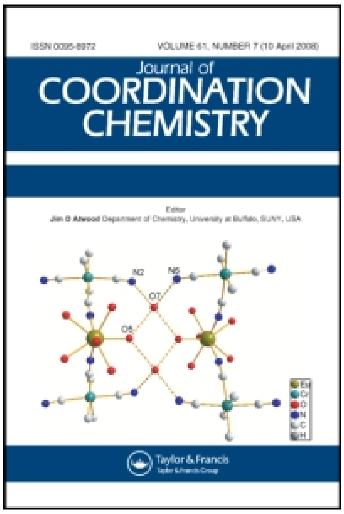

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SYNTHESIS AND STRUCTURE OF BIS(2-AMINO-5-CYANOPYRIDINIUM) DIAQUADICHLOROCOPPER(II) DICHLORIDE

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The reaction of $CuCl_2$ with 2-amino-5-cyanopyridine and HCl in 1-propanol gave bis(2-amino-5-cyanopyridinium) diaquadichlorocopper(II) dichloride (**1**). Crystal data for **1** are: monoclinic, space group: $P2_1/c$, $a = 8.461(3)$ Å, $b = 14.665(5)$ Å, $c = 7.883(3)$ Å, $\beta = 96.105(4)°$, $V = 972.6(6)$ Å^3, $Z = 2$, $D_{calc} = 1.645\,Mg/m^3$, $\mu = 1.691\,mm^{-1}$, $F(OOO) = 486$, $MoK_\alpha(\lambda = 0.71073$ Å$)$, $R1 = 0.0431$ for $[|I| \geq 2\sigma(I)]$ and $R1 = 0.0680$ for all 1944 unique reflections and 130 parameters. The structure exists as square planar $Cu(H_2O)_2Cl_2$ units with long semi-coordinate bonds to the cyano nitrogens of the 2-amino-5-cyanopyridinium ions. Hydrogen bonding from the water molecules and N—H hydrogens to the chloride ions stabilizes the lattice.

Keywords: 2-Amino-5-cyanopyridine copper(II); Hydrogen bond; Square planar; Structure

INTRODUCTION

Our interest in low-dimensional magnetic lattices has led us to study a series of compounds of formula $A_2[MX_4]$ where A is an organic cation, M is a 2+ transition metal ion and X is a halide (Cl, Br, I). A wide variety of these complexes are known where the A-group is a protonated alkyl amine [1], or heterocycle such as pyridine [2] or morpholine [3]. The magnetic exchange in these materials is propagated by van der Waals contacts between the halide

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ions of the MX_4 pseudo-tetrahedra. The distances between the halides, bond angles, and dihedral angles between M—X bonds are all factors in determining the sign and strength of the exchange and these are determined by the crystal packing. Several complexes are known where the organic base is a 2-aminopyrimidine derivative [4]. We had previously observed that the compounds A_2CuX_4 where X = Cl, Br and A = 5-methyl-[4e], 5-chloro-[4e], 5-bromo-2-aminopyridinium [4f] crystallized in the space group C2/c and generated two-dimensional, square magnetic lattices. It was apparent that the size of the substituent in the 5-position on the pyridine ring controlled the separation between MX_4^{2-} units within the layer, and thus the strength of the magnetic exchange. At the same time, the overall length of the substituted pyridinium ion controlled the separation between the magnetic layers, and thus the two-dimensional isolation. We believed that a long, narrow substituent in the 5-position should lead to strong magnetic exchange and good isolation, and thus attempted the preparation of the 5-cyano compound. However, instead of isolating the desired $(5\text{-CNAP})_2CuCl_4$[5-CNAP = 5-cyano-2-aminopyridinium], we obtained the unusual dihydrate, $(5\text{-CNAP})_2[CuCl_2(H_2O)_2]Cl_2$ (**1**).

EXPERIMENTAL

2-Amino-5-iodopyridine was synthesized according to a modification of the literature procedure [5]. $CuCl_2 \cdot 2H_2O$ was purchased from Alfa and used without further purification. All solvents were reagent grade and used without further purification.

2-Amino-5-cyanopyridine, $C_5H_5N_3$ **2** [6] – A solution of 2-amino-5-iodopyridine (2.47 g, 11.2 mmol) and anhydrous cuprous cyanide (1.06 g, 11.8 mmol) in dry pyridine (3.5 mL) was refluxed for three hours. The pyridine was removed *in vacuo* and the residue sublimed to give **2** as off-white needles, 0.75 g (56%). mp 163-4. [Lit. 164]. IR (KBr): ν 3414 s, 3318 m, 3143 m-br, 2210 s, 1652 s, 1599 s, 1508 s, 1408 s, 1211 m, 695 m cm^{-1}. ^{1}H-NMR (acetone-d_6): δ6.47 (s, br, 2H) 6.64 (d, 1H, J = 8.7 Hz) 7.66 (d, 1H, J = 8.7), 8.31 (s, 1H). ^{13}C-NMR-δ97.2, 108.7, 119.0, 140.3, 153.8, 162.5.

Bis(2-amino-5-cyanopyridinium) diaquadichlorocopper(II) dichloride, $(C_5H_6N_3)_2[Cu(H_2O)_2Cl_2]Cl_2$ (**1**) – A solution of copper(II) chloride (0.085 g, 0.5 mmol) dissolved in 15 ml of 1-propanol was added with stirring to a solution of 2-amino-5-cyanopyridine (0.119 g, 1.0 mmol) in 3 ml of concentrated $HCl_{(aq)}$. Green crystals of **1** were harvested after slow evaporation of the solution over $\approx$ 3 weeks (0.126 g, 50%). No attempt

TABLE I Crystal data and structure refinement for **1**

Empirical formula	$C_{12}H_{16}Cl_4CuN_6O_2$	Formula weight	481.65
Temperature	158(2) K	Wavelength	0.71073 A
Crystal system	Monoclinic	Space group	$P2_1/c$
Unit cell dimensions:	a = 8.461(3) Å	b = 14.665(5) Å	
	c = 7.883(3) Å	$\beta = 96.105(4)^\circ$	
Volume	972.6(6) $Å^3$	Z = 2	
Calculated density	1.645 Mg/m^3	$\mu = 1.691\ mm^{-1}$	
F(000)	486	Crystal size 0.39 × 0.11 × 0.08 mm	
Theta range for data collection	2.42° to 26.32°		
Limiting indices	$-10 \le h \le 10, -18 \le k \le 18, -3 \le 1 \le 9$		
Reflections collected/unique	6847/1944 [$R_{int} = 0.0403$]		
Completeness to theta = 26.32°	98.5%		
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	1944/0/130		
Goodness-of-fit on F^2	1.129		
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0431, wR2 = 0.0852		
R indices (all data)	R1 = 0.0680, wR2 = 0.0917		
Largest diff. peak and hole	0.562 and $-0.526\ e^{-}A^3$		

was made to maximize the yield. IR (KCl) - ν 3243 m-br, 3169 m-br, 2236 s, 1703 m, 1669 s, 1339 m, 1210 m, 834 s, 541 s cm^{-1}. Anal. Calc. for $C_{12}H_{16}N_6CuCl_4O_2$: C, 29.9; N, 17.44; H, 3.32. Found: C, 29.80; N, 17.20; H, 3.24.

X-ray Structure Determination

Data collection, cell refinement and data reduction were done *via* a Bruker SMART system [7]. The structure was solved via direct methods [8] and refined [9] *via* full-matrix least-squares. Absorption corrections were made *via* SADABS [10]. Hydrogen atoms bonded to carbon were refined as a riding model with fixed isotropic U's. Hydrogen atoms bonded to nitrogen were located in the difference map and their positions refined with a fixed, isotropic U. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [11]. Full crystallographic data may be found in Table I. Selected bond distances and angles are given in Table II. Significant hydrogen bonds within the

TABLE II Bond lengths [Å] and angles [°] for **1**

Cu—O	1.935(3)	Cu—Cl(1)	2.2701(12)
Cu—N(3)	2.969(5)	N(1)—C(2)	1.361(5)
N(1)—C(6)	1.365(5)	C(2)—N(2)	1.335(5)
C(2)—C(3)	1.408(5)	C(3)—C(4)	1.375(6)
C(4)—C(5)	1.416(6)	C(5)—C(6)	1.360(6)
C(5)—C(7)	1.462(6)	C(7)—N(3)	1.142(6)
O—Cu—Cl(1)	89.75(9)	O—Cu—Cl(1)#1	90.25(9)
O#1—Cu—N(3)	87.63(14)	O—Cu—N(3)	92.37(14)
N(3)—Cu—N(3)#1	180	Cl(1)—Cu—N(3)	86.09(9)
Cl(1)#1—Cu—N(3)	93.91(9)		
C(2)—N(1)—C(6)	123.0(4)	N(2)—C(2)—N(1)	118.7(4)
N(2)—C(2)—C(3)	123.0(4)	N(1)—C(2)—C(3)	118.3(3)
C(4)—C(3)—C(2)	119.7(4)	C(3)—C(4)—C(5)	119.8(4)
C(6)—C(5)—C(4)	119.8(4)	C(6)—C(5)—C(7)	118.8(4)
C(4)—C(5)—C(7)	121.4(4)	C(5)—C(6)—N(1)	119.5(4)
N(3)—C(7)—C(5)	179.2(6)	C(7)—N(3)—Cu	108.6(4)

Symmetry transformation used to generate equivalent atoms: #1 −x, −y+1, −z+1.

TABLE III Hydrogen bonds for **1** [Å and °]

D—H...A	*d(D—H)*	*d(H...A)*	*d(D...A)*	<(*DHA*)
O—H(1S)...Cl(2)	0.82(5)	2.25(5)	3.057(3)	168(5)
O—H(2S)...Cl(2)#2	0.77(5)	2.38(5)	3.118(3)	163(5)
N(1)—H(1)...Cl(2)#3	0.92(4)	2.33(5)	3.186(4)	155(4)
N(2)—H(2A)...Cl(2)#3	0.83(5)	2.57(5)	3.309(5)	148(4)
N(2)—H(2B)...Cl(1)#4	0.80(5)	2.59(5)	3.341(4)	158(4)

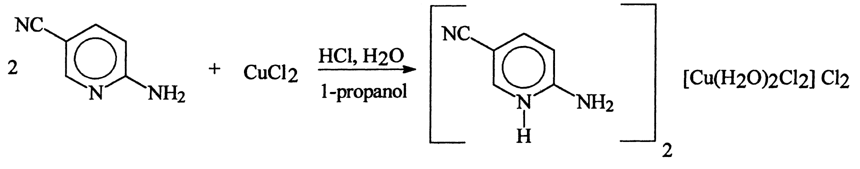
Symmetry transformations used to generate equivalent atoms: #1 −x, −y+1, −z+1; #2 −x, −y+1, −z; #3 x+1, y, z; #4 x+1, −y+1/2, z−1/2.

lattice are given in Table III. Atomic coordinates, observed and calculated structure factors, anisotropic thermal parameters, and H-atom positions and isotropic thermal parameters are given in the supplementary material.

RESULTS AND DISCUSSION

Synthesis and Structure

Reaction of 2-amino-5-cyanopyridine with copper chloride and HCl in I - propanol gave the title compound, **1**, in 56% yield. Green crystals suitable for X-ray diffraction were collected by slow evaporation of the mother liquor. The compound crystallized in the monoclinic space group, $P2_1/c$ as green needles. An ORTEP drawing of the molecular unit is shown in Figure 1. The structure consists of neutral $Cu(H_2O)_2Cl_2$ units co-crystallized with 5-CNAP chloride. The copper ion sits on a crystallographic inversion center and is principally square planar in geometry with typical Cu—O [1.935(3) Å] and Cu—Cl1 [2.270(1) Å] bond lengths and an O—Cu—Cl1 bond angle of 89.75(9)°. The uncoordinated chloride ions (Cl2) are held in the lattice by extensive hydrogen bonding to the water molecules and both the pyridinium and one of the amino hydrogens (H2A) of the 5-CNAP (see Tab. III and Fig. 2). In addition, hydrogen bonding between Cl1 and the other amino hydrogen (H2B) is also observed.



1

Bond lengths and angles within the pyridinium ion show only slight deviations in bond length and angle from ideal as is typical of protonated 2-aminopyridines [12]. The ring is planar with a mean deviation of 0.0048 Å for any atom within the ring. The amino and cyano nitrogens are only slightly distorted from the plane of the ring at 0.0107 Å and 0.0112 Å respectively. The cyano substituent is nearly linear [$< _{C5—C7—N3} = 179.2(6)°$] and the C5—C7 and C7—N3 bond lengths compare well with other aromatic nitriles [13].

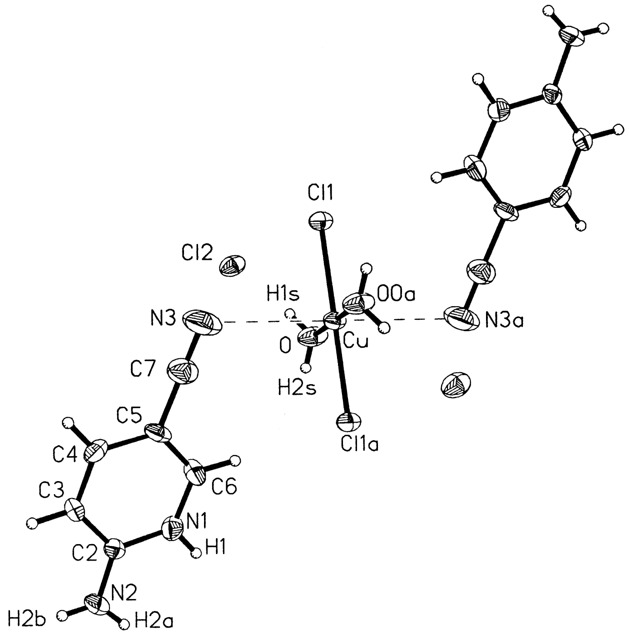


FIGURE 1 ORTEP drawing of the molecular unit of **1** with 50% probability ellipsoids, showing labeling for the asymmetric unit and those atoms bonded to the copper atom. Only hydrogens in refined positions have been labeled.

The cyano nitrogen is located 2.969(5) Å from the Cu in the position expected for axial ligands in a Jahn-Teller distorted complex, but this distance is significantly longer than even the semi-coordinate bond seen in a bridging 4-cyanopyridine complex [13]. The angle between the Cu—N3 vector and the mean plane of the water and chloride ligands about the copper is 85.4(5)°. The angle between the C≡N bond and the Cu—N3 vector is 108.6(4)°.

Figure 2 shows a packing diagram for **1**. The mean plane about the Cu ions is canted ± 16.8° from the B-face of the crystal depending on whether the copper is located at the cell origin, or at 0, 1/2, 1/2. The centroids of the pyridinium rings are stacked parallel to the *c*-axis and the rings are canted 23.4° from the C-face of the unit cell.

The presence of an interaction between the cyano nitrogen, N3, and the copper is clear from the packing diagram. As viewed down the *c*-axis (Fig. 2), the pyridinium rings are tipped alternately left and right such that N3 is brought closer to the adjacent copper ion. This is clearly contrary to steric congestion and suggests some kind of weak bonding interaction. The C7—N3 bond length supports a C≡N triple bond and sp-hybridization

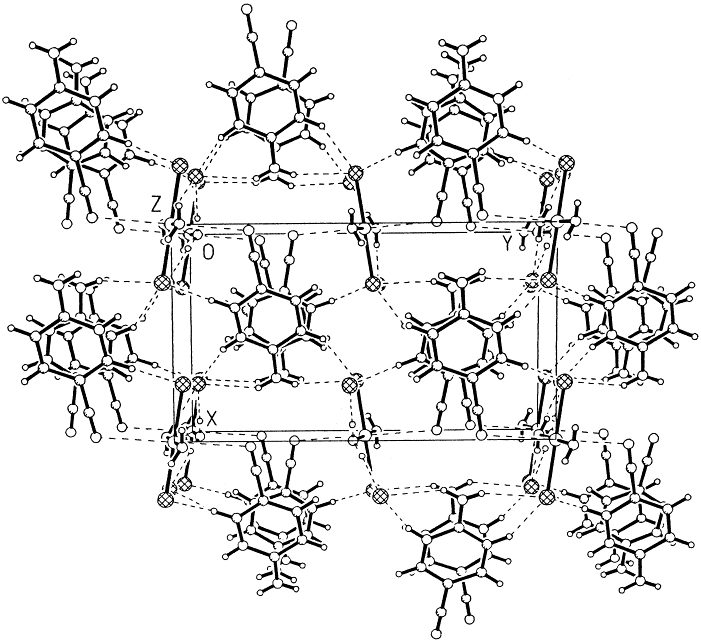


FIGURE 2 Packing diagram viewed parallel to the *c*-axis showing hydrogen bonds and close Cu—N3 contacts.

at N3. However, the 108.6(4)° C7—N3—Cu "bond angle" rules against a traditional bonding to the terminal lone-pair on N3. In addition, the long Cu—C7 distance, 3.506(6) Å, militates against coordination to the C—N π-bond, but a partial M—L π-interaction may contribute to the structure as seen in some alkali metal acetylides [14], although in cases of true π-coordination the C$\equiv$N bond is significantly lengthened and the C—C$\equiv$N bond angle greatly reduced [15]. The interaction may be electrostatic in nature since the *p*-amino substituent should serve to increase the electron density on N3, increasing its attraction to the copper(II) ion. This would also agree with the bond angle, as such electrostatic interactions are non-directional. Similarly, a high s-character in the N3 lone pair would also reduce the directionality of a Cu—N3 interaction, as demonstrated by theoretical energy calculations for the isoelectronic acetylides [16]. A reasonable analogue to the bond angles observed in **1** is found in alkali-earth acetylides. Crystal structures of Ca, Sr and Ba complexes of Ph$_3$Si—C$\equiv$C$^-$ show M—C$\equiv$C bond angles ranging from 126.6° to 164.0° with the deviation from linearity increasing with the size of the metal [17].

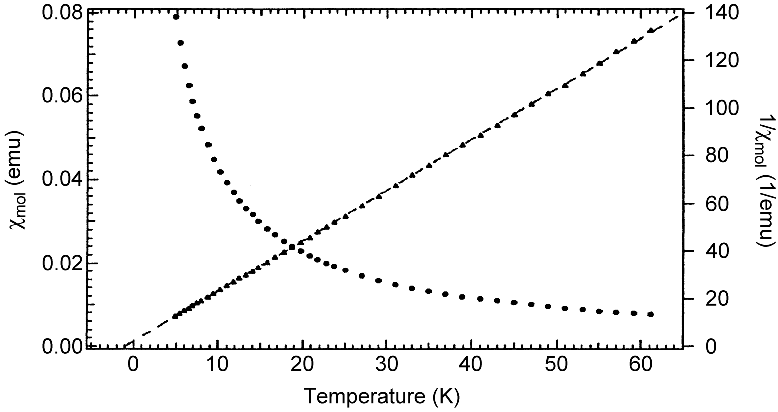


FIGURE 3 A plot of susceptibility (●) and inverse susceptibility (▲) as a function of temperature (K) for **1**.

Magnetic Measurements

The closest contacts between Cu ions occur parallel to the *c*-axis where the $Cu(H_2O)_2Cl_2$ units are linked into chains *via* hydrogen bonds between the coordinated water molecules and the uncoordinated chloride ion Cl2. Magnetic interactions through such a distance are expected to be vanishingly small. The magnetic susceptibility of **1** was collected as a function of temperature over the range 5–62 K on a Quantum Design SQUID magnetometer. A plot of χ *vs.* T and χ^{-1} *vs.* T is shown in Figure 3.

A Curie-Weiss fit (solid line in Fig. 3) gives a value for the Curie constant (C) of 0.47 and a θ_{cw} of -0.945, indicating that the interactions are indeed quite weak. The value of 0.47 for C requires $g_{ave} = 2.2$, somewhat high for Cu^{2+}, but not unreasonable considering the nearly square-planar nature of the ion in **1**. An EPR spectrum collected using an X-band Bruker EMX EPR spectrometer at room temperature displayed a standard, asymmetric powder adsorption pattern corresponding to principle g-values of $g = 2.05$ and 2.20, in reasonable agreement with the g-value obtained from the magnetic data.

CONCLUSIONS

Our attempt to manipulate the lattice dimensions in the family A_2CuX_4 [A = 5-substituted-2-aminopyridinium] by tuning the steric requirements of the 5-substituent to the long, narrow cyano group resulted in complete disruption of the previously observed C2/c structure and loss of the desired square magnetic lattice. Instead, a hydrated copper(II) complex was obtained in a lower symmetry space group. In spite of our previous success with methyl, chloro and bromo substituents, preliminary results from the 5-iodo, 5-fluoro and 5-nitro substituted pyridines suggests that the C2/c lattice is maintained only for a fairly narrow range of substituents. Attempts to prepare the desired anhydrous $(5\text{-CNAP})_2CuX_4$ complexes and examination of the parameters controlling the lattice structure continue.

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