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High-Field Magnetization Studies of Two-Dimensional Copper Antiferromagnets

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The magnetic susceptibilities and high-field magnetization data for members of two families of S = 1/2, two-dimensional, square antiferromagnetic lattices are reported. The known compounds bis-2-amino-5-methylpyridinium tetrabromocuprate, **1,** and bis-2-amino-5-chloropyridinium tetrabromocuprate, **2,** crystallize in the space group C2/c with the tetrabromocuprate ions related by the C-centering and unit cell translations, leading to a square magnetic lattice. Similarly bispyrazinecopper(II) perchlorate, **3,** and bispyrazinenitratocopper(II) hexafluoro-phosphate, **4,** crystallize in the space groups C2/m and I4/mcm respectively and also generate square magnetic lattices. High-field magnetization studies, up to 60 Tesla, have determined their saturation fields to be 21 T (**1**), 27 T (**2**), 53 T (**3**) and 32 T (**4**). All show upward curvature in plots of magnetization as a function of field and fall on a universal curve in good agreement with recent theoretical predictions.

Keywords: Heisenberg; two-dimensional; high-field; magnetization; quantum antiferromagnets

INTRODUCTION

Over the course of a little more than a decade, workers in the field of molecular-based magnetism have produced many novel materials. Since the

recognition of this discipline,[1] scientists from all over the world have extended the field by developing novel materials based on metals,[2] organic radicals,[3] and hybrid organic radical/transition metal systems.[4] Molecular-based magnetism has also been used to engineer the properties of compounds by starting with a known material and adjusting its properties through subtle (or some times not so subtle) changes in its composition or structure. We have been using this idea of crystal engineering, or molecular architecture, to develop new examples of low-dimensional antiferromagnetic lattices.

We have continued our 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 a new two-dimensional S=1/2 Heisenberg antiferromagnet and the high-field magnetization behavior of other members of that family. (Our recent work on new one-dimensional S=1/2 Heisenberg antiferromagnets is described elsewhere in these proceedings.)

A NEW BISPYRAZINECOPPER LAYER

Two known examples of the square magnetic lattice are $Cu(pz)_2(ClO_4)_2$[5] and $Cu(pz)_2(BF_4)_2$[6] where the pyrazine ligands bridge the Cu(II) ions to form a two-dimensional coordination polymer. While a large number of compounds with the formula $M(pz)_2X_2$ have been prepared,[7] most show canting angles for the pyrazine rings relative to the plane of the Cu(II) ions near 45° and they in general exhibit only very weak magnetic interactions.[8] We have been attempting the synthesis of additional members of this family to investigate

the nature of the relationship between the canting angle of the pyrazine and the strength of the magnetic exchange and have recently prepared the complex $[Cu(pz)_2(NO_3)]PF_6$, **4**.

Reaction of $Cu(NO_3)_2$ with two equivalents of pyrazine and a 5-fold excess of KPF_6 in aqueous solution gave crystals of **4** after slow evaporation at room temperature. The compound crystallizes in the tetragonal space group I4/mcm[9] and the structure is shown in Fig. 1.

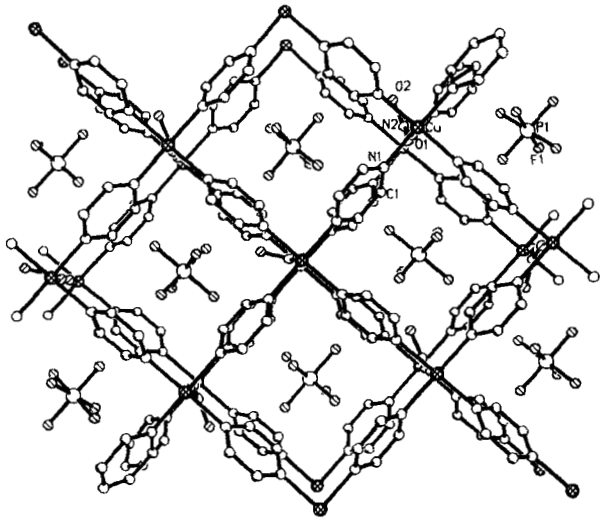

Fig. 1 - The extended structure of $[Cu(pz)_2(NO_3)]PF_6$ (**4**)

As previously seen in the perchlorate and tetrafluoroborate analogues, the Cu(II) ions are linked into a square lattice by the bridging pyrazine, but unlike the previous compounds, **4** shows a true propeller twist to the canting

of the pyrazine rings. The rings are tipped approximately 61° out of the plane, a much smaller value than that seen for the ClO_4 and BF_4 complexes. The second notable feature is the NO_3 ions linking the Cu(II) layers together (Note: Both the PF_6 and NO_3 ions are disordered in the lattice by the four-fold rotation axis. Only one site is shown in Fig. 1 for clarity). Thus, **4** represents a somewhat different structure from the other members of the bispyrazine bridged family since the Cu(II) ions are bridged *between* layers as well. We anticipate that the reduced canting angle for the pyrazine will lead to a lower value for J and that the bridge between layers may lead to a higher relative temperature transition to long-range order.

Magnetic Susceptibility Data

Powder magnetic susceptibility data for the four two-dimensional Heisenberg antiferromagnets are shown in Figure 2.

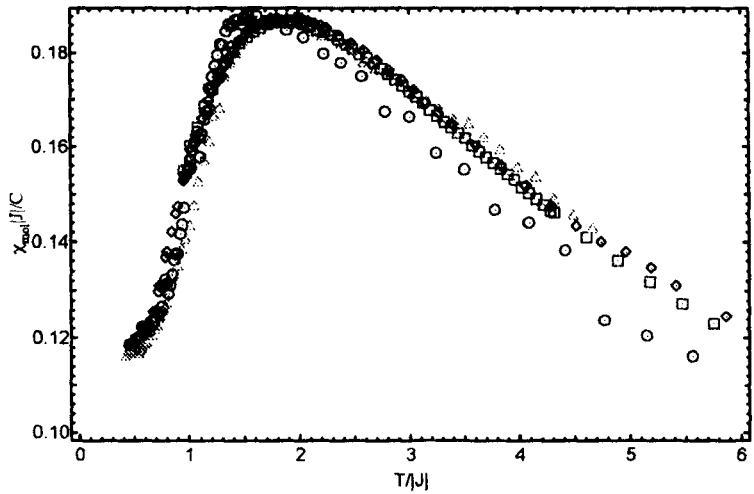

Fig. 2 - Reduced susceptibility ($\chi|J|/C$) as a function of temperature (as $T/|J|$) for (2-NH_2-5-Me-py)$_2CuBr_4$ **1** (◊); (2-NH_2-5-Cl-py)$_2CuBr_4$ **2** (□); Cu(pz)$_2$(ClO_4)$_2$, **3** (o); and [Cu(pz)$_2$(NO_3)]PF_6, **4** (Δ).

The data are plotted on a universal curve in terms of $\chi|J|/C$ vs. $T/|J|$ to show that the four compounds exhibit similar magnetic behavior and are all, in fact, good examples of two-dimensional Heisenberg antiferromagnets. Each of the data sets is well described by the predictions for the susceptibility of the two-dimensional antiferromagnetic model with exchange constants of -3.4 K (**1**), -4.3 K (**2**), -8.8 K (**3**) and -5.2 K (**4**).

HIGH-FIELD MAGNETIZATION DATA

Thus assured that these compounds constituted good representations of two-dimensional quantum Heisenberg antiferromagnets, we measured their low temperature magnetization curves. Figure 3 shows the results of these experiments at 1.8 K in fields up to 60 Tesla.

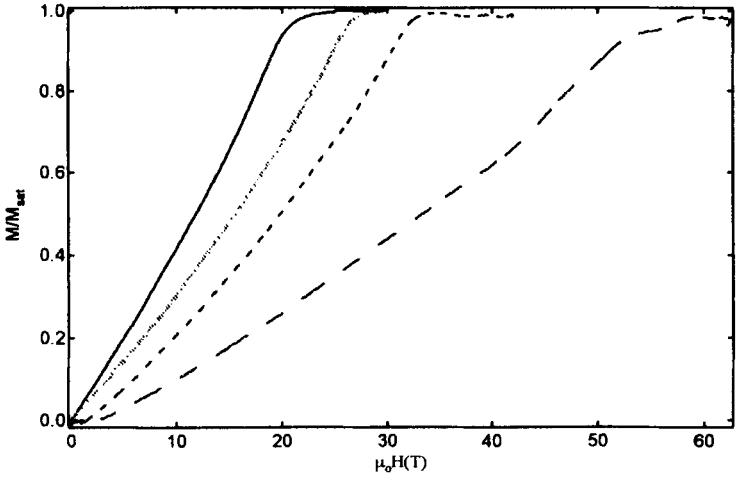

Fig. 3 - Reduced magnetization (M/M_{sat}) as a function of applied field (μ_oH) for (2-NH_2-5-Me-py)$_2CuBr_4$ **1** (——); (2-NH_2-5-Cl-py)$_2CuBr_4$ **2** (·····); $Cu(pz)_2(ClO_4)_2$, **3** (— — —); and $[Cu(pz)_2(NO_3)]PF_6$, **4** (– – –).

The saturation fields for these compounds are estimated be 21 T (**1**), 27 T (**2**), 53 T (**3**) and 32 T (**4**).We believe these to be the first measurements of the full magnetization curves for the class of two-dimensional S = ½ Heisenberg antiferromagnets. Further evidence of the uniform nature of the magnetic lattices in these systems can been seen by plotting the reduced magnetization (M/M_{sat}) as a function of the reduced field (H/H_{sat}, see Fig. 4). As was seen in the susceptibility data, the magnetization data for all four compounds fall onto a single universal curve. The theoretical predictions at T = 0 for the one-dimensional S = ½ Heisenberg model[10] and a two-dimensional S = ½ Heisenberg model[11] are also shown in Figure 4.

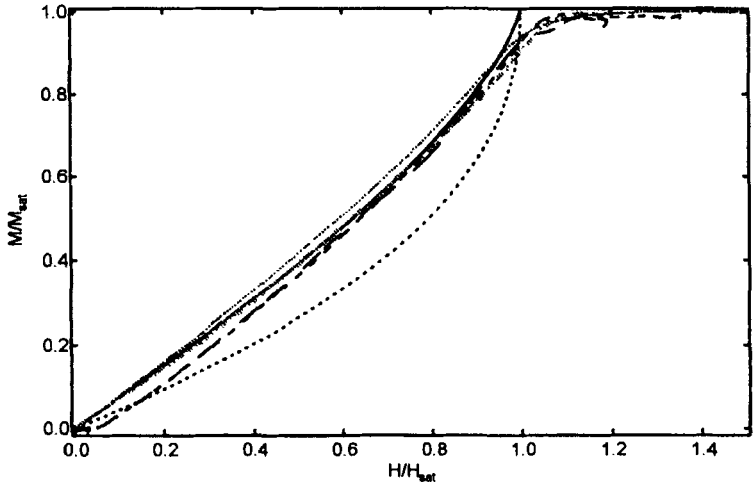

Fig. 4 - Reduced magnetization (M/M_{sat}) as a function of the reduced field (H/H_{sat}) for the compounds (2-NH_2-5-Me-py)$_2CuBr_4$ **1** (·····); (2-NH_2-5-Cl-py)$_2CuBr_4$ **2** (— - — -); $Cu(pz)_2(ClO_4)_2$, **3** (————); and $[Cu(pz)_2(NO_3)]PF_6$, **4** (– – –); and for the 1-D (-----) and 2-D (——) models.

The agreement between the data and the two-dimensional model is clear allowing for minor deviations near the saturation magnetization resulting from the finite temperature of the experiment, while the calculation is for T = 0 K. (Note: The line showing the two-dimensional model is the result of the calculation at T = 0 K. It is *not* a fit to the data.) It is also important to note that even though the layers in compound **4** are bridged by the nitrate groups, the magnetization behavior for the complex is dominated by the two-dimensional layers (as shown by the upward curvature).

Knowledge of the saturation field H_{sat}, provides an independent assessment of the exchange strength with the mean field relation $g\mu_B H_{sat} = zJ/2$. Based on the measured saturation fields, the exchange strengths are calculated to be -3.5 K (**1**), -4.8 K (**2**), -9.3 K (**3**) and -5.6 K (**4**), uniformly somewhat higher than the values obtained via fits to the susceptibility. we attribute this difference to the fact that the magnetization data were collected at finite temperature. Comparison of the data to calculations of the finite temperature magnetization M(H,T) are in progress.

Having clearly demonstrated through their magnetic behavior, that these compounds are good examples of two-dimensional quantum Heisenberg antiferromagnets, further experiments are in order. Heat capacity measurements are in progress, and the syntheses of perdeuterated versions of these compounds for neutron scattering experiments are also underway. In addition, we are preparing additional members of both families of compounds to provide related compounds with varying exchange strengths. We hope to use these compounds to continue our investigations into magneto-structural relationships in low-dimensional magnetic lattices.

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