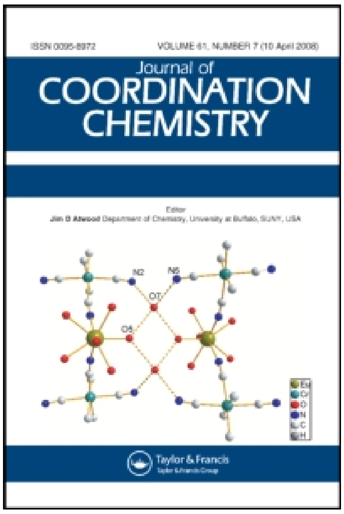

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Copper(II) Halide Complexes of 2-Aminopyrimidines: Crystal Structures of [(2-aminopyrimidine)$_{<i>n</i>}$CuCl$_2$] (n=1,2) and (2-amino-5-bromopyrimidine)$_2$CuBr$_2$

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To cite this Article Prince, Barry J. , Turnbull, Mark M. and Willett, Roger D.(2003) 'Copper(II) Halide Complexes of 2-Aminopyrimidines: Crystal Structures of [(2-aminopyrimidine)$_{<i>n</i>}$CuCl$_2$] (n=1,2) and (2-amino-5-bromopyrimidine)$_2$CuBr$_2$', Journal of Coordination Chemistry, 56: 5, 441 — 452

To link to this Article: DOI: 10.1080/0095897031000099983

URL: http://dx.doi.org/10.1080/0095897031000099983

J. Coord. Chem., 2003, Vol. 56, No. 5, pp. 441–452

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COPPER(II) HALIDE COMPLEXES OF 2-AMINOPYRIMIDINES: CRYSTAL STRUCTURES OF [(2-AMINOPYRIMIDINE)$_n$CuCl$_2$] ($n = 1,2$) AND (2-AMINO-5-BROMOPYRIMIDINE)$_2$CuBr$_2$

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(Received 22 January 2002; Revised 7 August 2002; In final form 7 January 2003)

The reaction of CuX$_2$ (X = Cl, Br) with 2-aminopyrimidine in aqueous solution, or 2-amino-5-bromopyrimidine in aqueous acid yields compounds of the forms [LCuCl$_2$]$_n$ (**1**), [L$_2$CuCl$_2$] (**2**) and [L$'_2$CuBr$_2$] (**3**) [L = 2-aminopyrimidine; L$'$ = 2-amino-5-bromo-pyrimidine]. The three compounds all form layered structures in which each copper ion is coordinated to two 2-aminopyrimidine molecules and two halide ions. Common structural threads involve bridging ligation [either by monomeric (**1**) or hydrogen bonded ligand dimers (**2** and **3**)], N–H$\cdots$X and N–H$\cdots$N hydrogen bonding and π–π stacking interactions as well as semi-coordinate Cu$\cdots$X bond formation (**1** and **2**) or Br$\cdots$Br interactions (**3**). Compounds **1** and **2** crystallize as two-dimensional coordination polymers with asymmetrically bihalide bridged (CuX$_2$)$_n$ chains cross-linked into sheets by the 2-aminopyrimidine molecules (**1**) or by hydrogen bonded L$_2$ dimers (**2**). The halide bibridged chains expand their primary copper coordination spheres to give 4 + 2 coordination spheres in **1** and **2**. In **3**, the layer structure involves coordination of the hydrogen bonded L$'_2$ dimers and C–Br$\cdots$Br$^-$ interactions. Crystal data: (**1**): monoclinic, $P2_1/m$, $a = 3.929(1)$, $b = 12.373(2)$, $c = 7.050(1)$ Å, $\beta = 91.206(4)^\circ$, $V = 342.7(1)$ Å^3, $Z = 2$, $D_{\text{calc}} = 2.225$ Mg/m^3, $\mu = 3.878$ mm^{-1}, $R = 0.0269$ for [$|I| \geq 3\sigma(I)$]. For (**2**): triclinic, P-1, $a = 4.095(4)$, $b = 7.309(5)$, $c = 10.123(6)$ Å, $\alpha = 86.28(6)$, $\beta = 78.44(6)$, $\gamma = 74.55(8)^\circ$, $V = 286.1(4)$ Å^3, $Z = 1$, $D_{\text{calc}} = 1.884$ Mg/m^3, $\mu = 2.360$ mm^{-1}, $R = 0.0506$ for [$|\mathrm{I}| \geq 2\sigma(\mathrm{I})$]. For (**3**): triclinic, P-1, $a = 6.074(4)$, $b = 7.673(3)$, $c = 8.887(3)$ Å, $\alpha = 108.43(3)$ $\beta = 100.86(5)$, $\gamma = 106.96(4)^\circ$, $V = 357.0(3)$ Å^3, $Z = 1$, $D_{\text{calc}} =$ 2.657 Mg/m^3, $\mu = 12.714$ mm^{-1}, $R = 0.0409$ for [$|\mathrm{I}| \geq 2\sigma(\mathrm{I})$].

Keywords: Copper(II); 2-Aminopyrimidine; Crystal structures; Hydrogen bonding

INTRODUCTION

We have been studying the packing motifs of the coordination complexes and salts of nitrogen heterocycles with divalent transition metal ions. Our early efforts focused on 2-aminopyridine and derivatives thereof where the metal complexes were arrayed in a

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000099983

variety of sheets, chains and ladders [1–3]. We have recently studied some nickel and cobalt compounds of 2-aminopyrimidine and its salts [4] and found common packing forms including the formation of hydrogen-bonded dimers of the 2-aminopyrimidinium cations which tend to form sheets in the crystal lattice and control the packing in that fashion. Such influence on lattice packing has been observed in the past for a variety of 2-aminopyrimidine and pyrimidinium complexes such as organic co-crystals of 2-aminopyrimidine with carboxylic acids, [5] 2-aminopyrimidine copper(II) dicyanamides [6], and bis(2-aminopyrimidine)ethene derivatives [7]. We have also seen how these hydrogen-bonded dimers may be interrupted by protonation of the pyrimidine nitrogen atoms or by the addition of waters of hydration in our previous work with Ni(II) and Co(II) [4], as well as our studies with $CuBr_2$ complexes [8] and with $CuCl_2$ in acidic media [9]. Here, we extend the previous work with the addition of neutral copper(II) chloride complexes as well as reporting our initial results with Cu(II) compounds of 2-amino-5-bromopyrimidine.

EXPERIMENTAL

Metal salts and acids, 2-aminopyrimidine and 2-amino-5-bromopyrimidine were purchased from Aldrich Chemical. All materials were used as received. Infrared spectra were recorded as KBr pellets; w = weak, m = medium, s = strong, br = broad. Combustion analyses were performed at the Department of Chemistry, University of Otago, Dunedin, NZ. All compounds gave satisfactory combustion analyses, except **1** where no combustion analysis was obtained.

μ-2-Aminopyrimidine-μ-dichlorocopper(II), **1** [10a] – A 1 : 1 ratio of 2-aminopyrimidine and $CuCl_2 \cdot 2H_2O$ was dissolved in a 50 : 50 mixture of water and ethanol. The resulting solution was allowed to evaporate slowly at room temperature resulting in green plates. The crystals were separated by filtration and air-dried.

Bis(2-aminopyrimidine)dichlorocopper(II), **2** [10b] – $CuCl_2 \cdot 2H_2O$ (20 mmol) was dissolved in 5 mL of H_2O and added to a solution of 2-aminopyrimidine (40 mmol) in 10 mL of H_2O. The majority of the product (4.87 g, 75%) precipitated immediately as a green powder and was isolated by filtration. The filtrate was allowed to evaporate and green needles were recovered after two days. The IR and CHN analyses for the powder and crystals were identical. IR: ν 3396 m, 3120 m, 1645s, 1568s, 1490 m, 1361 m, 1197 m, 788 m cm^{-1}.

Bis(2-amino-5-bromopyrimidine)dibromocopper(II), **3** – $CuBr_2$ (0.065 g, 0.29 mmol) was dissolved in 4 mL of ethanol and added to a solution of 2-amino-5-bromopyrimidine (0.985 g, 0.57 mmol) and HBr (1.14 mL of 1.0 M in H_2O) in 6 mL of ethanol. The solution was heated to reflux whereupon the 2-amino-5-bromopyrimidine dissolved giving a dark green solution. The solution was allowed to cool giving crystals of **3** (0.030 g, 18%) and (2-amino-5-bromopyrimidine)bromocopper(I) as the major product [11]. IR – ν 3408 m, 1647s, 1552s, 1491s, 1128 m, 781 m cm^{-1}.

X-ray Structure Determination

Data collections for **1–3** were carried out on a Siemens P4 diffractometer employing MoKα radiation ($\lambda = 0.71073$) and a graphite monochromator. Data collections *via* ω-scans, cell refinement and data reduction were performed using SHELXTL (VMS)

TABLE I Crystal data and structure refinement for **1**–**3**

	1	**2**	**3**
Empirical formula:	$C_4H_5N_3Cl_2Cu$	$C_8H_{10}N_6Cl_2Cu$	$C_8H_8N_6Br_4Cu$
Formula weight	229.6	324.66	571.38
Crystal system	Monoclinic	Triclinic	Triclinic
Crystal habit	Thin green plate	Green plate	Irreg. red chunk
Space group	$P2_1/m$	P-1	P-1
Unit cell dimensions:			
a (Å)	3.929(1)	4.095(4)	6.074(4)
b (Å)	12.373(2)	7.309(5)	7.673(3)
c (Å)	7.050(1)	10.123(6)	8.877(3)
α (°)	90	86.28(6)	108.43(3)
β (°)	91.206(4)	78.44(6)	100.86(5)
γ (°)	90	74.55(8)	106.96(4)
Volume	342.67(1)	286.1(4)	357.0(3)
Z	2	1	1
Density$_{\mathrm{calc}}$ (Mg/m^3)	2.225	1.884	2.657
Size (mm)	0.1 × 0.15 × 0.25	0.9 × 0.25 × 0.07	0.2 × 0.15 × 0.06
F(000)	226	163	267
μ (mm^{-1})	3.878	2.360	12.714
Data collection:			
Temperature (K)	303(2)	158(2)	158(2)
Max., min. trans	0.7556, 0.3177	0.847, 0.114	0.5159, 0.1853
Reflections collected	2951	758	1834
Independent refl.	993	734	917
θ range (°)	1.5–25.0	2.05–22.49	2.54–22.49
Range h, k, l	$-5 \le h \le 5$	$-4 \le h \le 0$	$-6 \le h \le -6$
	$-17 \le k \le 11$	$-7 \le k \le 7$	$-7 \le k \le 7$
	$-7 \le l \le 9$	$-10 \le l \le 10$	$-9 \le l \le 9$
Refinement:			
Data/rest./para.	993/0/56	734/0/85	917/0/88
Goodness-of-fit on F^2	1.055	1.066	0.875
Final R indices [$I > 2\sigma(I)$]			
R_1	0.0269	0.0506	0.0409
wR_2	0.0661	0.1250	0.0962
R indices (all data)			
R_1	0.0366	0.0661	0.0592
wR_2	0.0697	0.1333	0.1012
Largest diff. peak (e/Å^3)	0.416	0.751	0.830
Largest diff. hole (e/Å^3)	−0.324	−0.687	−0.811

software [12]. Absorption corrections were made *via* ψ-scans. The structures were solved using the heavy atom Patterson method [SHELXS-97] and full-matrix least squares refinement was done via SHELXL-97 [13]. The aromatic hydrogen atoms were refined *via* a riding model with fixed isotropic thermal displacement parameters. The coordinates of the NH hydrogens in **2** were located in the difference maps and allowed to refine with fixed isotropic U's. Attempts to refine the coordinates of the NH hydrogens in **3** resulted in unusually short bond lengths and thus they were placed geometrically and refined with a riding model. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [14]. Crystallographic data may be found in Table I. Selected bond lengths and angles are given in Table II. Significant hydrogen bonds are listed in Table III. Full crystallographic details, atomic coordinates and isotropic thermal parameters, full tables of bond lengths and angles, observed and calculated structure factors and anisotropic thermal parameters are available [15].

TABLE II Selected bond lengths (Å) and angles (°) for **1**–**3**

	1		**2**		**3**	
Cu–X1	Cu–Cl	2.2529(6)	Cu–Cl1	2.240(3)	Cu1–Br1	2.404(2)
Cu–X2	Cu–Cl#1	3.0815(7)	Cu–Cl1#2	3.486(3)		
Cu–N	Cu–N2	2.089(2)	Cu–N1	2.060(5)	Cu–N1	1.988(9)
X1–Cu–X2	Cl–Cu–Cl#1	93.59(2)	Cl–Cu–Cl#2	88.53(8)		
X1–Cu–N	Cl–Cu–N3	91.33(5)	Cl–Cu–N1	90.5(2)	N1–Cu1–Br1	89.1(3)
X2–Cu–N	N2–Cu–Cl#1	94.65(5)	N1–Cu–Cl#2	96.0(2)		

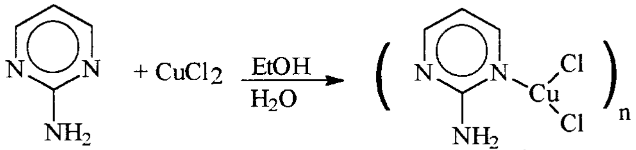
Symmetry transforms used to generate equivalent atoms: #1 = 1+*x*, *y*, *z*; #2 = *x*−1, *y*, *z*.

TABLE III Hydrogen bonds for **1**–**3** [Å and °]

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*<(DHA)*
For Compound **1**				
N2–H1A···Cl#1	0.758	2.467	3.193(3)	161.04
For Compound **2**				
N2–H2A···N3#2	0.73(7)	2.27(7)	3.003(7)	176(8)
N2–H2B···Cl1#1	0.95(7)	2.30(8)	3.191(7)	156(6)
For Compound **3**				
N3–H3A···N2#3	0.88	2.12	3.001(12)	175.9

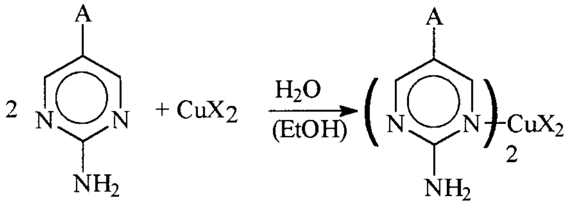
RESULTS AND DISCUSSION

Reaction of an equimolar ratio of 2-aminopyrimidine (2-apm) with $CuCl_2$ in water/ethanol gave $[CuCl_2(2\text{-apm})]$ (**1**) as green crystals.



1

Reaction of two equivalents of 2-apm with $CuCl_2$ in water, or of 2-amino-5-bromopyrimidine (2,5-abp) and $CuBr_2$ in ethanol/water gave the corresponding ML_2X_2 complexes.



2 - A=H, X=Cl; **3** - A, X=Br

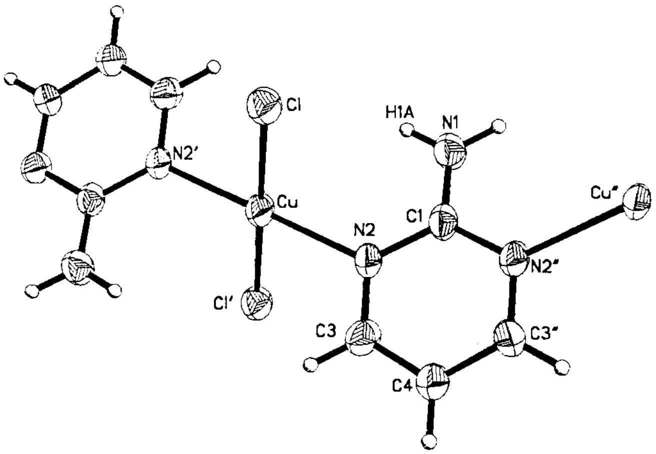


FIGURE 1 Thermal ellipsoid drawing of the molecular unit of **1**. The asymmetric unit is labeled and symmetry equivalents are denoted by ″(x−1, y−1, −z) or ′(x, 3/2−y, z). Hydrogen atoms are shown as circles of arbitrary size.

The poor solubility of 2,5-abp in H_2O and H_2O/ethanol mixtures, even in the presence of acid, required heating the mixture to dissolve all the components. Upon cooling, the major product was the yellow copper(I) compound (2-abp)CuBr, as reported previously [11]. Red crystals of compound **3** were easily separated from the mixture under a stereomicroscope. The complexes were analyzed by single crystal X-ray diffraction. Crystallographic data for **1–3** are given in Table I and selected bond lengths and angles in Table II.

Compound **1** crystallizes in the monoclinic space group $P2_1/m$. The molecular unit is shown in Fig. 1. The copper atom sits on a crystallographic inversion center while the 2-aminopyrimidine ring sits athwart a crystallographic mirror plane.

The Cu–Cl bonds are 2.253(1) Å while the Cu–N2 bonds are 2.089(2) Å. The geometry about the Cu is slightly distorted from square planar as seen by the N2–Cu–Cl bond angle of 91.33(5)°. The bond lengths within the 2-apm rings are typical for compounds where the ligand bridges two metal ions with the N2–C3 bond [1.335(3) Å] being shorter than either the N2–C1 [1.358(2) Å] or C3–C4 [1.370(3) Å] bonds [8,16]. The N2–C1–N2″ [123.1(3)°] and N2–C3–C4 [122.4(2)°] bond angles (see Fig. 1) are the largest within the ring as is usual in bridging 2-apm structures, but are slightly smaller than the typical values of 123–124° [8,16]. The 2-apm rings are nearly planar (mean deviation of the ring atoms from the mean plane = 0.0125 Å) with the copper atom lying only 0.0057 Å out of the plane and the amino nitrogen (N1) lying 0.1834 Å out of the plane on the opposite side. The copper coordination plane is tilted 55.0° relative to the plane of the ring.

The combination of the bridging capabilities of the 2-apm ligand and the propensity for copper(II) halides to form semi-coordinate Cu· · ·Cl bonds leads to the formation of a compact two-dimensional supramolecular structure for this compound. This layer structure is further stabilized by efficient N–H· · ·Cl bonds. The bridging 2-apm ligands link the copper atoms into chains parallel to the b-axis (see Fig. 2). Successive copper coordination planes along the chain are canted ±34.2° relative to each other. Planes of successive 2-apm molecules are parallel within experimental error, but have opposite orientations with respect to the direction of the amino

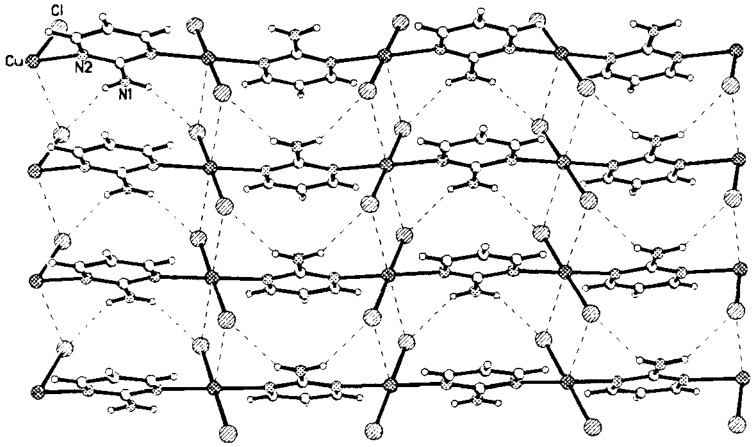


FIGURE 2 Diagram showing packing of one layer of **1** viewed parallel to the *c*-axis. Dotted lines represent H-bonds and semi-coordinate Cu–Cl bonds.

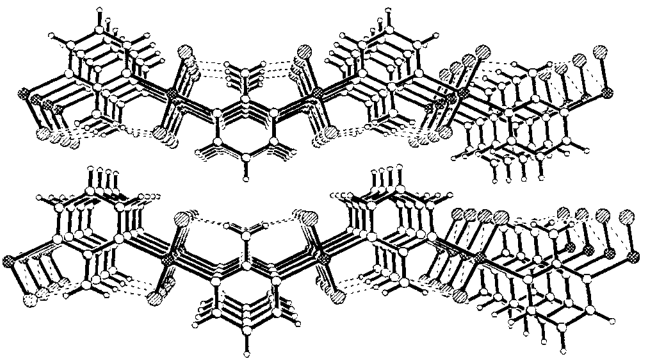


FIGURE 3 Diagram of the packing of **1** showing the relationship of adjacent planes. Dotted lines represent H-bonds.

substituent. The 2-apm bridged Cu chains are further linked into sheets by semi-coordinate bonds between the Cu and chloride atoms of $CuLCl_2$ units separated by a unit cell translation along the *a*-axis [$d_{Cu\text{-}Cl1a} = 3.082(1)$ Å; symm. transform $a = x+1$, y, z]. This leads to π–π stacking interactions between the 2-apm rings with an interplanar separation of 3.725 Å.

The templating effect of ligation and hydrogen bonding by the 2-apm ligands, clearly seen in Fig. 3, leads to a pleated sheet structure for the coordination polymer. The sheets are layered in register with each other (see Fig. 3). The closest contacts between chloride ions in successive layers is 4.060(1) Å [symm. transform = $-x$, $1-y$, $1-z$] and the Cu ions are separated by 7.050(1) Å due to a unit cell translation along the *c*-axis.

Many of the same supramolecular interactions present in **1** carry over to the structure of **2**. Compound **2** crystallizes as green needles in the space group *P*-1. The molecular unit is shown in Fig. 4. The copper atom sits on a crystallographic inversion center and is coordinated to two chlorine atoms and two 2-apm molecules (one each in the asymmetric unit). The geometry about the copper is nearly square planar with the plane of

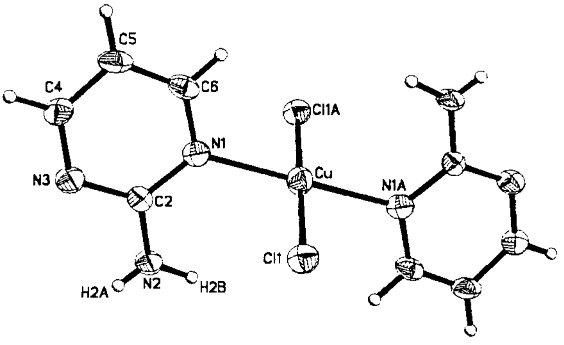


FIGURE 4 Thermal ellipsoid drawing of the molecular unit of **2**. The asymmetric unit, the copper coordination sphere and those hydrogens whose positions were refined are labeled. All hydrogens are shown as circles of arbitrary size.

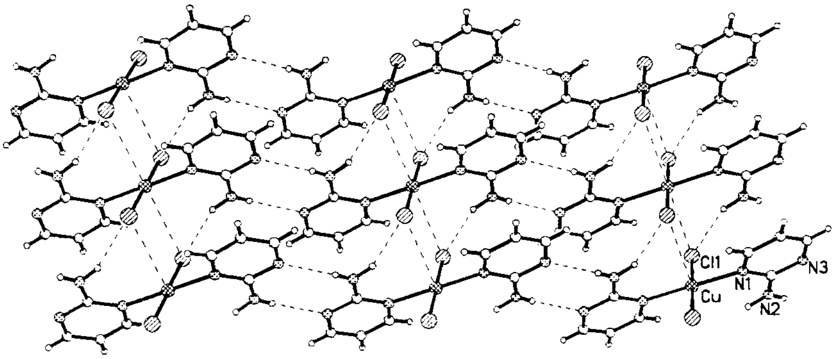


FIGURE 5 Packing diagram showing the formation of sheets in **2** *via* dimerization of the 2-aminopyrimidinium rings *via* hydrogen bonds and *via* semi-coordinate Cu–Cl bonds (dashed lines).

the 2-apm ligands tilted 61.7° out of the coordination plane, slightly larger than seen in **1**. The 2-apm ligands are not quite as planar as in **1** with a mean deviation of the ring atoms from the plane of 0.0193 Å. However, the amino nitrogen, N2, lays only 0.0753 Å out of the plane with the copper atom removed 0.3345 Å to the opposite face. Bond lengths and angles within the ring show the same trends as seen in **1** and are comparable to the corresponding bromo complex, $(2\text{-apm})_2CuBr_2$ [8] and to other 2-apm/copper(II) compounds [17] and while there are measurable changes in bond angles compared to the free ligand [18], none exceeds 3°.

As illustrated in Fig. 5, the molecular units of **2** are linked into chains *via* L_2 dimers formed by hydrogen bonds between amino N–H's and uncoordinated ring nitrogens of 2-apm rings [$d_{N2\text{–}H2A\cdots N3'} = 3.003(7)$ Å; symm. transform $N3' = -x, -y+1, -z$]. Since these two 2-apm rings are related by an inversion center, the planes of the rings are parallel (see Fig. 5). The chains so formed are then linked into sheets *via* very long semi-coordinate bonds between chlorine atoms and copper atoms in the next molecular unit parallel to the *a*-axis [$d_{Cu\text{–}Cl1'} = 3.486(3)$ Å; symm. transform $Cl1' = x-1, y, z$] as was the case with **1**. An additional hydrogen bond between the second amino hydrogen and a chloride ion in the next chain [$d_{N2\text{–}H2B\cdots Cl1'} = 3.191(7)$ Å] further stabilizes the

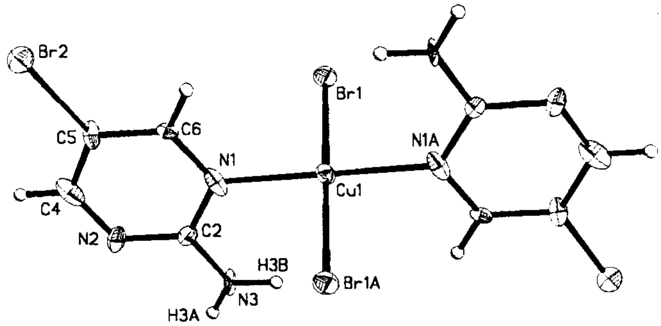


FIGURE 6 Thermal ellipsoid drawing of the molecular unit of **3**. The asymmetric unit, Cu coordination sphere and NH hydrogens are labeled. Hydrogen atoms are shown as circles of arbitrary size.

sheets. This leads to π–π stacking interactions between 2-apm ligands of 3.462 Å. The resulting sheets pack in a fashion very similar to that seen for **1**.

The molecular unit of compound **3** is the same as in **1** and **2**, with the substitution of 2,5-abp for 2-apm (see Fig. 6). The copper again sits on an inversion center and the complex is nearly square planar, with the absence of any semi-coordinate Cu $\cdots$ Br bonds. The Cu–N1 bond is somewhat shorter than in **2** [1.988(9) Å] perhaps because of this absence of semi-coordinate Cu $\cdots$ X interactions. The aromatic ring of the 2,5-abp ligand remains nearly planar (mean deviation of ring atoms = 0.0112 Å) with the amino nitrogen only 0.0381 Å and the Cu atom only 0.0456 Å out of the plane on one face while Br2 lies 0.0380 Å out of the plane on the opposite side. However, the angle between the plane of the ring and the copper coordination plane has increased significantly to 73.8°, as anticipated with the larger $\mathrm{Br^-}$ ion coordinated to Cu. The structure of $\mathrm{CuBr_2(2\text{-}apm)_2}$ also contains isolated square-planar complexes. Here the dihedral angle between the ring and the coordination plane is 81.0° [8]. In both of these bromide complexes, the large dihedral angle prevents formation of the semi-coordinate bonds. The bond lengths and angles within the ring are similar to the known structures of the hydrochloride salt [19] and the Cu(I)Br complex [11] of 2,5-abp, but differ significantly from the metanalinosulfonamide compound where conjugation of the amino nitrogen reduces its electron-donating character to the pyrimidine ring [20] (we note that the poor R-factor for the latter structure makes comparisons tenuous).

The supramolecular interactions leading to the layer structure in **3** contain an entirely different structural element than is present in **1** or **2**. This structure contains $\mathrm{CuX_2}$ units linked into chains by hydrogen bonded $\mathrm{L'_2}$ dimers, similar to the arrangement in **2**. The 2,5-abp rings still dimerize *via* hydrogen bonds between the 2-amino group of one ligand and the non-coordinated ring nitrogen of an inversion related second ligand [$d_{\mathrm{N3\text{–}H3A\cdots N2''}} = 3.001(12)$ Å; symm. transform for N2″ $= 2-x,\ 1-y,\ 2-z$] to form chains (see Fig. 7). However, those chains are not cross-linked into sheets *via* semi-coordinate bonds between the copper atoms and coordinated bromide ions, but rather *via* C–Br $\cdots$ $\mathrm{Br^-}$ interactions between the organic bromine atoms of the ligand and the $\mathrm{Br^-}$ ions in adjacent units [$d_{\mathrm{Br2\cdots Br1^*}} =$ 3.446 Å, $\angle_{\mathrm{C2\text{–}Br1^*\cdots Br2}} = 163.3°$; symm. transform for Br1* $= 1+x,\ 1+y,\ z$] (see Fig. 7). In addition, a longer Br1 $\cdots$ Br2″ contact of 3.909 Å [$\angle_{\mathrm{C2\text{–}Br1\text{–}Br2''}} = 67.6°$, symm. transform for Br1″ $= x,\ 1+y,\ z$] as well as Br1 $\cdots$ Br1* of 4.197 Å [$\angle_{\mathrm{C2\text{–}Br1\text{–}Br1^*}} = 67.6°$, symm. transform for Br1″ $= 2-x,\ 2-y,\ -z$] exist. This corresponds to the type II

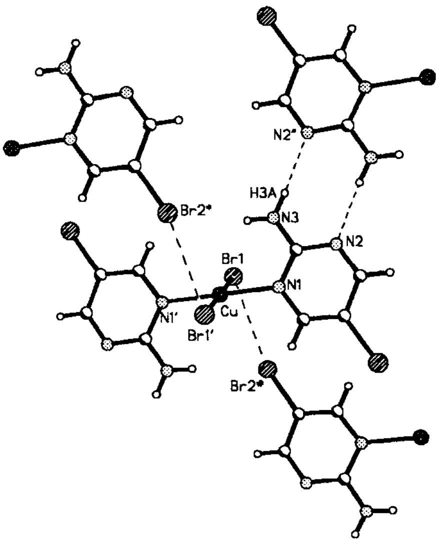


FIGURE 7 Partial view of layer structure for **3** showing dimerization of the 2-abp ligands through hydrogen bonding and the short intermolecular contacts between Br^- ions and ligand bromine atoms (both shown as dashed lines).

interaction of Desiraju and Parthasarathy [21], developed on the basis of their analysis of C-*hal* · · · *hal*-C interactions found in the Cambridge Structural Database. This arrangement is thought to arise through the electronic nature of the C-*hal* bond, that develops a δ^+ charge in the *hal* atom σ lone pair and a δ^- charge on the π lone pairs [22]. The extreme shortness of this Br · · · Br contact coupled with the near linearity of the C–Br · · · Br angle clearly indicates that this is a stabilizing feature of the layer structure. In the corresponding $CuBr_2$(2-apm)$_2$ structure, the C–Br · · · Br interactions are replaced by N–H · · · Br interactions to develop a layer structure.

Again, the 2,5-apb rings form π–π stacks, as illustrated in Fig. 8, with an inter-ring distance of only 3.338 Å. The 2,5-abp rings form layers lying in the ⟨1−11⟩ planes with the copper and bromide ions lying between these layers.

CONCLUSIONS

The 2-apm/coordination plane dihedral angle in the copper compounds increases in the order **1** < **2** < **3**. This increase is correlated with an increase in the Cu · · · X semi-coordinate distance as the dihedral angle increases. In fact, in the Br compound (**3**), no semi-coordinate bond exists.

All three copper complexes attain a two-dimensional layer structure. However, the interactions that lead to the layer structures are different in the three compounds. In **1**, the interactions are semi-coordinate Cu · · · Cl bonds and bridging 2-apm ligands. This mode of lattice development is similar to that found in CuBr(2-apm) and Cu_2Br_4(2-apm) in our previous study of the copper bromide complexes of 2-apm [8]. This is a very common lattice engineering technique utilizing ligands with multiple coordination sites [23]. In **2**, the semi-coordinate interactions are retained, but the bridging linkages are now replaced by (2-apm)$_2$ dimers. A similar dimerization is

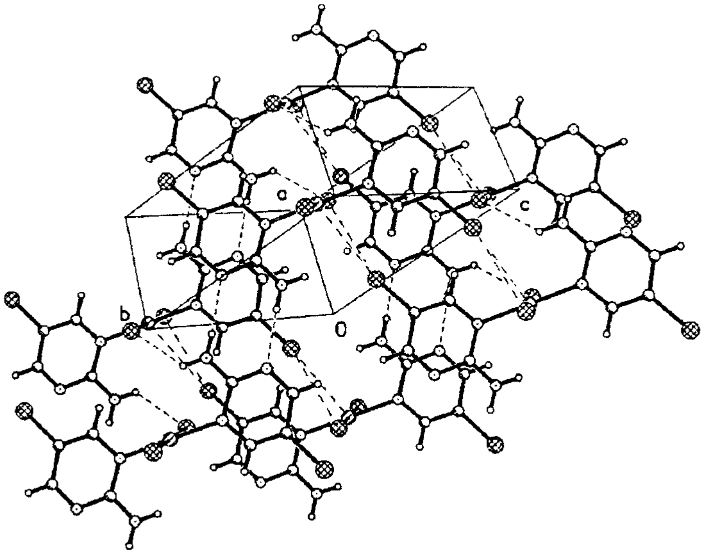


FIGURE 8 Illustration of the π–π packing interactions in **3**.

found in $CuBr_2(2\text{-apm})_2$ [8]. The utilization of self-complementary hydrogen bonded ligand dimers to create two-dimensional coordination polymers has recently been enunciated by Aakeröy, *et al.* [24] Finally, in **3**, the semi-coordinate linkages are replaced by Cu–Br···Br–C interactions. While the existence of C–Br···Br–C interactions are well documented [25], we know of only two reports of the interaction of C–Br with ionic bromide species [26]. However, we have encountered this phenomena quite frequently in our study of copper bromide salts of brominated organic cations [27]. The *pseudo*-linear feature of the short C–Br···Br^- contacts is a common feature observed in these structures.

The effects of these changes are reflected in the expected magnetic dimensionalities of the lattices that decrease from 2-D to 1-D to 0-D in the sequence **1** to **2** to **3**. Both the semi-coordinate linkages and the Cu-(2-apm)-Cu linkage in **1** should give rise to small but significant exchange coupling. However, for **2**, the $Cu\text{-}(2\text{-apm})_2\text{-}Cu$ linkage would be too long to give any substantial exchange coupling, leading to a 1-D magnetic system. In addition, the substantially longer Cu···Cl bonds will lead to weaker coupling *via* that pathway than in **1**. Finally, in **3**, neither pathway should be capable of transmitting substantial exchange coupling, so simple Curie behavior would be expected. Preliminary magnetic measurements from 4–300 K on **1** agree with the prediction of low-dimensional anti-ferromagnetic behavior, but our initial efforts to fit the data to any of the known models for Heisenberg systems have been unsuccessful. More detailed measurements and analysis are in progress. Compound **2** shows weak antiferromagnetic interactions at low temperatures. A Curie–Weiss plot of susceptibility *vs* temperature yields $C = 0.41$ and $\theta = -1.2\,K$. Data for **3** give $C = 0.42$ and $\theta = -0.3\,K$, confirming the prediction that interactions are negligible.

An evaluation of the π–π stacking interactions in metal compounds containing nitrogen-based coordinating ligands has recently been made by Janiak [28]. He found that while parallel planar stacking was typically observed in these structures, electrostatic interactions between the σ and π frameworks lead to a parallel displacement of the ring centers relative to each other. The statistical analysis of nearly 5000 structures showed that the most probable center-to-center distance was about 3.8 Å with an angle between the center-to-center vector and the normal to the ligand ring of approximately 27°. Our results fall well within the range of values observed by Janiak, with corresponding values of distance and angle pairs, (δ, φ) observed of (4.095 Å, 32.2°) for **1**, (3.721 Å, 29.7°) for **2**, and (3.818Å, 28.7°) for ring1-ring2 and (3.649Å, 17.0°) for ring1-ring1′ in **3**.

Acknowledgments

This work was supported by the NSF (Grants DMR-9006470 and DMR-9803813) and ACS-PRF Grant 34779-AC5. The assistance of George Pon, Firas Awwadi and Dr. Brendan Twamley (U. of Idaho) with the structure of Compound **1** is appreciated.

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