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New Square S=1/2 Heisenberg Antiferromagnetic Lattices: Pyridinium Tetrahalocuprates and Bispyrazinecopper(II) Tetrafluoroborate

Andrew S. Albrecht [a] , Christopher P. Landee [a] , Zoran Slanic And [a] & Mark M. Turnbull [a]
[a] Carlson School of Chemistry and Dept. of Physics, Clark University, 950 Main St., Worcester, MA, 01610, USA

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NEW SQUARE S=1/2 HEISENBERG ANTIFERROMAGNETIC LATTICES: PYRIDINIUM TETRAHALOCUPRATES AND BISPYRAZINECOPPER(II) TETRAFLUOROBORATE

ANDREW S. ALBRECHT, CHRISTOPHER P. LANDEE, ZORAN SLANIC AND MARK M. TURNBULL

Carlson School of Chemistry and Dept. of Physics, Clark University, 950 Main St., Worcester, MA 01610 USA

Abstract: As part of a program to create new low dimensional S=1/2 antiferromagnetic Heisenberg compounds with moderate exchange, we have prepared four new copper complexes with square magnetic lattices. The complexes $L_2[CuX_4]$ have been prepared (L = 2-amino-5-methylpyridinium, X = Cl, Br; L = 2-amino-5-chloropyridinium, X = Br). The compounds are isomorphous, giving monoclinic crystals; space group C2/c. The tetrahalometallate ions lie in C-centered layers, forming a square magnetic lattice. The layers are separated by the organic cations. Preliminary analysis of the magnetic data shows that the exchange constant, J, increases in the order Br > Cl and 2-amino-5-chloropyridinium > 2-amino-5-methylpyridinium. A new member of the pyrazine bridged family $M(pyrazine)_2X_2$ has also been prepared and studied. $Cu(pz)_2(BF_4)_2$ also crystallizes in the space group C2/c. Analysis of the temperature dependence of the susceptibility yields and exchange value of -7.98 K, similar to that found for the known $Cu(pz)_2(ClO_4)_2$ complex.

INTRODUCTION

The effects of quantum fluctuations and lattice dimensionality upon the ability of a magnetic lattice to spontaneously order have received a great deal of interest in the recent theoretical literature. This activity has been stimulated by the discovery of high-temperature superconductivity[1] in doped La_2CuO_4, a compound in which the copper(II) ions are antiferromagnetically coupled in a two-dimensional square lattice. It has now been concluded that a 2D S=1/2 Heisenberg antiferromagnetic lattice will order,[2] at least at T = 0 K, but that a similar one-dimensional chain remains disordered even at absolute zero.[3] In an effort to understand the influence of lattice dimensionality upon order, various systems of intermediate dimensionality (such as spin ladders[4] and rectangular lattices[5]) are being studied theoretically.

Our laboratory has begun a program of synthesizing and studying new S=1/2 low-dimensional Heisenberg antiferromagnets with small exchange constants, with the goal of creating model magnetic systems with which to examine theoretical predictions. We report here recent results on the synthesis, structure and magnetic properties of four new two-dimensional S=1/2 Heisenberg antiferromagnetic complexes.

PYRIDINIUM TETRAHALOMETALLATES

The A_2MX_4 family of complexes was synthesized from commercial materials.[6] For example, reaction of copper(II) bromide with two equivalents of 2-amino-5-methylpyridine and two equivalents of HBr in aqueous solution yielded $(5\text{-MAP})_2CuBr_4$ after several days (5-MAP = 2-amino-5-methylpyridinium). The 2-amino-5-chloropyridinium (hence 5-CAP) complexes were prepared in similar fashion. No attempts were made to maximize yields, which ranged from 35-60%. Crystals of $(5\text{-CAP})_2CuBr_4$ suitable for single crystal X-ray study grew spontaneously from the solution. The compound crystallizes in the monoclinic space group C2/c and is isomorphous with the known $(5\text{-MAP})_2CuBr_4$ and $(5\text{-MAP})_2CuCl_4$ compounds.[6] The compounds grow as two-dimensional sheets of highly distorted CuX_4^{2-} tetrahedra separated by the organic cations. This is illustrated for $(5\text{-CAP})_2CuBr_4$. Figure 1

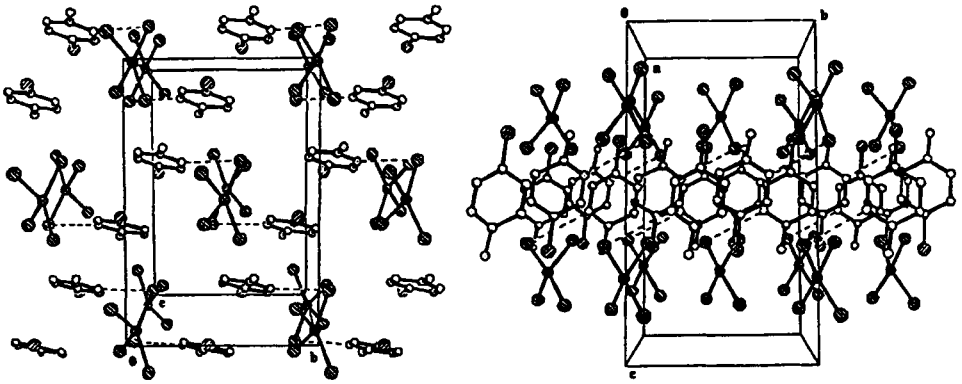

Figure 1 - The structure of $(5\text{-CAP})_2CuBr_4$. The left view is perpendicular to the $CuBr_4^{2-}$ layers. The right view shows the separation of the layers by the organic cations.

shows the relationship between the metal ions within a layer and the separation of the layers by the organic cations.

The separation between the halocuprate ions in the lattice, as measured by the shortest contact distances between the halide ions, is dependent upon both the halide ion and the organic cation. For $(5\text{-MAP})_2CuBr_4$ the separation within the layers is 4.56Å while the separation between layers is 4.98Å. The corresponding chloride complex shows smaller separations. The methyl substituent in the 5-position of the 5-MAP group lies partially within the halocuprate plane. Substitution of the sterically smaller chloride results in a decrease in the intraplanar separation to 4.28 Å and in the interplanar separation to 4.83Å. A study of the structure of $(5\text{-CAP})_2CuCl_4$ is in progress. Powder diffraction data suggests that the complex is isomorphous with the first three compounds of the series.

Powder susceptibility data was collected for $(5\text{-MAP})_2CuBr_4$, $(5\text{-MAP})_2CuCl_4$, and $(5\text{-CAP})_2CuBr_4$. Plots showing χ and χ^{-1} as a function of temperature are shown in Figures 2, 3 and 4, respectively. The susceptibility data was fit to the two dimensional model of Navarro[7] and the χ^{-1} data to the Curie-Weiss equation. The results are presented in Table 1. The susceptibility data for the bromide complexes show broad maxima between 4 K and 5 K.

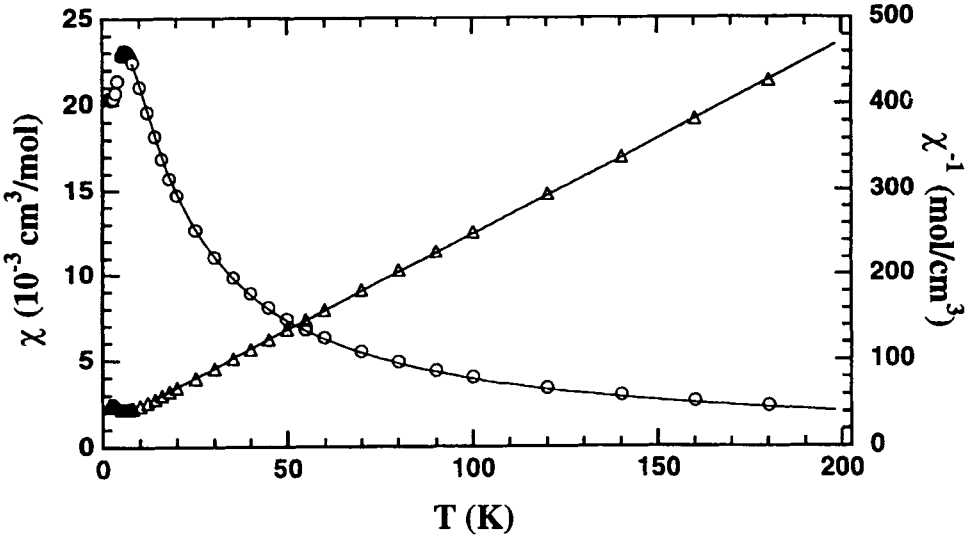

Figure 2 - Susceptibility (O) and inverse suseptibility (Δ) as a function of temperature for $(5\text{-MAP})_2CuBr_4$. The solid lines represent the calculate fit to the data.

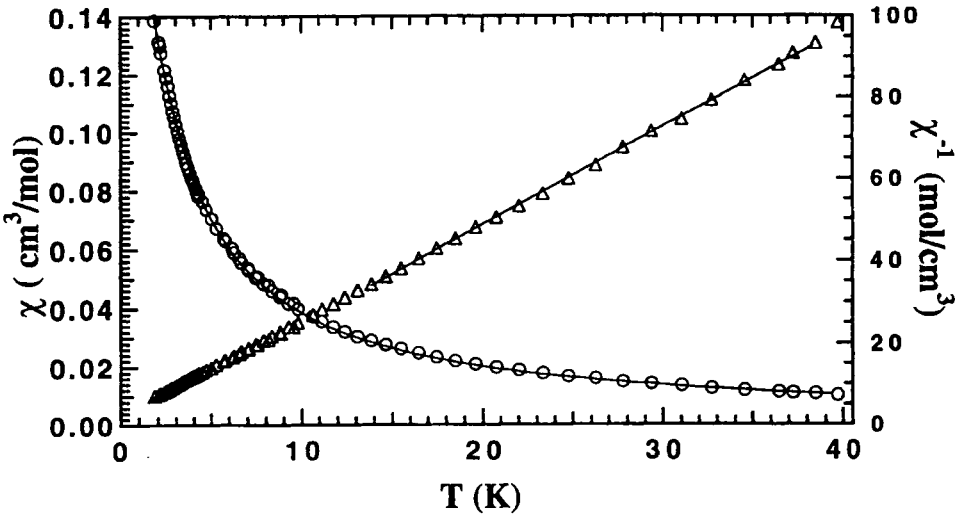

Figure 3 - Susceptibility (O) and inverse suseptibility (Δ) as a function of temperature for $(5\text{-MAP})_2CuCl_4$. The solid lines represent the calculate fit to the data.

Table 1	C (cm^3-K/mol)	θ (°)	g	J (K)
$(5\text{-MAP})_2CuBr_4$	0.43(2)	-10.6(2)	2.116(4)	-3.48(2)
$(5\text{-MAP})_2CuCl_4$	0.42(2)	- 0.4(1)	2.122(4)	-0.47(1)
$(5\text{-CAP})_2CuBr_4$	0.44(2)	-13.2(2)	2.117(5)	-4.33(3)

In this series of compounds, the principle superexchange pathway is via van der Waals contacts between the halide ions.The decrease in the exchange constant, J, from -3.48 to -0.47 on substituting chloride for bromide in the 5-MAP compounds reflects the both the increase in the distance between adjacent halides within the layer and the decrease in overlap of the smaller chloride orbitals compared to the bromide. Conversely, comparison of $(5\text{-MAP})_2CuBr_4$ to $(5\text{-CAP})_2CuBr_4$ shows the expected increase in the strength of the magnetic exchange (-3.48 K to -4.33 K) resulting from the shorter Br-Br contact distances. Low-temperature magnetic studies on single crystals of these materials are in progress. The perdeuterated $(5\text{-CAP})_2CuBr_4$ complex is also in preparation for elastic and inelastic neutron scattering experiments.

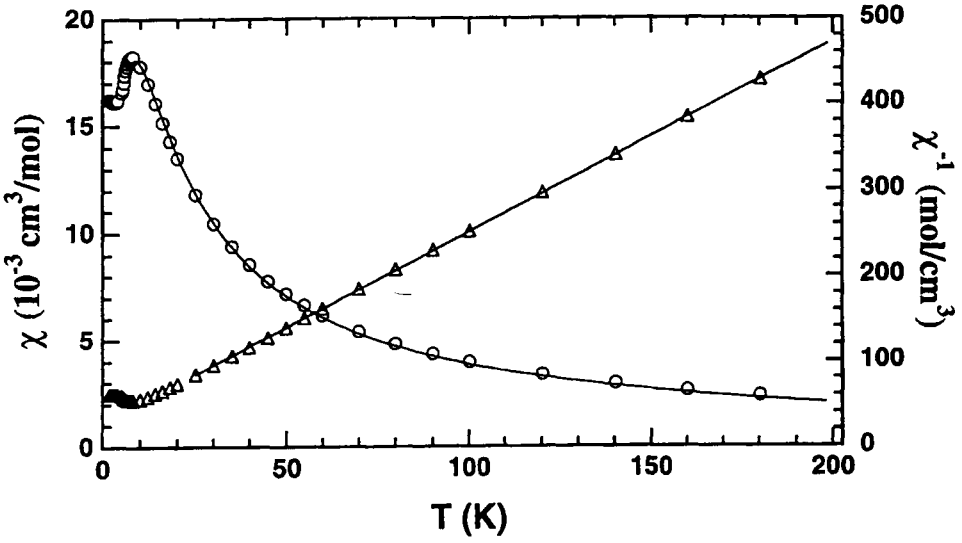

Figure 4 - Susceptibility (O) and inverse suseptibility (Δ) as a function of temperature for $(5\text{-CAP})_2CuBr_4$. The solid lines represent the calculate fit to the data.

BISPYRAZINECOPPER(II) TETRAFLUOROBORATE

One well studied example of a square magnetic lattice is $Cu(pz)_2(ClO_4)_2$ where the pyrazine ligands bridge the Cu(II) ions to form a two-dimensional coordination polymer.[8] While a large number of compounds with the formula $M(pz)_2X_2$ have been prepared,[9] they in general exhibit only very weak magnetic interactions.[10] One explanation for the significant antiferromagnetic interactions seen in $Cu(pz)_2(ClO_4)_2$ is the difference in the angle made by the pyrazine rings to the plane of the Cu(II) ions. While the other complexes show canting angles for the pyrazines of approximately 45°, the pyrazine rings of the perchlorate complex are tilted to 66.1°. We reasoned that the long Cu-O bonds in the axial Cu-sites allowed for the increased canting angle and provided a significant superexchange pathway. Earlier attempts to increase the canting angle by using methyl-substituted pyrazines to increase the steric demands were unsuccessful.[11] Therefore, we prepared the tetrafluoroborate analogue to determine if the poorly coordinating BF_4^- ion would allow for an even greater increase in the canting angle of the pyrazine rings.

Reaction of $Cu(BF_4)_2$ with two equivalents of pyrazine in aqueous solution generated the desired compound in 80% yield. Repeated recrystalization did not provide crystals suitable for x-ray study. However, *in situ* generation of the $Cu(BF_4)_2$ by reaction of CuO with 48% aqueous HBF_4 followed by dilution and addition of pyrazine generated reasonable sized (0.5 mm) single crystals. The extended structure of $Cu(pz)_2(BF_4)_2$ is shown in Figure 5. Like the previous compounds, the compound crystallizes in the monoclinic space group C2/c with the copper ions sitting on the 2-fold axis. Unfortunately, the canting angle of the pyrazine rings is 67.4°, nearly the same as that for the perchlorate complex. The temperature dependent magnetic susceptibility for $Cu(pz)_2(BF_4)_2$ is shown in Figure 6. The rounded maximum in the susceptibility, indicative of a low dimensional system is clearly seen at 15 K. A Curie-Weiss fit of χ^{-1} vs. T yields θ = -16.0(9) K and C = 0.452(2) cm^3-K/mol. Fitting χ vs. T to the Navarro model gives a g value of 2.197(5) and J equal to -7.98(9). These data are not significantly different from those reported for $Cu(pz)_2(ClO_4)_2$. This result leaves untested the hypothesis that the canting angle of the pyrazine ring is related to the

strength of the magnetic exchange. However, the ability to grow moderate sized single crystals of $Cu(pz)_2(BF_4)_2$ makes more detailed study of the material possible. Further efforts to vary the canting angle in these compounds are in progress.

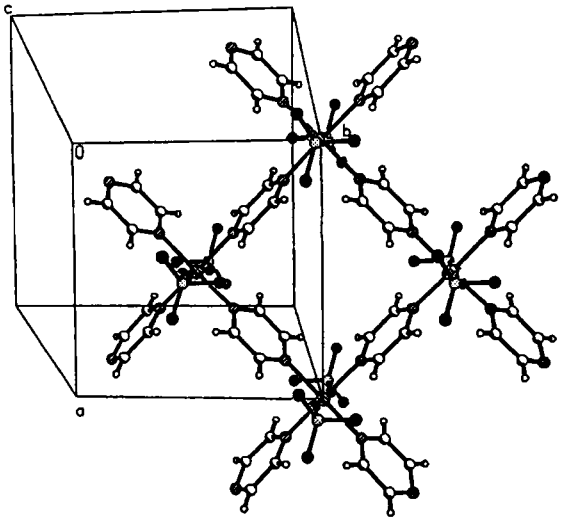

Figure 5 - The structure of $Cu(pz)_2(BF_4)_2$ seen perpendicular to the C-centered layers.

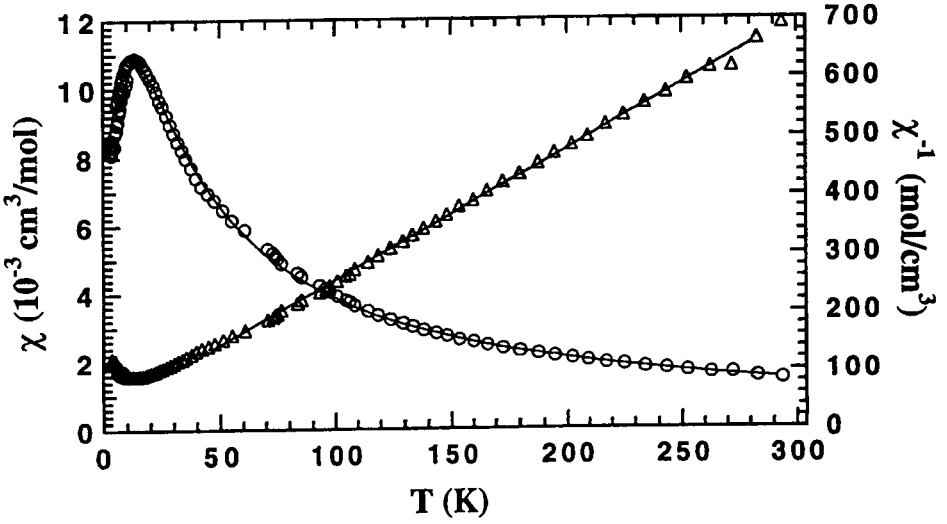

Figure 6 - Susceptibility (O) and inverse suseptibility (Δ) as a function of temperature for $Cu(pz)_2(BF_4)_2$. The solid lines represent the calculate fit to the data.

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REFERENCES

1. For a review see A.W. Sleight, M.A. Subramanian, and C.C. Toradi MRS Bulletin XIV, 45 (1989).
2. E. Manousakis Rev. Mod. Phys. 63, 1 (1991).
3. W.J. Caspers, Spin Systems, World Scientific, Singapore (1989) and references therein.
4. E. Dagotta and T.M. Rice Science, 271, 618 (1996).
5. M. Azzouz and B. Doucot Phys. Rev. B, 47, 8660 (1993).
6. The 5-MAP complexes have been previously prepared. See H. Place and R.D. Willett Acta Cryst., C43, 1050 (1987).
7. R. Navarro in Magnetic Properties of Layered Transition Metal Compounds ed. L.J. de Jongh, Kluwer, Dordrecht (1990).
8. J. Dariet, M.S. Haddad, E.N. Duesler and D.N. Hendrickson Inorg. Chem. 18, 2679 (1979).
9. a) A.B.P. Lever, J. Lewis, R.S. Nyholm Nature, 189, 58 (1961). b) J.R. Ferraro, J.Zipper, and W.Wozniak Appl. Spect., 23, 160 (1969).
10. a) R.L. Carlin, D.W.Carnegie Jr., J. Bartolome, D. Gonzalez and L.M. Flora Phys. Rev. B, 32, 7476 (1985). b) J.S. Haynes, J.R. Sams and R.C. Thompson Inorg. Chem., 25, 3740 (1986).
11. C. Navas, M.M. Turnbull, C. Giogas, C.P. Landee, W. Zhang, G.Pon and R.D. Willett Polyhedron 12, 1019 (1993).