between 0 and 50 kOe at 1.8

K. In order to determine if hysteresis was present, several data points were collected as the magnetic field returned to 0 kOe. No hysteresis was observed.  $M(H)$  for all samples was linear to at least 3 kOe. Magnetization was then measured between 1.8-310 K in an applied field of 1.0 kOe. Background corrections for the gelatin capsule and straw (measured independently) and the diamagnetic contributions of the constituent atoms (estimated via Pascal's constants [8]) were made. After magnetic measurements, powder X-ray diffraction was carried out on all SQUID samples and compared to the single crystal structure to confirm the phase of the complexes matched the single crystal structure for **1-3**; no impurities were detected.

### Single-crystal X-ray diffraction data

Data collections were carried out on a Bruker D8 Venture diffractometer fitted with a Photon 100 CMOS detector employing graphite-monochromated Mo-K $\alpha$  radiation, using  $\varphi$  and  $\omega$  scans. Using the SAINT+ software [9], the data were reduced and absorption corrections were made using the SADABS program [10]. Structure solution was carried out using the program SHELXS-97 [11] while refinements were performed using SHELXL-2014 [12]. Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically calculated positions and refined as a riding model with fixed isotropic thermal displacement parameters,  $U_{iso}(H) = 1.2 U_{eq}(C, N)$ . Crystallographic information for compounds **1** and **3** can be found in Table 1. Single crystal X-ray data was collected multiple times on crystals of **2**. All data collections resulted in the same crystal parameters, but the crystals were unstable and diffracted poorly. Although the general coordination environment of the Cu(II) ion and conformational geometry of the complex was clear, suitable refinements could not be obtained (minimum  $R_1 \sim 14\%$ ). We report here only the cell constants [13] and general geometry of the complex. The structures of **1** and **3** have been deposited with the CCDC as deposit numbers: 1896820, **1**; 1896822, **3**.

**Table 1:** Crystal data for compounds **1** and **3**.

	<b>1</b>	<b>3</b>
Empirical Formula	C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> Br <sub>4</sub> Cl <sub>2</sub> Cu	C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> Br <sub>2</sub> Cl <sub>4</sub> Cu
MW	608.25	519.33
T(K)	150(2)	150(2)
Wavelength(Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a (Å)	18.9530(17)	18.9284(16)
b (Å)	6.3155(6)	6.2543(5)

c (Å)	26.124(2)	25.695(2)
A(°)	90.00	90
$\beta$ (°)	96.279(4)	97.997(4)
$\gamma$ (°)	90.00	90
V (Å <sup>3</sup> )	3108.2(5)	3012.3(4)
Z	8	8
Abs. coeff. (mm <sup>-1</sup> )	12.018	7.449
F(0,0,0)	2264	1976
$\Theta$ range (°)	2.53 to 31.54	2.17 to 33.16
Index ranges	-26 ≤ h ≤ 26	-28 ≤ h ≤ 28
	-9 ≤ k ≤ 9	-9 ≤ k ≤ 9
	-37 ≤ l ≤ 37	-39 ≤ l ≤ 39
R <sub>fln</sub> total	56485	85614
Ind. rfln (R <sub>int</sub> )	4732 (0.1019)	5749 (0.0904)
Data/Res./para.	4732/ 0 / 174	5749/ 0 / 174
Final R index [I>2σ(I)]	R <sub>1</sub> =0.0448; wR <sub>2</sub> =0.1002	R <sub>1</sub> =0.0399 wR <sub>2</sub> =0.0874
R index (all data)	R <sub>1</sub> =0.0602; wR <sub>2</sub> =0.1051	R <sub>1</sub> =0.0540; wR <sub>2</sub> =0.0928
Largest peak(hole) (e/Å <sup>3</sup> )	1.294 (-1.109)	1.181 (-1.135)

**Table 2:** Bond Lengths (Å) and angles (°) for **1** and **3**.

Compound	<b>1</b>	<b>3</b>
Bond Lengths	Å	Å
Cu1-Br1	2.4207(4)	2.4132(3)
Cu2-Br2	2.3940(5)	2.3867(4)
Cu1-N11	1.985(3)	1.987(2)
Cu2-N21	2.006(3)	2.009(2)
Bond Angles	°	°
Br1-Cu1-Br1A	180.00	180.00
Br2-Cu2-Br2B	143.77(4)	145.32(3)
N11-Cu1-N11A	180.00	180.00
N21-Cu2-N21B	161.0(2)	162.09(15)
N11-Cu1-Br1	91.02(10)	90.99(7)
N21-Cu2-Br2	91.36(9)	91.39(7)
N21-Cu2-Br2B	94.53(9)	93.94(7)

Symm. Op. A: 1.5-x, 1-y, -z; B – 1-x, y, 0.5-z.

**Table 3:** Comparison of two-halide superexchange parameters of **1** and **3**

	<b>1</b>	<b>3</b>
X···X distance (Å)	4.945	4.912
Cu-X···X angle (°)	80.4°	79.9°

**Table 4:** Comparison of bi-bridged chain parameters of **1** and **3**

	<b>1</b>	<b>3</b>
X···Cu distance (Å)	5.192	5.079
Cu-X···Cu angle (°)	108.1°	107.8°

## RESULTS AND DISCUSSION

### Literature review of compounds with the general formula (sub-py)<sub>2</sub>CuX<sub>2</sub>:

*Criteria used for the selection of compounds:*

A search of the Cambridge Crystallographic Database [14] was conducted using the following search parameters:

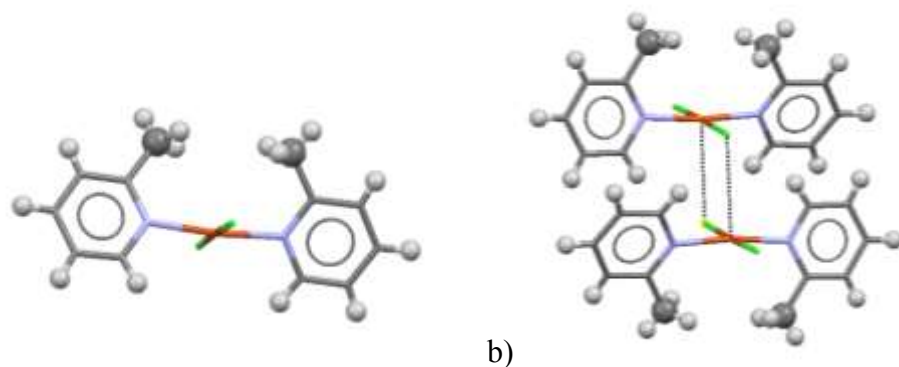
- Copper(II) complexes with two coordinated halide ions (no restriction on the identity of the halide ion) and two coordinated pyridine-based moieties (those containing a pyridine ring bonded through the N-atom to the Cu(II) ion). No restrictions were placed on the coordination number of the Cu(II) ion to allow for the possibility of bridging halide ions. However, complexes with bridging or chelating pyridine-based substituents were not generally included in the final list as they restricted the geometry of the copper coordination sphere, virtually always generating cis-configurations in the case of chelating ligands. Some exceptions were included (*vide infra*) as they represented particular and unusual coordination spheres within the general constraints. Further, all examples found were either copper(II) chloride or bromide complexes. We assume that this arises due to the generally poor solubility of copper(II) fluoride complexes, making crystallization and purification difficult, and the observation that iodide ion tends to reduce Cu(II) to Cu(I), although some exceptions are known.
- Complexes with more than four independent ligands were not included in the final selections as they restricted the ability of the complex to adopt either syn- or anti-geometries and reduced/prevented the complexes from developing bridging halide ion linkages.
- Complexes with excessively large substituents on the pyridine ring were not generally included as the final crystal packing could be controlled solely by the steric bulk and/or additional interactions between the ancillary groups (intermolecular) rather than by the central core of the complex.

d) Only square-planar compounds, or mildly distorted square-planar compounds, were considered as the lack of a well-defined coordination plane renders the definition of the syn- and anti-geometries moot.

In all, 101 compounds were identified and categorized based on the conformational geometry of the pyridine substituents (syn or anti) and the nature of the connectivity between molecular units (bihalide bridged chain, two-halide bridged chain, bihalide bridged dimer) if any. The following discussion is organized by the substitution pattern on the pyridine moiety and then, within each of those categories, by the nature of the conformation about the Cu(II) ion and type of intermolecular interaction.

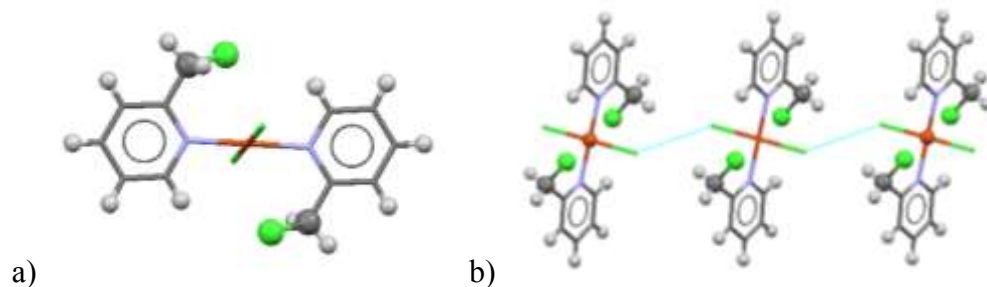
### 1) 2-Substituted pyridine moieties.

A significant number of copper(II) halide complexes have been reported where the pyridine moiety contains a single substituent in the 2-position. The syn/anti conformations of rings with a substituent in the 2-position and no substituent in the 6-position are perhaps the most likely to be affected by steric considerations because the difference between the two sides of the pyridine ring, close to the metal center, is the most distinct and most likely to be controlled by direct interactions between the substituents. In this category we find simple alkyl substituted pyridine moieties such as bis(2-methylpyridine)dichloridocopper(II)<sup>15</sup> and bis(2-methylpyridine)dibromidocopper(II).<sup>16</sup> In both cases, the complexes crystallize as the syn-conformers (see Fig. 3a),<sup>17</sup> although the ligands are not co-planar (due to steric repulsions between the methyl substituents). Syn-conformation molecules may form dimeric structures via short Cu...Cl contacts (3.382 Å) as observed in these molecules (Fig. 3b). One face of the molecule is blocked by the 2-substituents, effectively preventing close contact to a neighboring molecule on that face, but the other is free and this is the most common intermolecular structural synthon in such molecules if the metal geometry is planar (*vide infra*).



**Figure 3.** a) A model of bis(2-methylpyridine)dichloridocopper(II)<sup>1515</sup> showing the syn-ligand conformation. b) The dimer structure formed by short Cu...Cl contacts.

Increasing the size of the attached group by adding substituents to the methyl group can reverse the conformation as seen in the anti-conformation of bis(2-(chloromethyl)pyridine)dichloridocopper(II) (Fig. 4a).<sup>18</sup>

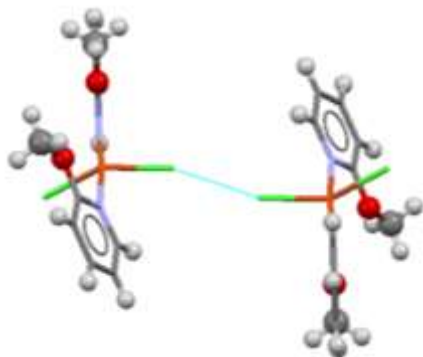


**Figure 4.** a) A of bis(2-(chloromethyl)pyridine)dichloridocopper(II)<sup>18</sup> showing its anti-conformation. b) Chain formation via the two-halide pathway.

The syn-conformation is presumably higher in energy due to the increased steric pressure of the larger substituent (compared to the simple methyl group) and the electrostatic repulsion of the chloro-groups. The geometry of the complex would make formation of a stabilizing halogen bond difficult. Given this, it is not at all surprising that bis(2-benzylpyridine)dibromidocopper(II) also adopts the anti-conformation.<sup>19</sup> Both of these molecules form intermolecular chains via the two-halide pathway as shown in Figure 4b, with X...X distances near 4.0 Å and 4.6 Å for the chloromethyl and benzyl substituted compounds, respectively.

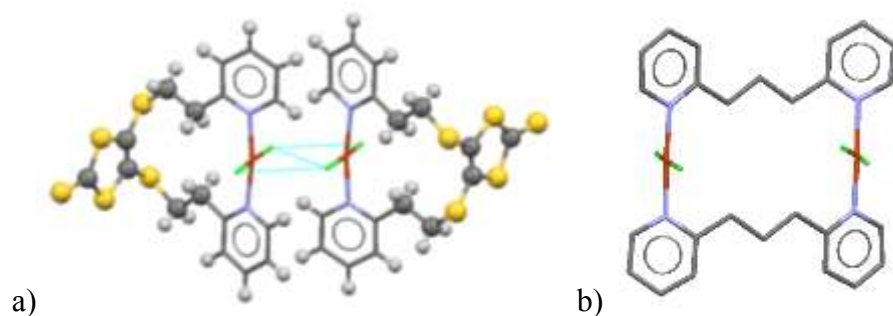
Replacement of the 2-substituent with a halogen atom provides similar results. The bis(2-chloropyridine)X<sub>2</sub>Cu (X = Cl, Br) complexes crystallize in the syn-conformation<sup>20</sup> and forms dimers similar to the 2-methylpyridine complexes (Figure 3) with intra-dimer Cu...X contacts of 2.956 Å and 3.710 Å for the chloride and bromide compounds, respectively. The corresponding 2-bromopyridine compounds, with the slightly larger bromine substituent, adopt the anti-conformation<sup>21</sup> (similar to the 2-chloromethyl compound), but while the CuCl<sub>2</sub> complex forms weak chains via the two-halide pathway (X...X ~ 4.6 Å), the bromide equivalent shows no such contacts at distances < 5.0 Å.

The methoxy-substituted compound bis(2-methoxypyridine)dichloridocopper(II) provides a somewhat unusual example in the 2-substituted complexes.<sup>22</sup> The complex crystallizes in the syn-conformation, but with a distinct distortion from planarity; the mean trans angle for the substituents is 151° with the Cl-Cu-Cl angle being the larger of the two (Figure 5). Interestingly, the molecule still forms dimers as is common in the case of syn-conformation compounds, but via the two-halide pathway (Cl...Cl = 3.69 Å), rather than the bihalide pathway. These contacts only link molecules into pairs and do not generate a more extended motif.



**Figure 5.** Two molecules of bis(2-methoxypyridine)dichloridocopper(II) showing the distorted planar geometry at the metal ion and the two-halide linkage, forming dimers.

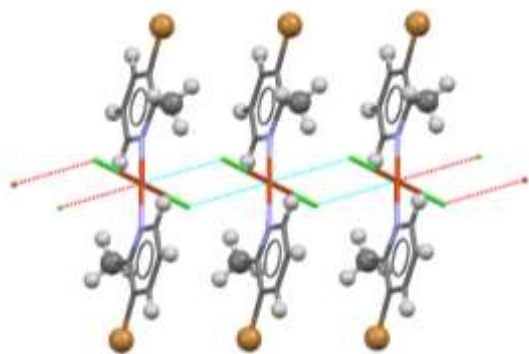
Finally, in the 2-substituted pyridine category, it is worth mentioning a small number of di-pyridyl compounds where the bridge between the pyridine rings is long enough to permit the formation of either cis- or trans-configurations. Most of the reported complexes show trans-configurations with syn-conformations<sup>23</sup> (as expected due to the chelation effect) and generate bihalide-bridged dimers with the opposite face blocked by the bridge linking the two pyridine rings [trans-dichlorido-(4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-thione)copper(II)<sup>23b</sup> is shown as an example in Figure 6a]. However, in the case of bis[dichlorido-( $\mu$ 2-1,3-di(2-pyridyl)propane-N,N')-copper(II)]<sup>24</sup>, the 1,3-dipyridylpropane ligands bridge between pairs of copper chloride units, holding the Cu(II) ions more than 7 Å apart in a pseudo-syn conformation (Figure 6b). A complex layer network is then formed by short two-halide contacts between the chloride ions.



**Figure 6.** a) The dimeric structure of trans-dichlorido-(4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiole-2-thione)copper(II). b) The structure of bis[dichlorido-( $\mu$ 2-1,3-di(2-pyridyl)propane-N,N')-copper(II)].

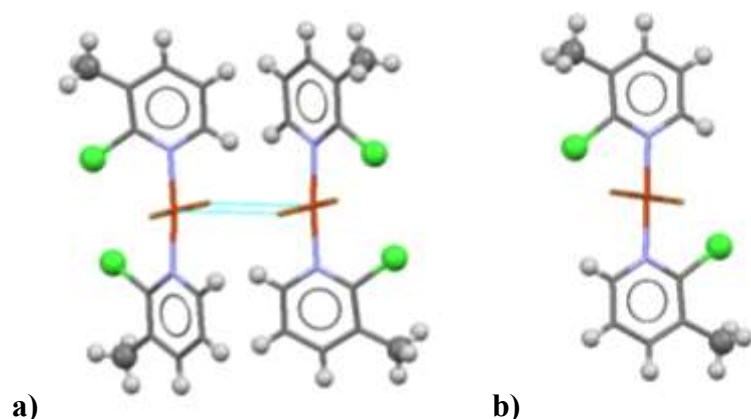
We will now consider complexes with 2,n-substitution on the pyridine ring, where  $n \neq 6$ . With respect to the interactions near the metal center, these compounds may be expected to behave similarly to their 2-substituent counterparts, but intermolecular interactions may be quite different due to the ancillary groups. A significant number of 2,3-disubstituted pyridine-based complexes have been reported. The

bis(2,3-dimethylpyridine) $X_2Cu$  complexes ( $X = Cl, Br$ ) both crystalize as anti-conformers,<sup>25</sup> but no halide...halide or metal...halide contacts link the molecules into more extended motifs. Although these are the only reported 2,3-dialkylpyridine compounds, a number of compounds with one methyl group and one halogen have been reported. The bis(2-methyl-3- $X'$ -pyridine) $X_2Cu$  complexes with  $X, X' = Br, Cl$  are known.<sup>26</sup> Of these, only the  $X' = Cl, X = Cl$  compound crystalizes in the syn-conformation and it forms the expected bihalide bridged dimer with  $Cu...Cl = 2.727 \text{ \AA}$ . The remaining three complexes crystalize in the anti-conformation and all form bihalide bridged chains with  $Cu...X$  distances between 4.3-4.7  $\text{\AA}$  (Figure 7).



**Figure 7.** Bihalide-bridged chain structure of bis(3-bromo-2-methylpyridine)dichloridocopper(II).

Reversing the positions of the substituents generated a very similar family of complexes, but with its own variations.<sup>27</sup> Bis(2-chloro-3-methylpyridine)dichloridocopper(II) crystalizes in the syn-conformation and forms the expected bihalide bridged dimeric structure ( $Cu...Cl = 3.579 \text{ \AA}$ ), while the bis(2-bromo-3-methylpyridine) $X_2copper(II)$  ( $X = Br, Cl$ ) compounds are both in the anti-form with the bromide compound forming two-halide bridged chains ( $Cu...Br = 4.482 \text{ \AA}$ ) and the chloride analogue failing to exhibit such intermolecular contacts. The most interesting member of this family is the bis(2-chloro-3-methylpyridine)dibromidocopper(II) complex which exhibits polymorphs where one is in the syn-conformation while the other is anti (Figure 8). Crystals of the syn-complexes exhibit the typical dimeric structure ( $Cu...Br = 3.579 \text{ \AA}$ ), while those of the anti-conformation form two-halide bridged chains ( $Br...Br = 4.505 \text{ \AA}$ ).



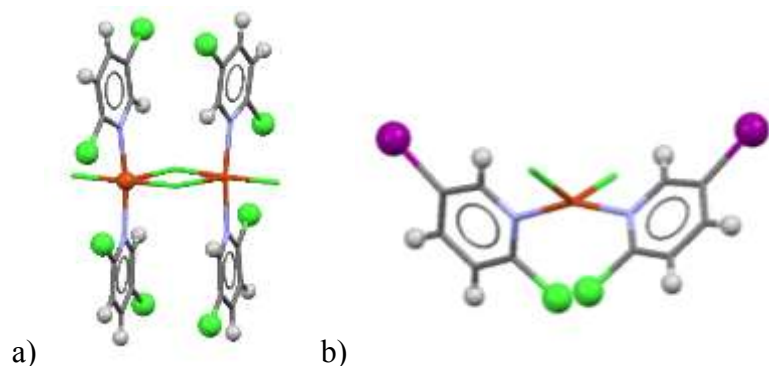
**Figure 8.** The a) syn- and b) anti-polymorphs of bis(2-chloro-3-methylpyridine)dibromidocopper(II).

2,3-Dihalopyridinecopper(II) complexes are rare, but bis(2-chloro-3-fluoropyridine)dibromide-copper(II) has been recently reported.<sup>28</sup> The molecules are not linked via either the bihalide or two-halide pathways, but do form chains via pairs of halogen-halide bonds between the chlorine substituents and the bromide ions.

2,3-Disubstituted pyridine complexes with larger substituents, such as phenyl,<sup>19</sup> are also known and form anti-conformers without significant halide/metal contacts between molecules. Systems with a second ring, fused to the 2,3-carbon atoms of the pyridine ring, also fall into this category, such as azafluorenones,<sup>29</sup> 4,5-diazafluorenes,<sup>30</sup> (although here there is some question whether the distal N-atom is weakly coordinated to the Cu(II), making the complex pseudo-octahedral) and azaindoles.<sup>31</sup> In all cases, the compounds crystallize in the anti-conformation and either pack as isolated molecules, or form extended motifs via the two-halide pathway.

Although we did not find any 2,4-disubstituted pyridine complexes which fit the search criteria, there are a number of 2,5-disubstituted compounds. As with the 3-substituents, one would not expect a 5-substitution group to have a significant effect on the local environment of the Cu ions, but it may cause changes in the crystal packing which could then affect the coordination sphere. A substantial number of 2,5-dihalopyridine copper(II) halide complexes have been reported with homo- and hetero-halogen substitution including fluoro, chloro, bromo and iodo substituted compounds in some cases with multiple temperature X-ray data available.<sup>32</sup> The vast majority of these complexes crystallize as halide bridged dimers of nearly square pyramidal Cu(II) ions, with the 2-halo substituents in the syn-conformation on a single metal ion (Figure 9a). Bis(2-chloro-5-(chloromethyl)pyridine)dichloridocopper(II) observes this

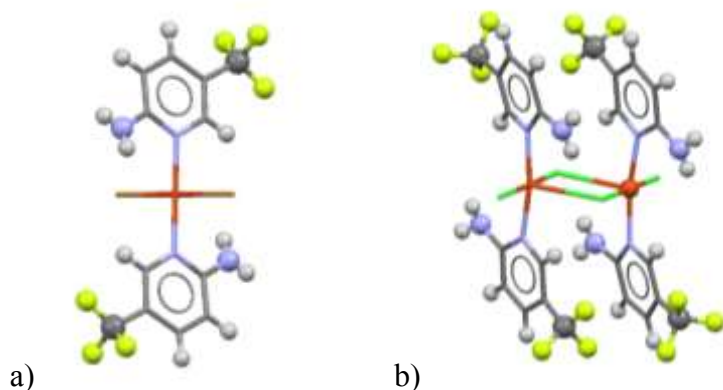
trend as well.<sup>33</sup> However, several of the complexes show significant distortions toward tetrahedral geometry (Figure 9b). In these cases, the dimer structure does not form and intermolecular interactions take place predominately through the two-halide pathway.



**Figure 9.** a) The dimeric structure of bis( $\mu$ -chloro)-dichlorido-tetrakis(2,5-dichloropyridine)-di-copper(II).<sup>32b</sup> b) The structure of dichlorido-bis(2-chloro-5-iodopyridine)-copper(II).<sup>32a</sup>

Here again, we see the existence of polymorphs for some of the compounds with the anti-conformer also known. This is true for bis(2-bromo-5-fluoropyridine)dichloridocopper(II), bis(2,5-dichloropyridine)dichloridocopper(II) and bis(5-bromo-2-chloropyridine)dichloride-copper(II).<sup>32</sup> The intermolecular contacts for these compounds occur via the two-halide pathway. Bis(2-chloro-5-methylpyridine)dichloridocopper(II) crystallizes in the same pattern.<sup>34</sup>

The copper chloride and bromide complexes of 2-amino-5-trifluoromethylpyridine provide an excellent example of the diversity that arises from the plasticity of the Cu(II) ion.<sup>35</sup> The bromide complex crystallizes in the anti-conformation (Figure 10a) and exhibits the formation of bihalide-bridged chains (similar to that shown in Figure 7), one of the common motifs for anti-conformation complexes. The chloride compound, however, provides a rare example of an anti-conformation compound which crystallizes as bihalide bridged dimers (Figure 10b). While for most anti-conformation molecules, the interactions between the pyridine substituents lead to destabilization of the dimer structure in favor of the more separated bibridged chains (greater X...Cu distances), the possibility of halogen bonding across the dimer exists between the fluorine substituents (shortest F...F distance is 2.99 Å) which may explain the stability of this unique compound.



**Figure 10.** The a) bromide and b) chloride copper(II) complexes of 2-amino-5-trifluoromethylpyridine.

We also note one example of a  $(2,5\text{-disubstitutedpyridine})_2\text{CuCl}_2$  complex which is perhaps best described as distorted square-planar, but where the pyridine ligands are *cis*, rather than *trans*.<sup>36</sup> This very uncommon configuration likely arises from the very bulky substituents on the pyridine ring (the ligand is ethyl 6-((4,4-dimethyl-3,4-dihydro-2H-thiochromen-6-yl)ethynyl)nicotinate). Possibly due to the length of the ligand, steric repulsions between molecules override the normal steric constraints at the metal center, which result in the bulk of members of this group of compounds having *trans*-configurations.

Finally, a small family of 2,3,5-substituted pyridine complexes have been reported. The four bis(2-amino-3,5- $\text{X}'_2$ pyridine) $_2\text{CuX}_2$  compounds ( $\text{X}, \text{X}' = \text{Cl}, \text{Br}$ )<sup>37</sup> all crystallize in the *anti*-conformation and pack into chains via bihalide linkages with  $\text{Cu}\dots\text{X}$  distances of  $\sim 3.0$  Å for the copper chloride complexes and  $\sim 4.1$  Å for the copper bromide complexes. The copper bromide and copper chloride complexes of 2-amino-5-chloro-3-fluoropyridine, however, show different coordination conformations and structures.<sup>38</sup> The  $\text{CuCl}_2$  complex crystallizes in the *anti*-conformation and generates halide bibridged chains ( $\text{Cu}\dots\text{Cl} = 2.97$  Å), similar to the 2-amino-3,5- $\text{X}'_2$ pyridine complexes, while the bromide analogue occurs in the *syn*-conformation and generates bibromide bridged dimers similar to Figure 8a ( $\text{Cu}\dots\text{Br} = 2.67$  Å). In the latter case, fluorine-fluorine halogen bonds ( $\text{F}\dots\text{F} = 3.1$  Å) further link the dimers into chains.

A small group of compounds have been reported with substituents in both the 2- and 6-positions (and more substituents in some cases) and as one might expect, the severe steric crowding around the metal center substantially reduces the possibilities for interactions. Dibromido- and dichloridobis(2,6-dimethylpyridine)copper(II) are both known<sup>39</sup> and while the bromide complex exhibits weak interactions via the two-halide pathway ( $\text{Br}\dots\text{Br} = 4.86$  Å), no such interactions are seen in the chloride analogue.  $(2,4,6\text{-Trimethylpyridine})_2\text{CuCl}_2$ <sup>40</sup> also exhibits weak interactions via the two-halide pathway ( $\text{Cl}\dots\text{Cl} =$

4.81 Å) while dichloridobis(2,6-dimethyl-3,5-dimethoxycarbonyl-4-(2-nitrophenyl)pyridine)copper(II)<sup>41</sup> shows no potential interactions between the metal centers.

Pyridine compounds that lack a substituent in the 2-position can still adopt syn- or anti-conformations as long as the substitution is not symmetric. In all cases of 3-substituted pyridine ligands that we found, the configuration at the metal center was uniformly trans and they crystalize in the anti-conformation. Virtually all of these compounds generate halide bibridged chains with Cu...X distances ranging from ~2.85 - 3.2 Å for copper chloride complexes<sup>32a,42</sup> and ~3.1 - 3.3 Å for copper bromide complexes.<sup>43</sup> The same trend is observed for the bis(isoquinoline)CuBr<sub>2</sub> complex (3,4-disubstituted by the ring fusion).<sup>5d</sup> In the case of bis(3-pyridinecarbonitrile)CuBr<sub>2</sub>, the shortest intermolecular contacts form weak chains via the two-halide pathway<sup>44</sup> and dichlorido-bis(4,4,5,5-tetramethyl-2-(pyridin-3-yl)-4,5-dihydro-imidazole-1-oxyl-3-oxide)copper(II)<sup>45</sup> forms chloride bibridged dimers (Cu...Cl = 2.67 Å) in spite of the apparent interactions between the bulky tetramethylimidazole substituents.

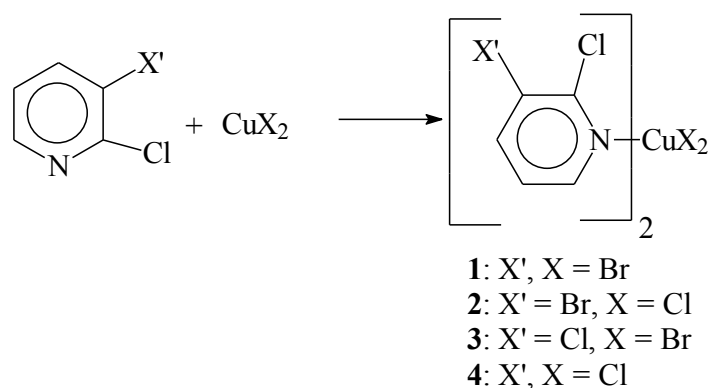
Symmetrically substituted pyridine ligands cannot adopt syn- or anti-conformations as rotation about the Cu-N bond produces a degenerate structure. However, some simple trends are observed in terms of the extended structural motifs that are worthy of brief mention here. The simplest members of this group are the copper chloride and bromide complexes of pyridine itself.<sup>46</sup> Both complexes form bihalide bridged chains with the chloride analogue having closer Cu...X contacts (2.98 Å) than the bromide (3.20 Å) as expected. Simple substituents, such as alkyl,<sup>47</sup> cyano<sup>48</sup> and halo<sup>49</sup> groups, in the 4-position on the pyridine ring all show the same type of structural packing between the molecular units. Dichloridobis(4-dimethylaminopyridine)copper(II)<sup>50</sup> is an exception to this pattern and generates bichloride bridged dimers without extension into a chain structure.

A number of 4-pyridinecarboxylic acid complexes and derivatives thereof have been reported. The parent molecule, dichloridobis(pyridine-4-carboxylic acid)copper(II) serves as a model compound for most of this family, crystallizing in a square-planar geometry and generating bihalide bridged chains through short Cu...Cl contacts (2.90 Å).<sup>42b</sup> Derivatives at the carboxylate function that follow the same packing motif include esters<sup>51</sup> and amides.<sup>35,47c,52</sup> Compounds with large substituents in the 4-position tend to crystallize as isolated molecular units lacking both bihalide and two-halide connections<sup>53</sup> although dichlorido-bis(2-pyridyl(4-pyridyl)methanone)-copper(II)<sup>54</sup> forms bihalide bridged chains. Dichlorido-bis(2,3,4,5,6-pentafluoro-N-(pyridin-4-yl)benzamide)copper(II)<sup>55</sup> provides another example where two different polymorphs are known which have unique packing arrangements. Both forms crystallize in the trans-configuration, but while one forms extended chains via the two-halide pathway (Cl...Cl =

4.03 Å), the other generates halide bibridged dimers which may be stabilized by halogen bonds between fluorine atoms on adjacent perfluorophenyl rings within the dimers (F...F = 2.92 Å). Two 3,5-disubstituted pyridine complexes in this category have been reported. Dibromidobis(3,5-dimethyl)copper(II) form chains via bibromide bridges (Cu...Br = 3.29 Å)<sup>56</sup> while the packing of bis(4-(*t*-butyl(oxido)azanyl)-3,5-dichloropyridine)dichloridocopper(II) does not produce significant potential superexchange interactions between the metal coordination spheres.<sup>57</sup>

### Synthesis and structure of bis-2,3-dihalopyridinedihalidocopper(II) complexes:

Reaction of one equivalent of  $\text{CuX}_2$  with two equivalents of 3- $\text{X}'$ -2-chloropyridine, where  $\text{X}'$  is chlorine or bromine, produced four compounds; (3-bromo-2-chloropyridine)<sub>2</sub>CuBr<sub>2</sub> (**1**), (3-bromo-2-chloropyridine)<sub>2</sub>CuCl<sub>2</sub> (**2**), (2,3-dichloropyridine)<sub>2</sub>CuBr<sub>2</sub> (**3**) and (2,3-dichloropyridine)<sub>2</sub>CuCl<sub>2</sub> (**4**). Good quality crystals of **1** and **3** were isolated from the reaction mixture for single x-ray diffraction data collection. Only poor quality crystals of **2** were obtained after multiple attempts using a variety of techniques and solvents and no crystals of **4** of X-ray quality could be prepared in our hands.

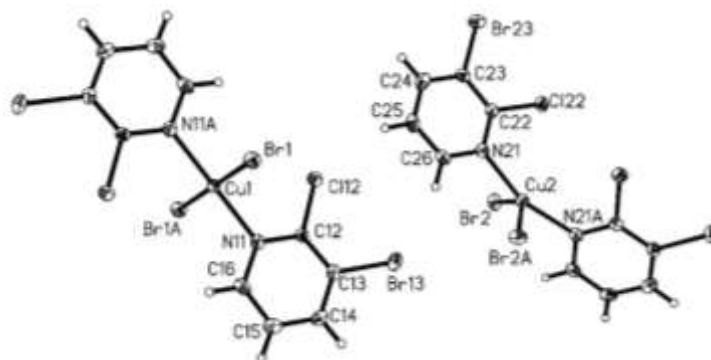


**Figure 11.** Preparation of compounds 1-4.

### X-ray Structure of Bis(3-bromo-2-chloropyridine)dibromidocopper(II)(1).

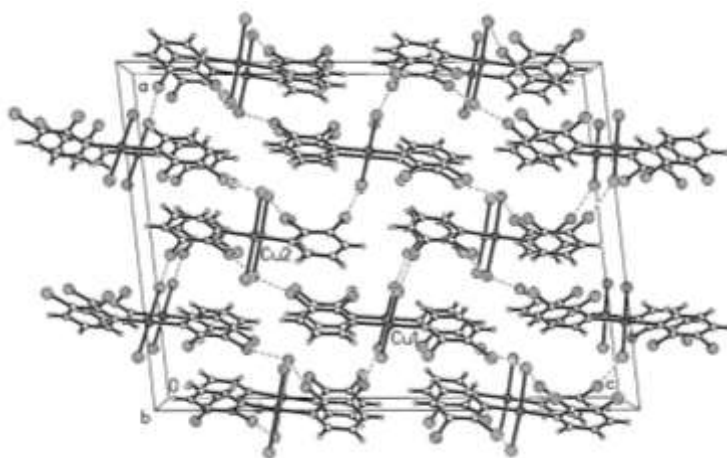
Compound **1** crystallizes in the monoclinic space group  $C2/c$ . The molecular unit is shown in Figure 12. Two independent molecules are seen in the unit cell, one in the anti-conformation (Cu1) and one in the syn-conformation (Cu2). Selected bond lengths and angles are given in Table 2. The Cu1 ion sits on an inversion center, creating a planar coordination environment and forcing trans bond angles to be  $180^\circ$  as required by symmetry; the Br1-Cu1-N11 angle is  $91.02(0)$ . The pyridine rings are nearly planar with a mean deviation of the constituent atoms of  $0.0044 \text{ \AA}$ . They are inclined  $78.1^\circ$  relative to the Cu1 coordination plane. Cu2 sits on a two-fold rotation axis and adopts a highly distorted tetrahedral environment with a mean trans angle [7] of  $152.4^\circ$ . The two independent N-Cu-Br angles are just over  $90^\circ$ . The N21-pyridine rings are only slightly less planar (mean deviation =  $0.0116 \text{ \AA}$ ) than seen for the N11 ring

ligands and adopt a syn-conformation. The N21 and N21A rings are canted 60.1° relative to each other, presumably to reduce steric hindrance between the halogen substituents. The Cu-Br and Cu-N distances are within the normal parameters for copper(II) bromide and copper(II) pyridine bond lengths as described in the literature review (vide supra).



**Figure 12.** Molecular unit of **1** shown as 50% probability thermal ellipsoids. Only the asymmetric unit and copper coordination spheres are labeled. Hydrogen atoms are shown as spheres of arbitrary size and not labeled.

As described in the literature review above, close contacts may be seen amongst nearest neighboring bromide ions and bromine and chlorine atoms on the pyridine ring which influence crystal lattice (Figure 13). Cu1 and Cu2 molecules are related by unit cell translations and stack parallel to the *b*-axis. The stacks then form layers parallel to the *bc*-plane which alternate between Cu1 containing layers and Cu2 containing layers in the *a*-direction. Halogen bonds provide significant stabilization. Br1 ions interact with Br23 atoms forming Type II halogen bonds [58] [ $d_{\text{Br1}\dots\text{Br23A}} = 3.421 \text{ \AA}$ ,  $\angle_{\text{Cu1-Br1}\dots\text{Br23A}} = 87.4^\circ$ ,  $\angle_{\text{Br1}\dots\text{Br23A-Cu2A}} = 169.3^\circ$ , Symm. Op. A:  $x+0.5, y+1.5, z$ ] which link Cu1 molecules to Cu2 molecules.



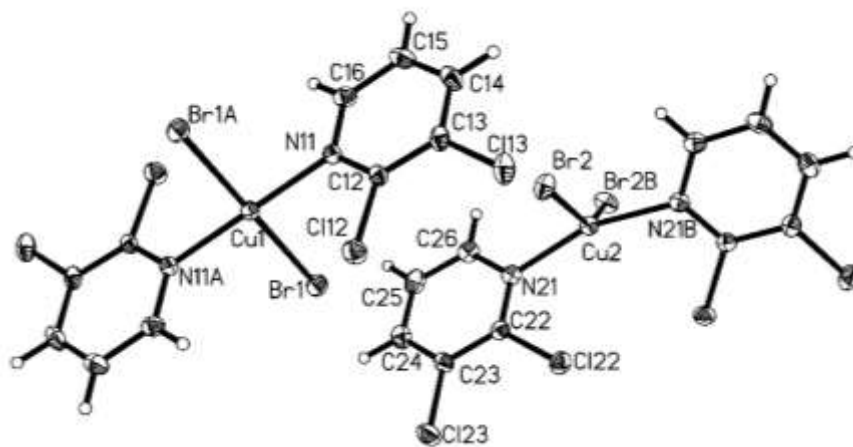
**Figure 13.** Packing of **1** viewed parallel to the *b*-axis. Dashed lines represent halogen bonds (see text for details).

Further, Cu2 molecules are linked to Cu2 molecules (parallel to the *b*-axis) via Type II halogen bonds between Br2 ions and Cl22 atoms [ $d_{\text{Br2}\dots\text{Cl22A}} = 3.766 \text{ \AA}$ ,  $\angle_{\text{Cu2-Br2}\dots\text{Cl22A}} = 108.7^\circ$ ,  $\angle_{\text{Br2}\dots\text{Cl22A-C22A}} = 159.5^\circ$ , Symm. Op. A:  $1.5-x, 1.5-y, -z$ ]. A number of weaker halogen bonds are also observed in the

lattice. The closest contacts between the bromide ions of either the Cu1 or Cu2 molecule are  $\sim 5$  Å or greater and the closest contacts between bromide ions and adjacent Cu ions are also greater than 5 Å. This suggests that neither the bi-halide, nor the two-halide bridging superexchange pathway will be significant in the structure and any magnetic interactions will be weak.

### X-ray Structure of (2,3-dichloropyridine)dibromidocopper(II)(3).

Compound **3** is isostructural to compound **1** and as such will be discussed briefly. The molecular unit is shown in Figure 14 and bond lengths and angles are given in Table 2. Again, two independent molecules are seen in the unit cell one each in the anti-(Cu1) and syn-conformation (Cu2). The Cu1 ion sits on an inversion center and the Cu2 ion sits on a two-fold rotation axis as in **1** with bond lengths and angles virtually identical to those in **1** except for the C-Cl bonds (C12-Cl12 and C22-Cl22) which replaced the corresponding C-Br bonds. In the Cu1 molecule, the pyridine rings are canted  $79.4^\circ$  relative to the Cu1 coordination plane compared to  $78.1^\circ$  in **1**. The mean trans angle of  $153.7^\circ$  (compared to  $152.4^\circ$ ) and the canting angle between the pyridine rings of  $58.5^\circ$  (compared to  $60.1^\circ$ ) for Cu2 are all good measures of the similarity.



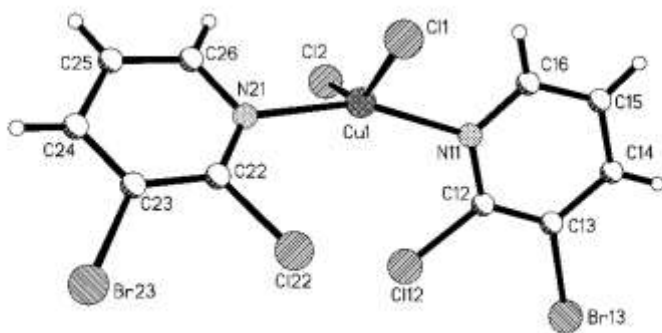
**Figure 14.** Molecular unit of **3** shown as 50% probability thermal ellipsoids. Only the asymmetric unit and copper coordination spheres are labeled. Hydrogen atoms are shown as spheres of arbitrary size and not labeled.

As seen in **1**, Cu1 and Cu2 molecules are related by unit cell translations and stack parallel to the *b*-axis similar to Figure 13. Again, halogen bonds provide significant stabilization with the two strongest being between Br1 and Cl23 atoms [Type II halogen bonds:  $d_{\text{Br1}\cdots\text{Cl23A}} = 3.481$  Å,  $\angle_{\text{Cu1-Br1}\cdots\text{Cl23A}} = 86.9^\circ$ ,  $\angle_{\text{Br1}\cdots\text{Br23A-Cu2A}} = 166.6^\circ$ , Symm. Op. A:  $x, y+1, z$ ] and between Br2 ions and Cl22 atoms [Type II halogen bond:  $d_{\text{Br2}\cdots\text{Cl22A}} = 3.436$  Å,  $\angle_{\text{Cu2-Br2}\cdots\text{Cl22A}} = 86.9^\circ$ ,  $\angle_{\text{Br2}\cdots\text{Cl22A-C22A}} = 161.9^\circ$ , Symm. Op. A:  $-x, y+1, z$ ]. As before, a number of weaker halogen bonds are also observed in the lattice. Also, as with **1**, the

intermolecular halide...halide and halide...copper contacts are nearly 5 Å or greater suggesting that only weak magnetic interactions are expected.

### Structure of (3-bromo-2-chloropyridine)dichloridocopper(II)(2).

Repeated attempts failed to produce crystals of sufficient quality and stability to allow for full data collection and refinement of and X-ray structure for compound **2**. However, repeated attempts did produce a reproducible unit cell (see Ref. 13) and well a defined coordination sphere for the complex. Compound **2** is the chloride analogue of compound **1**, but unlike **1**, only a syn-conformation, distorted tetrahedral environment is observed, rather than both syn- and anti-conformations (Figure 15). The mean trans angle at Cu1 is 150° and the angle between the pyridine rings is ~ 53°.



**Figure 15** – The coordination geometry of compound **2**. Full refinement of the X-ray structure was not possible (vide supra).

The general packing arrangement of the molecules can also be confirmed from the data available, but distances and angles must be considered to have potentially large esds given the poor quality of the refinement. Short Cl...Cl contacts [ $d_{\text{Cl1...Cl2A}} \sim 3.7$  Å,  $\angle_{\text{Cu1-Cl1...Cl2A}} \sim 157^\circ$ ,  $\angle_{\text{Cl1...Cl2A-Cu1A}} \sim 167^\circ$ ,  $\angle_{\text{Cu1-Cl1...Cl2A-Cu1A}} \sim 3^\circ$ , Symm. Opp. A:  $x+1, y, z$ ] create a uniform chain superexchange pathway parallel to the *a*-axis in the crystal. Additional halogen bonding is present in the structure (the closest Br...Br distance is ~ 3.5 Å), but detailed analysis will have to wait for higher quality, stable crystals.

### Magnetic behavior

Magnetic susceptibility data for compounds **1** - **4** were obtained on a Quantum Design MPMP-XL SQUID magnetometer using powdered samples. To verify that the powdered sample used for magnetic data collection was the same phase as the bulk material, IR analysis was performed on the sample prior to magnetic data collection. To verify the purity of the SQUID samples, powder X-ray diffraction patterns were collected on **1-3** after being run in the SQUID and compared to theoretical patterns deter-

mined from the single crystal data (calculated powder patterns were obtained using Mercury [17]). Parameters for the best fits to the data shown in Table 5. Models were taken from Reference 59 and fit using the  $H = -J \sum_{nn} S_i \cdot S_{i+1}$  Hamiltonian

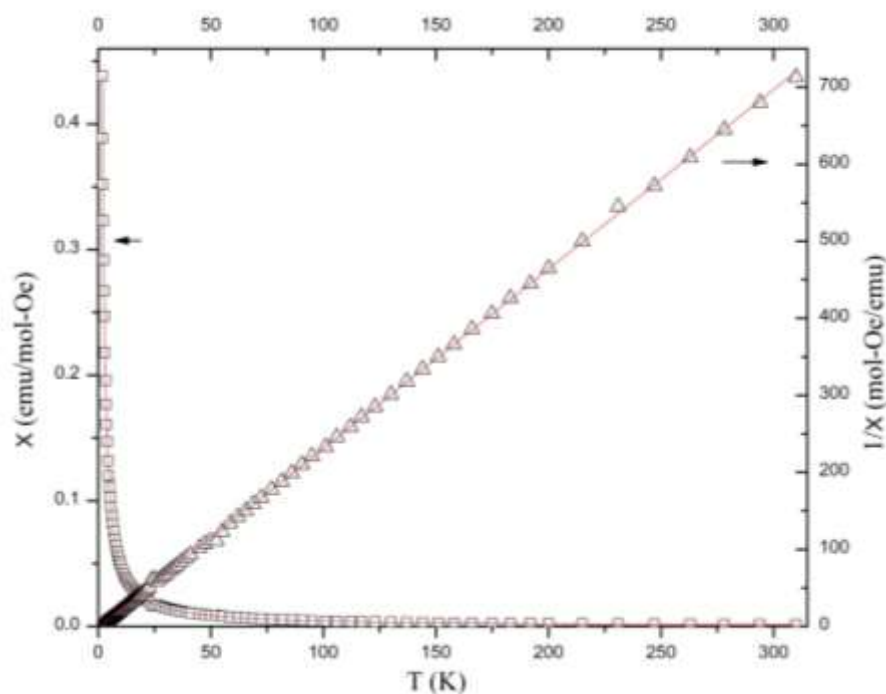
**Table 5:** Fitted values for the magnetic susceptibility data of compound **1-4**. [C = Curie Constant, J = exchange constant,  $\theta$  = Weiss constant, p = paramagnetic impurity]

Compound	Model	C (emu-K/mol-Oe)	J (K)	$\theta$ (K)	P (%)
<b>1</b>	Curie-Weiss	0.429(5)		-0.9(1)	1*
<b>2</b>	1D-AFM	0.433(1)	-19.6(1)		0.38(2)
<b>3</b>	1D-FM	0.416(2)	2.9(1)	0.29(5)	0.08(9)
<b>4</b>	1D-AFM	0.414(11)	-3.68(3)		1*

\* Paramagnetic impurity value fixed at 1%.

### Bis(3-bromo-2-chloropyridine)dibromidocopper(II)(1).

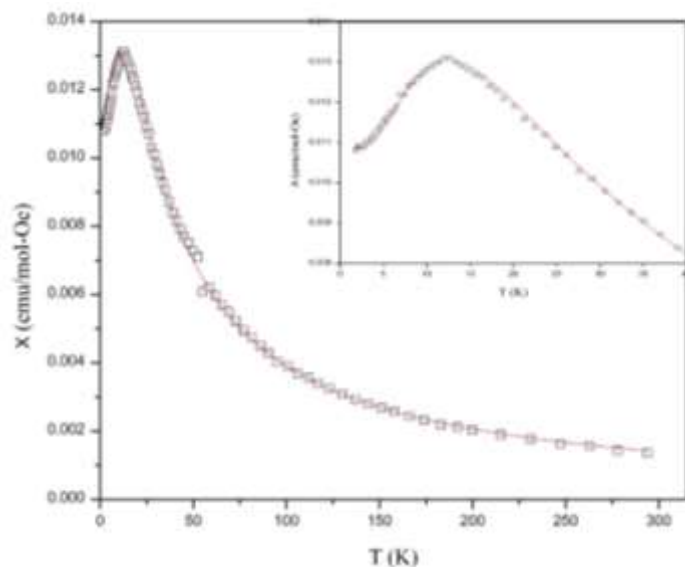
Magnetic interactions in compound **1** are vanishingly weak. No maximum is seen in  $\chi(T)$  down to 1.8 K (Figure 16) and only a slight downturn is visible in the data at low temperatures when plotted as  $\chi T(T)$ . The data were fit to the Curie-Weiss law from 5-310 K and yielded a very weak antiferromagnetic interaction ( $\theta = -0.9(1)$  K).



**Figure 16**  $\chi$  vs. T ( $\square$ ) and  $1/\chi$  vs. T ( $\Delta$ ) plots for compound **1**. Solid lines represent the best fit to the Curie-Weiss law.

### **Bis(3-bromo-2-chloropyridine)dichloridocopper(II)(2).**

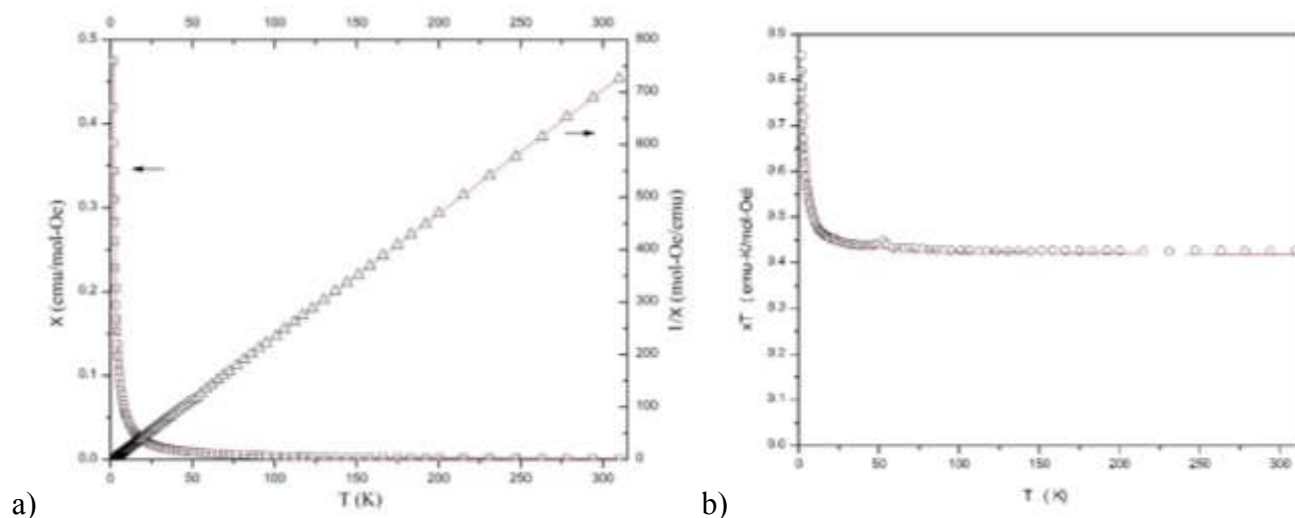
Magnetic data for **2** (Fig. 17) indicated moderate antiferromagnetic interactions. Based upon the connectivity suggested by the partial crystal structure, the data were fit to the uniform one-dimensional antiferromagnetic model<sup>59</sup> resulting in a Curie Constant of 0.433(1) emu-K/mol-Oe and an exchange constant  $J = -19.6(2)$  K.



**Figure 17**  $\chi$  vs.  $T$  ( $\square$ ) plot for compound **2**. The solid line represents best fit to the uniform 1D-antiferromagnetic model. The inset shows an expansion of the region near the maximum in  $\chi$ .

### **Bis(2-chloro-3-chloro-pyridine)dibromidocopper(II)(3).**

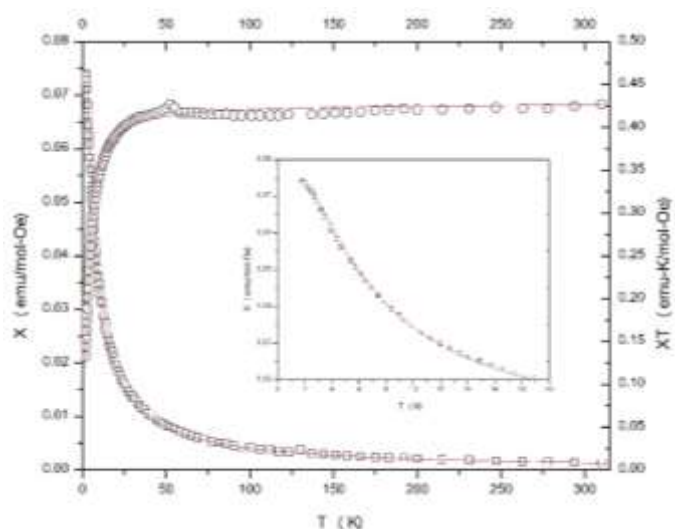
Weak ferromagnetic interactions are seen in compound **3** (Fig. 18), evident by the increase in  $\chi T$  as temperature decreased below 10 K. The data fit to a uniform one-dimensional ferromagnetic model with a Curie-Weiss( $\theta$ ) correction to account for weak inter-chain interactions. From the fitted data, the exchange constant ( $J$ ) and Weiss constant ( $\theta$ ) are 2.87(8) K and 0.29(1) K. Compound **2** exhibits weak one-dimensional ferromagnetic interactions with weaker (nearly zero) ferromagnetic interchain interactions, evident by the positive  $\theta$  value.



**Figure 18** a)  $\chi$  vs. T ( $\square$ ) and  $1/\chi$  vs. T ( $\Delta$ ) plots for compound **3**. b)  $\chi T$  vs. T ( $\circ$ ) plot for compound **3**. Solid lines represent the best fit to the uniform 1D-ferromagnetic model.

### Bis(2,3-dichloropyridine)dichloridocopper(II)(**4**).

Data for **4** (Fig. 19) clearly indicate the presence of antiferromagnetic interactions, as seen by the decrease in  $\chi T$  at low temperatures. The interactions must be weak as no maximum in  $\chi$  is seen down to 1.8 K, although the data hint at a maximum just below that temperature. In the absence of crystallographic data to suggest a superexchange pathway, the data were fit to a variety of models (Curie-Weiss Law, uniform 1D, uniform 2D) and the best fit was obtained for the one-dimensional uniform antiferromagnetic model yielding  $C = 0.414(5)$  emu-K/mol-Oe and  $J = -3.68(3)$  K. As seen in the inset to Figure 19, the quality of fit below 20 K is not particularly good, being systematically low from  $\sim 13$ -19 K and systematically high between  $\sim 4$ -6 K which suggests that this may not be the most appropriate model. However, given the weakness of the exchange and the absence of structural information, a more detailed analysis of the magnetic lattice would not be valid.



**Figure 19** a)  $\chi$  vs. T ( $\square$ ) and  $\chi T$  vs. T ( $\circ$ ) plots for compound **4**. The solid lines represent the best fit to the 1D-antiferromagnetic model. The inset show an expansion of the region below 20 K.

## DISCUSSION

As seen in the review of the current literature, substituted pyridine ligands in compounds of  $L_2CuX_2$  may adopt syn- or anti-conformations if the ring substitution is not symmetrical. Although a few compounds have been reported where both the syn- and anti-polymorphs are known, the vast majority adopt one conformation or the other. Of those, the majority of the syn-conformation complexes form halide bibridged dimers and the majority of the anti-conformation complexes adopt a bihalide-bridged chain structure, or fail to show significant intermolecular interactions involving the copper(II) ions (common in the case of complexes with large substituents). The current compounds **1** and **3** represent, to our knowledge, unique examples of complexes where both the syn- and anti-conformations occur in the same crystal lattice. However, neither conformation follows the expected intermolecular packing trend. In **1**, the shortest Br...Br distances are nearly 5.0 Å, on the borderline of the maximum distance where magnetic exchange has been reported via the two-halide pathway.<sup>7</sup> Further, the Cu-Br...Br angles are close to 90° which is also unfavorable for magnetic superexchange. These parameters are in good agreement with the observed magnetic data which, while clearly showing anti-ferromagnetic exchange, are barely distinguishable from a purely paramagnetic systems. The presence of the halogen substituents on the pyridine rings is likely the explanation for the failure of the two conformations to form their typical packing motifs; the significant halogen bonding observed controls the crystal packing. Several reports have appeared in the past few years showing the effects of halogen bonding on crystal lattices and indicating that it can provide major structural control, even over hydrogen bonding.<sup>32b,60</sup>

Although the crystal packing is very similar to **1**, complex **3** shows different magnetic behavior, exhibiting weak, but distinct, ferromagnetic interactions. As with **1**, there are no obvious superexchange pathways observed via the crystal structure, but the interactions are somewhat stronger (nearly three-fold) and of opposite sign. Weak ferromagnetic interactions have been observed previously in the dihalogen substituted pyridine complex (3-chloro-2-fluoropyridine)<sub>2</sub>CuCl<sub>2</sub>(H<sub>2</sub>O).<sup>28</sup> This may suggest a different superexchange pathway can operate in such compounds, but given the weakness of the exchange observed, more examples will be required before a supportable proposal may be made.

Compound **2** shows significant anti-ferromagnetic exchange and was well modeled as a uniform chain with  $J$  nearly -20 K. This is in good agreement with the proposed two-halide superexchange pathway via short ( $\sim 3.7$  Å) Cl...Cl contacts. Compound **2** exhibits a syn-conformation, but like **1** and **3** it does not form the halide bibridged dimers which are typical of such geometry. Again, it appears that halogen bonding in the structure has dominated control of the lattice. Finally, compound **4** exhibits weak

anti-ferromagnetic interactions as seen in the downturn in  $\chi T(T)$  at low temperatures as is the case for most compounds with the general formula  $L_2CuX_2$ .

## CONCLUSIONS

We report here the synthesis and characterization of two new complexes of the general formula (subpy)<sub>2</sub>CuBr<sub>2</sub> (**1** and **3**) which are unusual in that both syn- and anti-conformation molecules are found in the same crystal. The pyridine rings are disubstituted with halogen atoms in the 2 and 3 positions. Neither conformation exhibits the packing interactions typical of that structure, but significant halogen bonding between the bromide ions and halogen substituents appear to dominate the intermolecular interactions. Few complexes of 2,3-dihalogenatedpyridine molecules have been reported to date, suggesting that more data is needed to make a detailed analysis of the structural control parameters. The corresponding chloride complexes have also been prepared, but do not exhibit the presence of the two conformational forms. Variable temperature magnetic measurements show that the interactions in the bromide complexes, **1** and **3**, exhibit very weak magnetic exchange, while the chloride complexes show significantly stronger antiferromagnetic interactions. Further work on additional 2,3-dihalopyridine ligands is in progress.

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