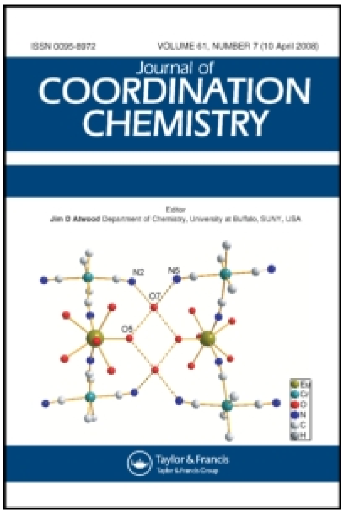

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SYNTHESIS AND STRUCTURE OF (2-AMINO-5-BROMOPYRIMIDINE)BROMOCOPPER(I)

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SYNTHESIS AND STRUCTURE OF (2-AMINO-5-BROMOPYRIMIDINE)BROMOCOPPER(I)

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The reaction of $CuBr_2$ with 2-amino-5-bromopyrimidine and HBr in aqueous solution gave as the major product (2-amino-5-bromopyrimidine)bromocopper(I) (**1**) in 58% isolated yield. Compound **1** crystallizes as small orange blocks in the rare space group 14mm. Crystal data for **1** are: tetragonal, space group: 14mm, $a = b = 15.646(3)$, $c = 6.705(3)$ Å, $V = 1641.3(8)$ Å^3, $Z = 8$, $D_{calc} = 2.634$ Mg/m^3, $\mu = 12.334$ mm^{-1}, F(OOO) = 1216, MoK$_a$ ($\lambda = 0.71073$ Å), $R = 0.0322$ for $[|I| \geq 2\sigma(I)]$ and $R = 0.0420$ for all 343 unique reflections and 70 parameters. The structure exists as a three-dimensional coordination polymer with sheets of pyrimidine bridged copper atoms, parallel to the *ab*-crystal plane, bridged by bromine atoms roughly parallel to the *c*-axis.

Keywords: coordination polymer; 14mm; reduction; copper I; pyrimidine

INTRODUCTION

Our interest in low-dimensional magnetic lattices has led us to study a series of compounds of the formula $A_2[MX_4]$ where A is an organic cation, usually a protonated base, M is a 2+ transition metal ion and X is a halide (Cl, Br). A wide variety 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 properties of these compounds are dominated by van der Waals contacts between the halide ions of the MX_4 *pseudo*-tetrahedra, and the contacts are determined by the crystal packing. Several complexes are known where the organic base is a 2-aminopyrimidine derivative.[4] Our attempt to improve the isolation between the MX_4^{2-} layers in the 2-aminopyrimidine complexes by increasing the steric bulk of the ligand resulted in reduction of the Cu(II) ions and the isolation of (2-amino-5-bromopyrimidine)bromocopper(I).

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EXPERIMENTAL

2-Amino-5-bromopyrimidine was purchased from Aldrich Chemical Corp. and used without further purification. $CuBr_2$ was purchased from Alfa and used without further purification. Ethanol refers to 95% ethanol.

(2-Amino-5-bromopyrimidine)bromocopper(I), $Cu(C_4H_4N_3Br)Br$(**1**) –Copper (II) bromide (0.065g, 0.29 mmol) was dissolved in 4 mL of ethanol and added to a mixture of 2-amino-5-bromopyrimidine (0.099g, 0.57 mmol, 2 eq) and HBr (0.1924g of 48% aqueous, 1.14 mmol, 4 eq) in 6 mL of ethanol. The mixture was heated to reflux at which point all of the pyrimidine dissolved and a dark green solution was formed. The solution was allowed to cool to room temperature overnight. The resulting precipitate was collected by vacuum filtration and the product was washed with water (2 mL) to remove traces of the red bis(2-amino-5-bromopyrimidine)dibromocopper(II) complex. The remaining orange solid was washed with ethanol and air dried to give 0.048 g (58%).

X-ray Structure Determination

Data collection was carried out at 158K on a Siemens P4 diffractometer employing MoKa radiation (l = 0.71073) and a graphite monochromator. Three standard reflections were monitored every 97 reflections and showed only 6.33% decay. The intensities of 1216 reflections were measured by using an omega scan of which 343 were unique (R_{int} = 0.0730). The structure was solved using the heavy atom Patterson method [SHELXS-86].[5] Full-matrix least-squares refinement [SHELXL-93][6] after absorption correction (*via* psi-scans; minimum and maximum transmission coefficients 0.19677 and 0.27001) gave R = 0.0322 and R_w = 0.0575 for $|I| \geq 2\sigma(I)$ (all data; R = 0.0420, R_w = 0.0592). The final refinement included 70 least-squares parameters with a goodness of fit of 0.887 (based on F^2). The hydrogen atoms were refined as a riding model with fixed isotropic U's. An absorption coefficient of 12.334 mm^{-1} was calculated. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton.[7] All data reduction, structure solution and refinement, and graphics were performed by using SHELXTL (VMS) software. Full crystallographic data may be found in Table I. Atomic coordinates and isotropic thermal parameters are listed in Table II, and selected bond distances and angles in Table III. Observed and calculated structure factors, anisotropic thermal parameters, and H-atom positions and isotropic thermal parameters are given in the supplementary material.

TABLE I Crystallographic data for (2-amino-5-bromopyrimidine)bromocopper(I) (1)

Formula:$C_4H_4Br_2CuN_3O_{0.5}$	Space group: I4mm
Fw = 325.46	Crystal system: tetragonal
$a = b = 15.646(3)$ Å	T = 158(2) K
$c = 6.705(3)$ Å	$\lambda = 0.71069$ Å
$\alpha = \beta = \gamma = 90$	$D_{calc} = 2.634$ Mg/m^3
	$\mu = 12.334$ mm^{-1}
$V = 2659.3(10)$ Å^3	$R(F_o) = 0.0322$
$Z = 8$	$R_w(F_o) = 0.0575$

TABLE II Atomic coordinates [$\times10^4$] and equivalent isotropic displacement parameters [Å$^2\times10^3$] for 1.U(eq) is dee third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U(eq)*
Cu	-1907(1)	1907(1)	4303(3)	20(1)
Br1	-2010(1)	2010(1)	563(3)	19(1)
Br2	0	3819(2)	9971(4)	42(1)
N1	-762(6)	2369 (6)	5297(19)	17(3)
N2	0	1693(13)	2844(31)	26(6)
C2	0	2138(12)	4501(33)	18(5)
C4	-749(8)	2850(8)	6926(20)	15(4)
C5	0	3128(11)	7761(52)	19(5)
O1A	-674(31)	674(31)	-903(126)	251(48)
O1B	-317(36)	317(36)	-2078(164)	198(51)

TABLE III Selected bond lengths [Å] and [°] for 1

Cu—N1	2.044(10)	Cu—N1#1	2.044(10)
Cu—Br1	2.518(3)	Cu—Br1#2	2.540(3)
Br1—Cu#3	2.540(3)	Br2—C5	1.83(3)
N1—C4	1.33 (2)	N1—C2	1.355(13)
N2—C2	1.31(3)	C2—N1#4	1.355(13)
C4—C5	1.37(2)	C5—C4#4	1.37(2)
O1B—O1B#5	0.99(11)	O1B—O1B#6	0.99(11)
O1B—O1B#7	1.4(2)		
N1—Cu—N1#1	120.9(6)	N1—Cu—Br1	111.0(3)
N1#1—Cu—Br1	111.0(3)	N1—Cu—Br1#2	103.9(3)
N1#1—Cu—Br1#2	103.9(3)	Br1—Cu—Br1#2	104.23(10)
Cu—Br1—Cu#3	114.60(10)	C4—N1—C2	117.5(13)
C4—N1—Cu	118.8(8)	C2—N1—Cu	123.3(10)
N2—C2—N1	118.4(9)	N2—C2—N1#4	118.4(9)
N1—C2—N1#4	123(2)	N1—C4—C5	122(2)
C4—C5—C4#4	118(2)	C4—C5—Br2	121.1(12)
C4#4—C5—Br2	121.1(12)	O1B#5—O1B—O1B#6	90.002(4)
O1B#5—O1B—O1B#7	45.004(4)	O1B#6—O1B—O1B#7	44.997(6)

Symmetry transformation used to generate equivalent atoms: #1 -y, -x, z #2 -x-1/2, -y+1/2, z+1/2 #3 -x 1/2, -y+1/2, z-1/2 #4 -x, y, z #5 -y, x, z #6 y, -x, z #7 -x, -y, z.

RESULTS AND DISCUSSION

Reaction of $CuBr_2$ with two equivalents of 2-amino-5-bromopyrimidine and HBr in aqueous solution gave the reduced product (2-amino-5-bromopyrimidine) bromocopper(I) (**1**) in 58% yield. Crystals suitable for x-ray diffraction study crystallized spontaneously from the solution. A small amount of red bis(2-amino-5-bromopyrimidine)dibromocopper(II) also precipitated with **1**, but it could be easily removed due to its greater water solubility. Reduction of Cu(II) in solutions of heterocyclic amines is well documented,[8] especially in the presence of halide ions.[9] It is likely that aminobromopyrimidine is the actual reducing agent, with the 2:1 ligand to metal ratio in the mixture providing more than sufficient material to account for the 58% yield.

Compound **1** crystallizes as nearly octahedral orange prisms in the unusual space group 14mm. Only five organic related structures have been previously reported in this space group.[10] Crystallographic data are given in Table I. Atomic coordinates and equivalent isotropic thermal parameters are given in Table II. Selected bond lengths and angles are given in Table III. The structure of one complete molecule is shown in Figure 1 (symmetry equivalent atoms generated by one of the mirrors are labeled with 'A'). Packing diagrams viewed along the *c*-axis and the *b*-axis are shown in Figures 2 and 3, respectively.

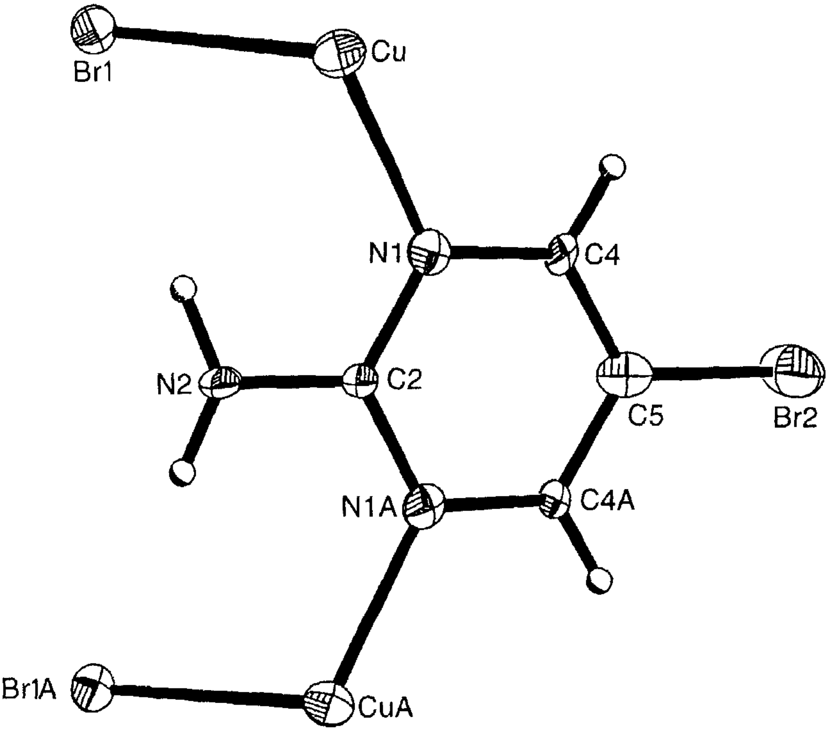

FIGURE 1 ORTEP drawing of 1 showing a complete 2-amino-5-bromopyrimidine ring. Symmetry generated atoms are labeled with A.

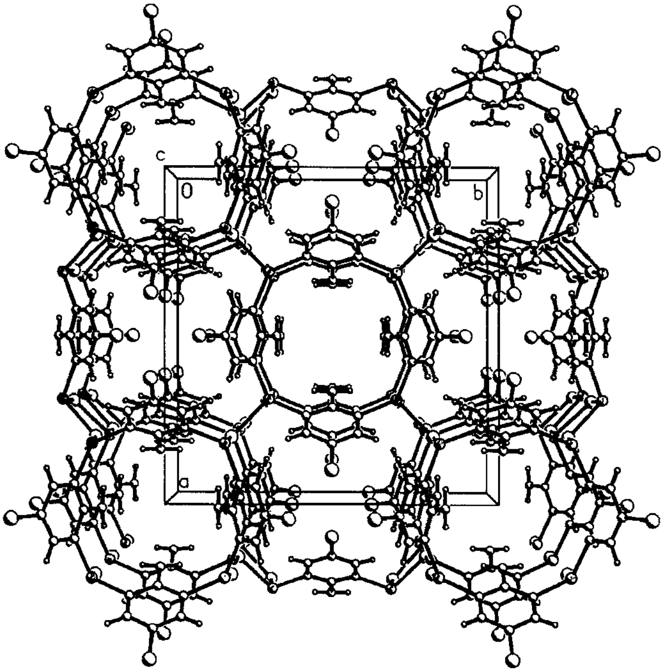

FIGURE 2 Packing diagram of 1 viewed parallel to the four-fold axis (*c*-axis).

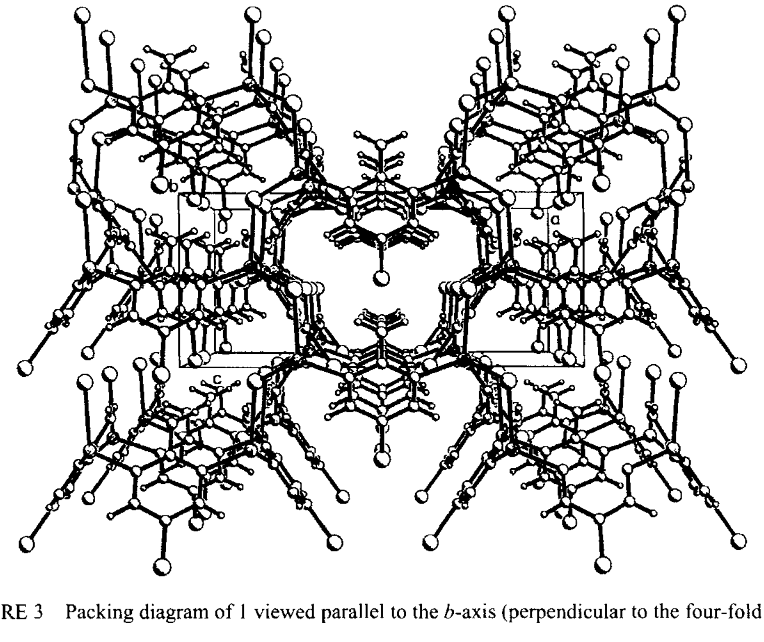

FIGURE 3 Packing diagram of 1 viewed parallel to the *b*-axis (perpendicular to the four-fold axis).

The structure of **1** may be described as gear-toothed —Cu—Br—Cu—Br— chains running parallel to the *c*-axis (the four-fold axis) and contained in the crystallographic mirrors along the *ab*-diagonals. The Cu atoms in the chains are cross-linked by the pyrimidines into *pseudo*-squares roughly parallel to the *ab* face (see Figure 2). The pyrimidine rings are bisected by the crystallographic mirrors perpendicular to the *ac*- and *bc*-faces. The layers of squares are staggered in the *c* direction (see Figure 3). The Cu—Br bond lengths in the chain are nearly identical, alternating between 2.518(3) Å and 2.540(3) Å, while the Cu—N bond is 2.044(10) Å. The geometry about the Cu atom is distorted tetrahedral with two of the bond angles expanded (N1—Cu—N1′ = 120.9(6), N1—Cu—Br1 = 111.0(3)) and two of them slightly contracted (Br1—Cu—Br1′ = 104.2(1), N1—Cu—Br1′ = 103.9(3)). Bond lengths and angles within the pyrimidine ring are comparable to those of the free base[11] and the hydrochloride salt.[12]

The pyrimidine rings are canted relative to the *ab*-plane such that all the amino substituents lie on the same side and all of the bromo substituents lie on the opposite side (Figure 3). This results in two types of channels in the crystal running parallel to the *c*-axis; those ‘lined’ with amino groups and those ‘lined’ with bromine atoms. The diameter of the Br channels (measured as the Br-Br separation) is small at 3.69 Å. The diameter of the amino channels (measured as the N-N distance), however, is significant at 5.30 Å. This is large enough to admit or trap small molecules. In fact, toward the end of the structure refinement an additional peak arose in the difference map located near the N2 nitrogen. The peak was successfully modeled as a two-site disordered oxygen atom (see Figure 4) (presumably a water molecule, but no attempts were made to locate or fix the hydrogen atoms). Even allowing for the disorder the total electron density was too small for a water molecule,

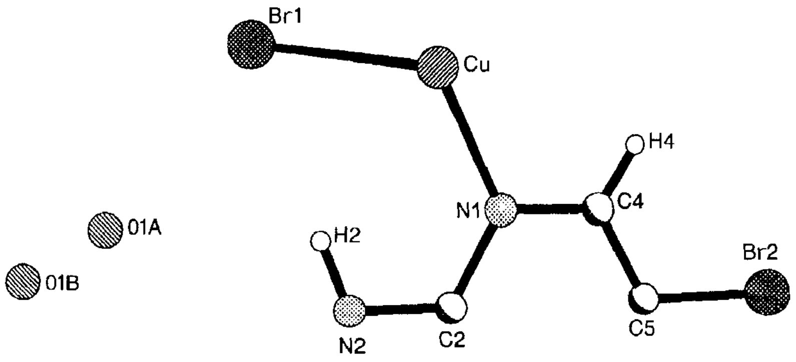

FIGURE 4 Drawing of the asymmetric unit of 1 showing the positions of the disordered water oxygen atoms relative to the coordination unit (spheres are of arbitrary size).

and the final model included a fixed occupancy for the water molecule of only 50% (25% for each disordered position). Even at this reduced occupancy, the equivalent isotropic thermal parameter for the oxygens was still unusually large, suggesting that the actual occupancy may be even lower. Work is in progress to determine whether the molecules located in these channels are mobile or trapped, and to investigate the size limits of such molecules.

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