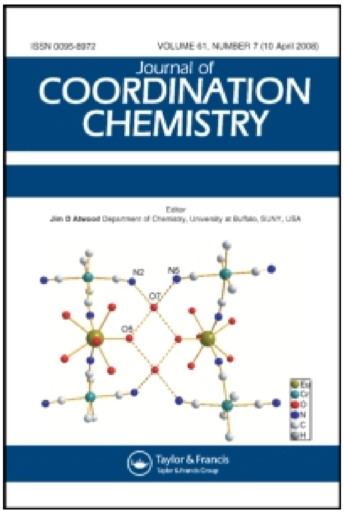

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Giantsidis, John , Galeriu, Calin , Landee, Christopher and Turnbull, Mark(2002) 'Transition Metal Halide Salts of 2-Amino-5-Substituted-Pyridines: Synthesis, Crystal Structure and Magnetic Properties of Two Polymorphs of (5-IAP)$_2$CuCl$_4$[5-IAP = 2-Amino-5-Iodopyridinium]', Journal of Coordination Chemistry, 55: 7, 795 — 803
To link to this Article: DOI: 10.1080/0095897022000001548
URL: http://dx.doi.org/10.1080/0095897022000001548

J. Coord. Chem., 2002, Vol. 55(7), pp. 795–803

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TRANSITION METAL HALIDE SALTS OF 2-AMINO-5-SUBSTITUTED-PYRIDINES: SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF TWO POLYMORPHS OF $(5\text{-IAP})_2CuCl_4$ [5-IAP = 2-AMINO-5-IODOPYRIDINIUM]

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(Received 23 January 2001; Revised 7 June 2001; In final form 28 August 2001)

The reaction of anhydrous $CuCl_2$ with HCl and 2-amino-5-iodopyridine in 1-propanol resulted in two polymorphs of $(5\text{-IAP})_2[CuCl_4]$ [5-IAP = 2-amino-5-iodopyridinium], one as red rods (**1**) and one as orange prisms (**2**). The two polymorphs have been characterized by single crystal x-ray diffraction and variable temperature magnetic susceptibility. Crystal data: triclinic, $P\text{-}1$, $F(000) = 606$, MoK_α ($\lambda = 0.71073$ Å): for (**1**): $a = 9.248(6)$, $b = 10.202(7)$, $c = 10.368(7)$ Å, $\alpha = 102.451(9)$, $\beta = 96.662(8)$, $\gamma = 96.725(8)^\circ$, $V = 938.4(11)$ Å^3, $Z = 2$, $D_{\text{calc}} = 2.291$ Mg/m^3, $\mu = 5.020$ mm^{-1}, $R = 0.0392$ for $[|I| \geq 2\sigma(I)]$. For (**2**): $a = 8.966(2)$, $b = 10.755(2)$, $c = 11.359(2)$ Å, $\alpha = 89.63(3)$, $\beta = 68.04(3)$, $\gamma = 69.07(3)^\circ$, $V = 938.6(3)$ Å^3, $Z = 2$, $D_{\text{calc}} = 2.291$ Mg/m^3, $\mu = 5.019$ mm^{-1}, $R = 0.0217$ for $[|I| \geq 2\sigma(I)]$. The crystal packing for both polymorphs suggests that their magnetic behavior should be that of weakly interacting alternating linear chains. Temperature dependent susceptibility measurements yield: for **1**, $C = 0.43$, $g = 2.14$, $\theta = -1.98$; for **2**, $C = 0.45$, $g = 2.19$, $\theta = -4.15$.

Keywords: Copper; Pyridine; Crystal structure; Magnetic properties

INTRODUCTION

We are interested in the preparation of low-dimensional magnetic lattices. One route for generating such lattices is *via* crystal packing of transition metal ion complexes. In this vein, we have been preparing and studying 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) [1]. A number of these complexes have been prepared where the cation is a protonated N-heterocycle such as pyridine [2], morpholine [3], or pyrimidine [4]. The magnetic exchange in these compounds is

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897022000001548

mediated by van der Waals contacts between the halide ions of the MX_4^{-2} *pseudo*-tetrahedra and the contacts are determined by the crystal packing. We have been studying the use of substituted 2-aminopyridines as potential bases for this purpose and have recently reported our work with 2-amino-3-methylpyridine [1d], 2-amino-5-chloro- and 2-amino-5-methylpyridine [1a,b,f], 2-amino-5-cyanopyridine [1e], and 2-amino-5-bromopyridine [5]. We are especially interested in how the size of the 5-substituent affects the symmetry of the crystal lattice and separation between the MX_4^{-2} ions. This paper reports the results of our synthesis and characterization of two polymorphs of the iodo-substituted complex $(5\text{-IAP})_2CuCl_4$ [5-IAP = 2-amino-5-iodopyridinium].

EXPERIMENTAL

$CuCl_2$ dihydrate was purchased from Alfa-Aesar and dried at 140°C for 24 h to generate the anhydrous salt. 1-Propanol was dried over 4 Å molecular sieves for 48 h prior to use. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR. NMR spectra were taken on a Varian Mercury200 and referenced to TMS (^{1}H) or solvent (^{13}C). Combustion analysis were performed at the University Instrumentation Center, University of New Hampshire, Durham, NH.

2-Amino-5-Iodpyridine [6]

2-Aminopyridine (10.0 g, 0.016 mmol) was dissolved with stirring in a mixture of 14 mL of H_2O and 70 mL of glacial acetic acid, followed by iodine (10.85 g, 0.0427 mmol) and H_5IO_6 (4.853 g, 0.0213 mmol). The mixture was treated dropwise with conc. H_2SO_4 (1.9 mL), stirred for four hours and then allowed to cool to room temperature. The solution was treated with solid KOH until precipitation of a yellow solid was complete. The residue was collected and recrystallized from hexanes/toluene to give a white solid, 11.29 g (48%). m.p. 125–126°C [Lit. 128°C] [6]. IR (KBr): ν 3391 m, 3305 m, 3138 m, 1636 s, 1584 s, 1482 s, 1381 s, 1142 m, 822 s cm^{-1}. ^{1}H-NMR (acetone-d$_6$): δ 5.63 (2H, s, br, NH_2) 6.48 (1H, d, $J = 8.8$ Hz, NH_2–C=C*H*) 7.62 (1H, dd, $J = 2.35$ Hz, 8.8 Hz, I–C=C*H*–CH) 8.12 (1H, d, $J = 2.35$ Hz, N-C*H*=). ^{13}C-NMR (acetone-d_6): δ 76.3, 111.6, 145.5, 154.4, 159.7.

2-Amino-5-Iodopyridinium Chloride

Dry HCl was bubbled through a solution of 2-amino-5-iodopyridine (5.7 g, 25.9 mmol) in diethyl ether (100 mL) until precipitation was complete. The salt was recovered by filtration and dried under vacuum to give a white solid, 6.65 g (98%). IR (KBr): ν 3279 m, 3116 m, 1654 s, 1606 m, 1419 m, 1326 m, 1237 m, 1145 m, 813 s cm^{-1}.

Bis(2-Amino-5-iodopyridinium)tetrachlorocuprate(II), (1) and (2)

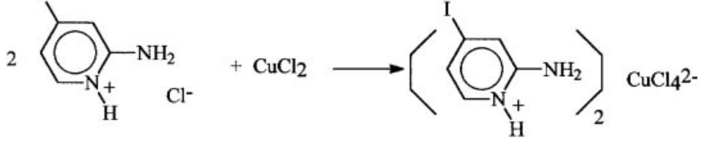
2-Amino-5-iodopyridinium chloride (0.477 g, 1.86 mmol) was dissolved in 70 mL of 1-propanol and combined with a solution of anhydrous $CuCl_2$ (0.128 g, 0.95 mmol) dissolved in 70 mL of 1-propanol. After addition of an extra 70 mL of propanol to reduce the crystallization rate, the solution was placed in a Schlenk flask under a slow stream of argon at room temperature to evaporate. Crystals were harvested after two weeks (51%). No attempt was made to maximize the yield. Examination of the product under a stereomicroscope revealed two types of crystals, red rods (**1**) and orange prisms (**2**), a sufficient quantity of which were separated manually to obtain IR, x-ray and CHN analyses. IR (KCl): ν 3287m, 3182m, 1660s, 1602s, 1534m, 1442m, 1325m, 1150m, 828m, 500m cm^{-1}. [Note: the spectra of the two polymorphs are identical within instrument resolution.] CHN: Calc. for $C_{10}H_{12}N_4Cl_4CuI_2$: C, 18.53; H, 1.85; N, 8.64. Found: (**1**) C, 18.31; H, 2.04; N, 8.33; (**2**) C, 18.41; H, 2.01; N, 8.45%.

X-ray Structure Determination

All data collections were carried out at 158 K on a Siemens P4 diffractometer *via* ϕ and ω-scans employing MoKα radiation ($\lambda = 0.71073$) and a graphite monochromator. The structures were solved using the heavy atom Patterson method [SHELXS-97] and full-matrix least-squares refinement was done *via* SHELXL-97 [7]. The aromatic hydrogen atoms were refined *via* a riding model with fixed isotropic U's while the coordinates of the NH hydrogens were allowed to refine with fixed isotropic U's. Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [8]. Data collection, cell refinement and data reduction were performed by using a Bruker SMART system [9]. Crystallographic data may be found in Table I. Bond lengths and angles about the Cu ion are given in Table II. 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 given in the supplementary material [10].

RESULTS

2-Amino-5-iodopyridine was prepared *via* a modification of the procedure of Ogura and co-workers [6]. This method proved vastly superior to previously published techniques as it eliminated the need to remove large quantities of unreacted I_2 [12] or to separate 2-amino-3,5-diiodopyridine from the product [13]. The pyridine was then converted to the corresponding hydrochloride salt, 5-IAP chloride, by treatment with dry HCl in ether. The reaction of 5-IAP chloride with anhydrous copper(II) chloride in 1-propanol upon slow evaporation under argon gave *bis*(5-IAP) tetrachlorocuprate(II) in 51% yield.



The compound crystallized as a mixture of small orange prisms and red rods in approximately a 1 : 2 ratio. Infrared spectra of the two types of crystals were indistinguishable and characterized by strong absorptions for the N–H and C–H stretching vibrations (3075–3290 cm^{-1}) and the NH_2 bending vibration at 1600 cm^{-1}. Combustion analysis revealed both to have the stoichiometry $(5\text{-IAP})_2CuCl_4$. Single crystal x-ray diffraction showed that the two types of crystals are polymorphs.

TABLE I Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula:	$C_{10}H_{18}N_4Cl_4CuI_2$	$C_{10}H_{18}N_4Cl_4CuI_2$
Formula weight	647.38	647.38
Crystal system	Triclinic	Triclinic
Crystal habit	Red rods	Orange prisms
Space group	*P*-1	*P*-1
Unit cell dimensions:		
a (Å)	9.248(6)	8.966(2)
b (Å)	10.202(7)	10.755(2)
c (Å)	10.368(7)	11.359(2)
α (°)	102.451(8)	89.63(3)
β (°)	96.662(8)	68.04(3)
γ (°)	96.725(8)	69.07(3)
Volume	938.4(11)	938.6(3)
Z	2	2
Density (calc)(g/cm^3)	2.291	2.291
F(000)	606	606
μ (mm^{-1})	5.020	5.019
Data collection:		
Absorption correction [11]	SADABS	SADABS
Max., min. transmission	1.000, 0.5469	1.0000, 0.7052
Reflections collected	8640	6546
Independent reflections	3601	3386
θ range	2.80–26.55	3.72–26.36
Range h, k, l	$-5 \leq h \leq 11$	$-11 \leq h \leq 10$
	$-12 \leq k \leq 12$	$-12 \leq k \leq 13$
	$-12 \leq l \leq 12$	$-12 \leq l \leq 14$
Refinement:		
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3601/1/208	3383/0/208
H atom refinement	Mixed	mixed
Goodness-of-fit on F^2	1.159	1.111
Final R indices [$I > 2\sigma$(I)]		
R_1	0.0374	0.0217
wR_2	0.1168	0.0532
R indices (all data)		
R_1	0.0478	0.0238
wR_2	0.1431	0.0543
Largest difference peak (e/Å^3)	1.312 (near I1)	0.623
Largest difference hole (e/Å^3)	-1.800 (near I1)	-0.738

TABLE II Selected bond lengths (Å) and angles (°) for **1** and **2**

Bond	*1*	*2*	*Angle*	*1*	*2*
Cu–Cl1	2.245(2)	2.233(1)	Cl1–Cu–Cl2	133.46(7)	142.64(4)
Cu–Cl2	2.249(2)	2.251(1)	Cl1–Cu–Cl3	97.61(8)	96.78(4)
Cu–Cl3	2.263(2)	2.284(1)	Cl1–Cu–Cl4	99.87(8)	96.85(4)
Cu–Cl4	2.248(2)	2.246(1)	Cl2–Cu–Cl3	100.45(8)	97.04(4)
			Cl2–Cu–Cl4	99.55(7)	97.01(4)
			Cl3–Cu–Cl4	131.30(7)	135.79(4)

Figure 1 shows the asymmetric unit of **1**, the red polymorph. Bond lengths and angles about the Cu ion are given in Table II.

The $CuCl_4^{-2}$ ions show distinct Jahn–Teller distortion from tetrahedral. The mean *trans*-angle (defined as the average of the X–Cu–X angles > 109.5°) about the Cu is 132.4°, but the Cu–Cl bond lengths are typical and average 2.249 Å. The average

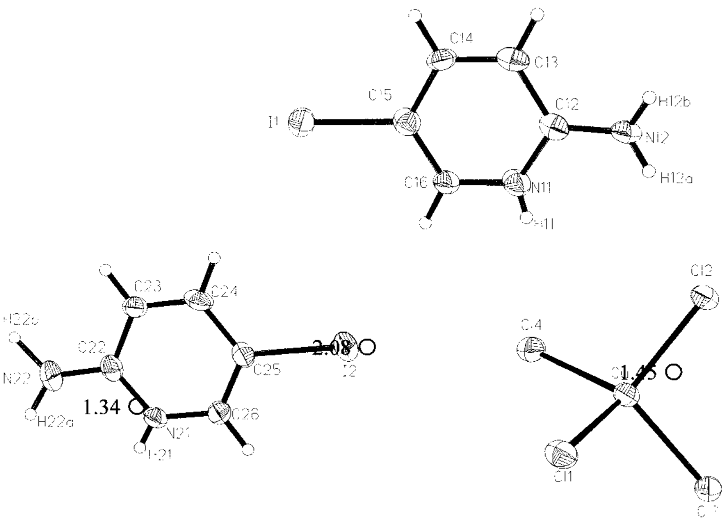


FIGURE 1 ORTEP diagram of **1**, the red polymorph of $(5\text{-IAP})_2CuCl_4$, showing 50% probability ellipsoids. Only hydrogens whose positions were refined are labeled.

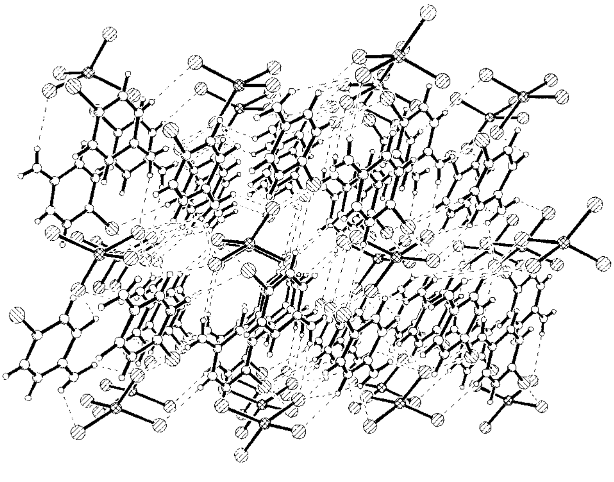


FIGURE 2 Packing diagram of **1**, viewed parallel to the *c*-axis, showing the layer structure. The Jahn–Teller distortion of the $CuCl_4^{-2}$ ions is also clear. The dashed lines show the hydrogen bonds within the lattice.

bond lengths and angles within the two 5-IAP rings are comparable to those of other 5-substituted-2-aminopyridinium ions [14]. The C–I bond is 2.09(1) Å in both rings, and makes the overall length of the 5-IAP cation significantly greater than compounds we have previously studied, such as the 5-bromo and 5-chloro analogues. The two 5-IAP rings are nearly parallel, but opposite in orientation. The angle between the major axes (defined as the C2–C5 direction) of the two rings is 170° while the angle between the mean ring planes is 11°. The mean deviation from planarity for both rings is less than 0.008 Å.

The compound packs in layers with the 5-IAP cations separating sheets of the tetrachlorocuprate anions (Fig. 2). The three-dimensional structure is stabilized

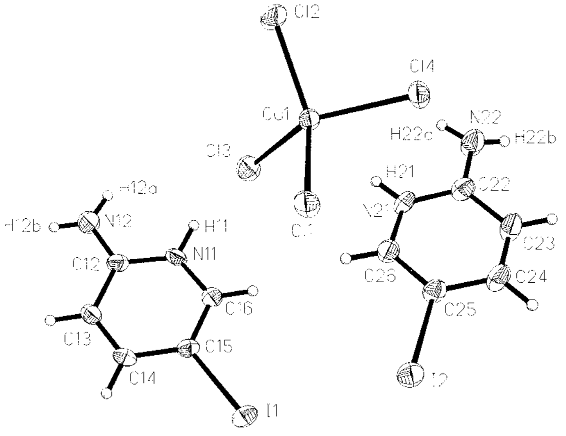


FIGURE 3 ORTEP diagram of **2**, the orange polymorph of (5-IAP)$_2$CuCl$_4$, showing 50% probability ellipsoids. Only hydrogens whose positions were refined are labeled.

by numerous hydrogen bonds between the N–H protons and the chlorine atoms. The strongest hydrogen bonds occur between chlorines and the amino and pyridinium hydrogens of a single 5-IAP cation [$d_{\mathrm{N11-H11\cdots Cl4}} = 3.16(1)\,\text{Å}$, $\angle = 166(10)°$; $d_{\mathrm{N12-H12A\cdots Cl2}} = 3.31(1)\,\text{Å}$, $\angle = 165(7)°$; $d_{\mathrm{N12-H12B\cdots Cl3'}} = 3.29(1)\,\text{Å}$, $\angle = 165(7)°$ (Symmetry transform for C13′: x-1,y, z)].

Within a layer, the shortest contacts between the CuCl_4^{-2} ions resemble an alternating chain. Single contacts ($d_{\mathrm{Cl\cdots Cl}} = 3.74\,\text{Å}$) are observed between Cl3 atoms related by the crystallographic inversion center at (0, 0, 0), while double contacts ($d_{\mathrm{Cl\cdots Cl}} = 3.84\,\text{Å}$) are observed between Cl2···Cl4 pairs related by the inversion center at (0.5, 0.5, 0.5). The closest contacts between chains within the layer ($d_{\mathrm{Cl\cdots Cl}} = 4.33\,\text{Å}$) and between layers ($d_{\mathrm{Cl\cdots Cl}} = 4.42\,\text{Å}$) are significantly longer.

Crystals of the orange phase of (5-IAP$_2$CuCl$_4$, **2**, were also suitable for single crystal x-ray study. The asymmetric unit of **2** is shown in Fig. 3. Selected bond lengths and angles are given in Table II.

The CuCl_4^{-2} ions of **2** show an even larger distortion from tetrahedral than was observed in **1**. The mean *trans*-angle about the Cu is 139.2°, almost 7° larger. The bond lengths and angles within the two 5-IAP rings agree with those of **1** within ± 0.03 Å. The two 5-IAP rings of **2** are closer to being co-planar as the angle between the mean planes of the rings is only 6.6°. However, the relative orientation of the rings is significantly more skewed. The angle between the major axes of the two rings is 53.9°. The mean deviation from planarity for both rings is less than 0.006 Å.

Initial examination of the packing of **2** suggests that it is similar to **1**, with layers of 5-IAP cations separating layers of tetrachlorocuprate anions (see Fig. 4). Again, the structure is stabilized by numerous hydrogen bonds, the strongest of which are seen between a pyridinium hydrogen and Cl4 [$d_{\mathrm{N11-H11\cdots Cl4'}} = 3.17(1)\,\text{Å}$, $\angle = 156(3)°$] and an amino hydrogen on the other ring and Cl3 [$d_{\mathrm{N22-H22A\cdots Cl3'}} = 3.315(1)\,\text{Å}$, $\angle = 162(4)°$] (Symmetry transform for Cl3′ and Cl4′: $-x+1$, $-y+1$, $-z-1$).

As was observed in the red polymorph, **2** also exhibits short alternating intermolecular Cl···Cl distances that could lead to magnetic superexchange. However, here the shortest contacts are observed between Cl atoms in different packing layers. Examination of Fig. 4 reveals that one chlorine in each CuCl_4^{-2} moiety; (Cl4)

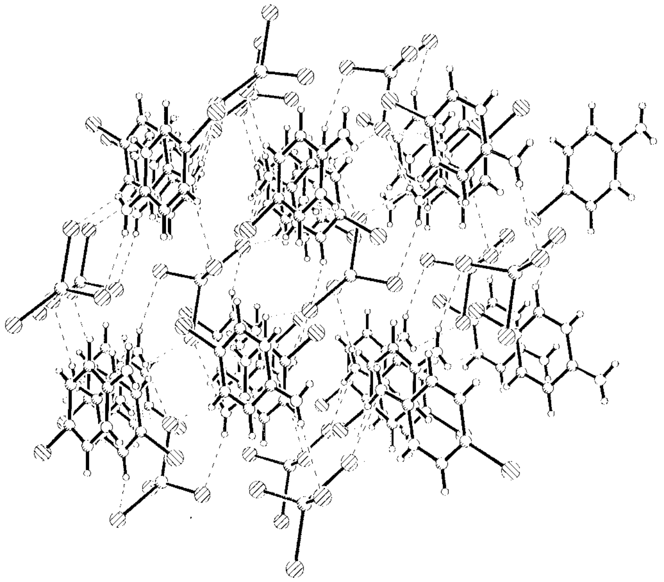


FIGURE 4 Packing diagram of **2** viewed parallel to the *c*-axis. The dotted lines show hydrogen bonds within the lattice.

protrudes into the layer of 5-IAP cations where it comes in close contact (3.65 Å) with an inversion related chlorine from the next layer (inversion center at 0.5, 0, 0.5). The alternating chains then continue through short contacts (3.82 Å) between Cl3 atoms related by the inversion center at (0.5, 0.5, 0.5). The ions so related are so close that the non-bonded Cl···Cu distance here is only 4.32 Å. The next shortest Cl···Cl distance within the layer is 4.74 Å (parallel to the C-face diagonal) and the closest contact between these layers is 5.72 Å (parallel to the *c*-axis) suggesting that the chains should be well isolated from each other in space.

MAGNETIC DATA

Magnetic susceptibility (χ) was collected as a function of temperature between 2–100 K on a Quantum Design SQUID magnetometer. Both complexes show weak antiferromagnetic interactions. Curie–Weiss fits to the data above 30 K yield the following: for **1**, $\theta = -1.98$ K, C = 0.43, $g = 2.14$; for **2**, $\theta = -4.15$, C = 0.449, $g = 2.19$. While the g-factors are somewhat high for Cu^{+2}, they are not unreasonable considering the largest distortion from tetrahedral geometry about the copper ions.

DISCUSSION

The discovery of two polymorphs of $(5\text{-IAP})_2CuCl_4$, both of which crystallized in the triclinic space group *P*-1 was unexpected. We had previously prepared a number of complexes with the general formula $(5\text{-SAP})_2CuX_4$ [5-SAP = 5-substituted-2-amino-pyridinium, X = Cl,Br] including the 5-methyl [1a,2], 5-chloro [1b,1c], and 5-bromo [5] compounds, all of which crystallized in the monoclinic space group $C2/c$ and generated square magnetic lattices. In these complexes, the MX_4^{-2} anions are related by the C-centering and lie in planes. The planes are separated by stacks of the 5-SAP cations which are oriented such that their major axis (the C2–C5 axis) is perpendicular to the MX_4^{-2} planes. This provides maximum separation between the MX_4^{-2} planes as it points the amino- and 5-substituents toward the MX_4^{-2} planes. We have been investigating the effect of varying the size and shape of the 5-substituent of the pyridinium ion on the spacing between the MX_4^{-2} anions and hence the magnetic exchange between them. The intent was that the long C–I bond would serve to isolate the layers better. However, there appears to be a limit to the separation between those layers which is tolerated by the $C2/c$ lattice. Increasing the length of the cation to the size of the 5-IAP ion leaves such voids between the layers that the cations reorient to reduce the free volume in the unit cell. For example, in the $C2/c$ compound (2-amino-5-bromopyridinium)$_2$CuBr$_4$, there is a single 5-BAP cation in the asymmetric unit and its major axis is only 22° from the normal to the plane of the Cu ions [5]. In compound **1**, the two rings are rotated such that their major axes lie 65.4° (C12 ring) and 69.8° (C22 ring) from the mean plane of the Cu ions.

Magnetic exchange interactions between the tetrachlorocuprate ions *via* the non-bonding overlap of the chloride ions are significantly weaker that those between the corresponding bromide ions [1b] and as a result no maximum in χ was observed above 2 K. Attempts to fit the magnetic data to both the uniform and alternating $S = 1/2$ Heisenberg chain models were inconclusive. The two models only differ significantly in their predictions as T approaches the temperature at χ_{max} and as a result the data fit both models equally well.

We are continuing our investigations of the (5-SAP)$_2MX_4$ family of compounds. We hope to determine the limits on the size and shape of the 5-substituent that will allow the previously observed $C2/c$ lattice for members of the family. We anticipate that both the overall length of the 5-SAP ion and the effective radius of the 5-substituent will play roles.

Acknowledgements

This work was supported in part by the NSF (Grants DMR-9006470 and DMR-9803813). We are grateful for additional financial support (JG) through a James and Ada Bickman Summer Undergraduate Research Fellowship. The authors are indebted to Prof. Joseph Budnick (U. Conn.) for the use of his SQUID and Prof. Ward T. Robinson (U. Canterbury) for the x-ray data collection. In addition, we appreciate helpful discussions with Prof. Daniell Mattern (U. Mississippi).

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