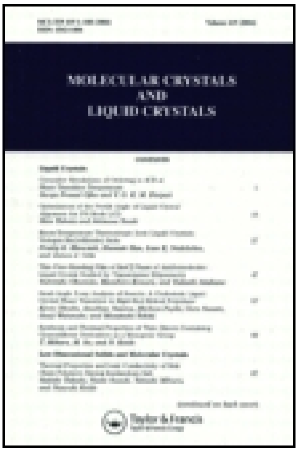

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Synthesis, Structure and Magnetic Susceptibility of two 5-Nitro-2-Aminopyridinium Cuprates: (5-NAP) 2 CuCl 4 and the Quantum Magnetic Ladder (5-NAP) 2 CuBr 4 ·H 2 O

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Synthesis, Structure and Magnetic Susceptibility of two 5-Nitro-2-Aminopyridinium Cuprates: (5-NAP)$_2$CuCl$_4$ and the Quantum Magnetic Ladder (5-NAP)$_2$CuBr$_4$·H$_2$O

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Abstract: The synthesis, x-ray crystal structures and magnetic susceptibilities for two tetrahalocuprate salts are reported. Bis(2-amino-5-nitropyridinium) tetrabromocuprate monohydrate [(5-NAP)$_2$CuBr$_4$•H$_2$O], **1** is triclinic, P-1. The tetrabromocuprate ions pack to form quasi-Heisenberg, S=½ quantum antiferromagnetic ladders with two identical Br…Br contacts of 4.07 Å forming the rungs and a single Br… Br contact of 3.93 Å forming the rails. Bis(2-amino-5-nitropyridinium) tetrachlorocuprate [(5-NAP)$_2$CuCl$_4$], **2**, is monoclinic , P2$_1$/n. The tetrachlorocuprate ions are square planer and pack in layers to form a rectangular lattice with Cl…Cl contacts of 4.09 Å and 4.31 Å. Preliminary magnetic data on **1** yields exchange constants of J_{rung} = 25.4 K and J_{rail} = 13.3 K.

Keywords: Heisenberg; magnetic ladder; tetrabromocuprate; quantum antiferromagnets.

INTRODUCTION

Low-dimensional, quantum antiferromagnets are providing a rich field for the study of exchange theory and superconductivity. It has become evident that spin-ladders are particulary interesting systems for such study.[1] Even-legged ladders are expected to have singlet ground states with a finite energy gap (Δ). The gaps can be closed by application of a magnetic field to generate a quantum critical point.

Few systems are known which behave as spin ladders. The family of Sr/Cu/O compounds, of which the simplest is $SrCu_2O_3$, form a significant body of high symmetry complexes with both two- and three-leg ladders known.[2] However, the exchange constants in these materials are exceedingly strong (400-1500 K), making measurements of field-dependent properties impossible. In addition, it means that the magnetic moments being measured are always small and uncertainties due to diamagnetic corrections or trace impurities can cause large errors. $[(DT\text{-}TTF)_2][Au(mnt)_2]$ suffers similar problems.[3]

Cu_2(1,4-diazacycloheptane)$_2Cl_4$ has been well studied.[4] While the rail and rung magnetic exchange (2-14 K) can be overcome with accessible fields, the site symmetry is low and additional approximations are needed to analyze the magnetic behavior. However, the moderate exchange strengths generate an experimentally accessible critical point and have allowed for extensive study of the compound.[5]

We have been interested in the design and preparation of low-dimensional magnetic systems for some time, both through the design of coordination polymers and through the effects of crystal packing. Recently, the structures and magnetic behavior of three additional complexes which also crystallize as magnetic ladders, $(2\text{-AP})_2CuBr_4$,[6] $(5\text{-IAP})_2CuBr_4{\bullet}2H_2O$[7] and $(C_5H_{12}N_2)_2CuBr_4$,[8] have been reported. These compounds are similar to Cu_2(1,4-diazacycloheptane)$_2Cl_4$ in that they exhibit moderate exchange constants which allow for extensive study of their magnetic behavior, but more importantly, all show higher packing symmetry. In these materials, the superexchange paths are formed via non-bonding contacts between the Br ions on the $CuBr_4^{2-}$ units which are related by either unit cell translations or inversion centers. This means that for these systems, there are truly only two magnetic exchange pathways, one across the rungs of the ladders and one along the rails. We report here the synthesis, structure and preliminary magnetic properties of a new member of this family of S=1/2 magnetic ladders, bis(2-amino-5-nitropyridinium) tetrabromocuprate monohydrate $[(5\text{-NAP})_2CuBr_4 \cdot H_2O]$, **1**, and the synthesis and structure of its chloro analogue, bis(2-amino-5-nitropyridinium) tetrachlorocuprate [$(5\text{-NAP})_2CuCl_4$], **2.**

SYNTHESIS AND STRUCTURE OF $(5\text{-NAP})_2CuBr_4 \bullet H_2O$

Dark red (nearly black), laminar crystals of $(5\text{-NAP})_2CuBr_4 \bullet H_2O$, **1**, were grown by slow evaporation of a solution of 0.204g (1.5mmol) of 2-amino-5-nitropyridine, 0.164g (0.75mmol) of $CuBr_2$ and 4 ml of 48% $HBr_{(aq)}$ in 30 ml of 1-propanol. Crystal data for **1** is given in Table 1.[9]

TABLE 1 Crystal data for Compounds **1** and **2**

		1	**2**
Empirical Formula		$C_{10}H_{14}N_6O_5CuBr_4$	$C_{10}H_{12}N_6O_4Cl_4Cu$
Molecular Weight		681.45 g/mol	485.60
Crystal Class		Triclinic	monoclinic
Space Group		P-1	$P2_1/n$
Lattice constants:	a	7.566(3)Å	8.080(3)Å
	b	9.359(4)Å	7.874(3)Å
	c	14.909(6)Å	14.080(5)Å
	α	77.07(1)°	90°
	β	75.91(1)°	106.41(4)°
	γ	76.39(1)°	90°
Temperature		163(2)K	158(2)K
F(000)		650	486
Z		2	2
Total Reflections		11529	10642
Unique Reflections		3907 (3228h $I>2\sigma$)	1733(1666 $I>s\sigma$)
Structure solution		SHELXS-97	SHELXS-97
Structure refinement		SHELXL-97	SHELXL-97
Final agreements:	R	0.0636	0.0178
	R_w	0.1677	0.0487
	GooF	1.015	1.117

A drawing of the molecular unit of **1** is presented in Figure 1. The bond lengths and angles within the 2-amino-5-nitropyridinium ions are in good agreement with those observed for 2-amino-5-nitropyridinium ions[10] and are unremarkable. The tetrabromocuprate ion is a distorted tetrahedron with a mean Cu-Br bond length of 2.391(1)Å and a mean trans Br-Cu-Br angle of 129.95(2)°. The angle distortion is greater than it first appears as the individual trans Br-Cu-Br angles are 141.15(5)° and 118.77(4)°.

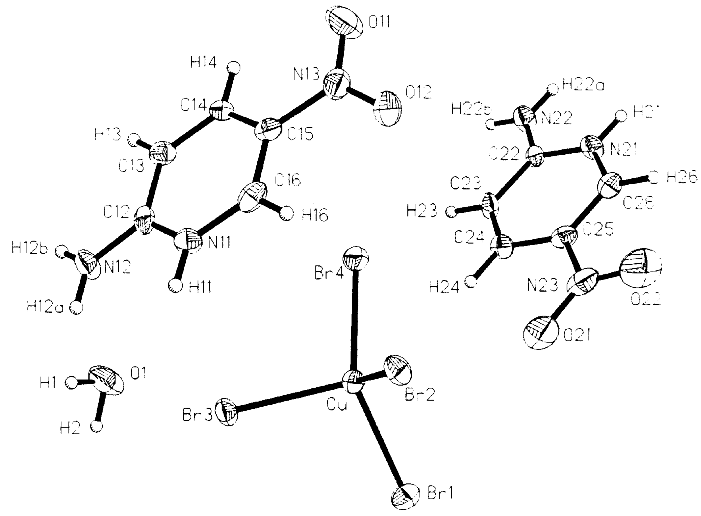

FIGURE 1 - ORTEP drawing of **1** showing 50% probability ellipsoids.

This may be explained by the proximity of one of the oxygen atoms of one of the nitropyridinium ring (O12_1655, $d_{Cu...O12}$ = 3.439(1)Å). The water molecule (O1) forms a strong hydrogen bond to a hydrogen on one of the amino groups ($d_{O1...N22}$ = 2.84(1)Å, $\angle_{O1..H..N22}$ = 171(2)°) and weaker hydrogen bonds to bromine atoms and another water molecule related by a crystallographic inversion center.

The tetrabromocuprate ions pack such that the closest Br...Br contacts form ladders (see Figure 2a). The rails of the ladder are formed by unit cell translations along the *a*-axis ($d_{Br1a...Br2b}$ = 3.93Å) and the rungs of the ladder are formed by two close Br...Br contacts between $CuBr_4^{-2}$ ions related by an inversion center ($d_{Br2a...Br3d}$ = $d_{Br3a...Br2d}$ = 4.07Å). Although the bromine-bromine distance is slightly larger across the rungs, the dual exchange pathway may lead to larger values for J. The ladders are well isolated from each other by stacks of the pyridinium ions and the water molecules (see Figure 2b).The closest Br...Br contacts between ladders are 5.24Å.

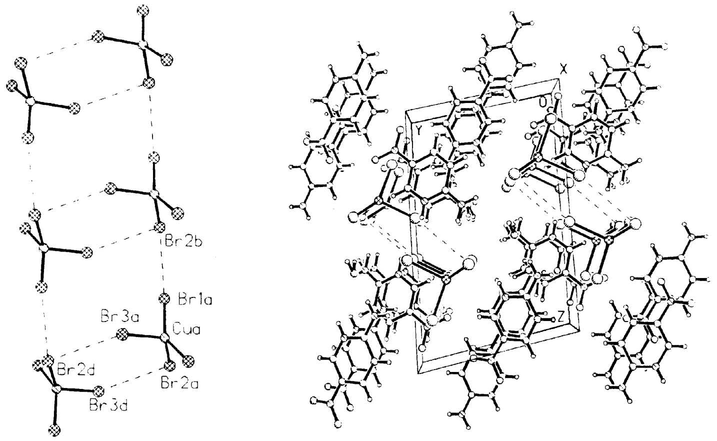

FIGURE 2 - a) The ladder structure of **1**. b) Packing diagram of **1** showing the stacking of the organic cations. The dashed bonds show the rungs of the ladders.

SYNTHESIS AND STRUCTURE OF $(5\text{-NAP})_2CuCl_4$

Slow evaporation of a solution of 2-amino-5-nitropyridine (0.214g, 1.53mmol) with $CuCl_2{\bullet}2H_2O$ (0.131g, 0.75mmol) and 2 ml of 36% $HCl_{(aq)}$ in 10 ml of 1-propanol resulted in bright green crystals of bis(2-amino-5-nitropyridinium) tetrachlorocuprate, **2**, suitable for x-ray study.[9]

The molecular unit of **2** is shown in Figure 3. The compound crystallizes as monoclinic crystals in the space group $P2_1/n$ with the Cu atom locate upon an inversion center. The coordination of the chloride ions about the copper atom is nearly perfectly square planar ($\angle_{Cl1\text{-}Cu\text{-}Cl2}$ = 90.34(2)°) with an average Cu-Cl bond length of 2.279(1)Å. There are also interactions between the Cu atom and one of the oxygens of the organic cations ($d_{Cu...O11}$ = 2.741(1)Å, $\angle_{O11\text{-}Cu\text{-}Cl}$ = 89.14(3)°) generating a tetragonal environment. This represents a distinct polymorph from that previously reported by Bagieu-Beucher, *et al.*[9b]

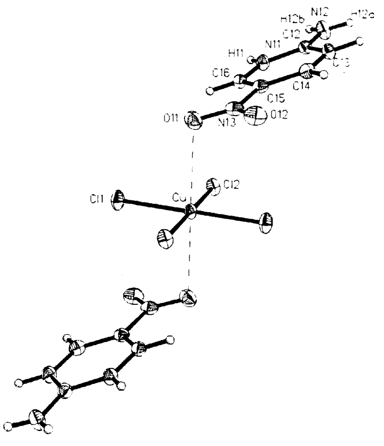

FIGURE 3 - ORTEP drawing of **2** with the asymmetric unit labeled.

The packing of the molecules generates layers ($CuCl_4^{-2}$; cation; cation) which run parallel to the crystallographic C-face. The $CuCl_4^{-2}$ ions lie in 2D-rectangular sheets (see Figure 4) with Cl...Cl contacts within the sheet of 4.09Å (parallel to the *a*-axis) and 4.31Å (parallel to the *b*-axis).

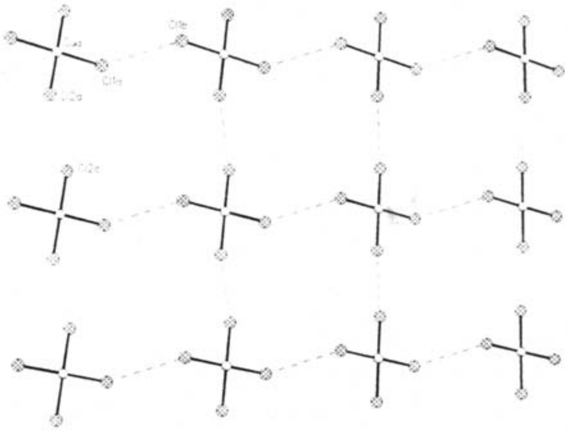

FIGURE 4 - One layer of $CuCl_4^{-2}$ ions. The *a*-axis is horizontal and the *b*-axis is vertical.

While the packing of **2** lends itself to the study of rectangular lattices, chloride-chloride distances of this size will generate only very weak exchange and will require very low temperatures to study.

Magnetic Susceptibility Data

Powder magnetic susceptibility data for **1** is shown in Figure 5. A preliminary fit of the data using a high-temperature series expansion[5b] determined that the exchange across the rungs was much greater than that along the rails, and thus an analytical expression resulting from perturbation theory was applied.[11]

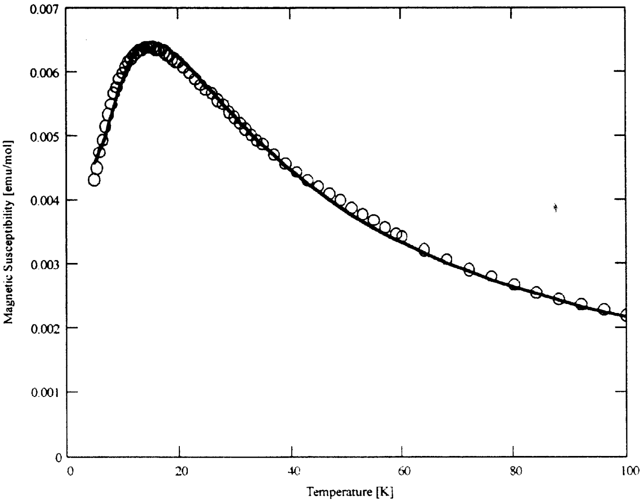

FIGURE 5 - Powder magnetic susceptibility as a function of temperature for **1**. The solid line is the fit to the data.

This resulted in exchange parameters of J_{rail} = 13.3K and J_{rung} = 25.4K, allowing for a 6% paramagnetic impurity. Lower temperature data will be required to verify these preliminary values and high field magnetization experiments are scheduled to determine the magnetic energy gap.

Acknowledgments

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