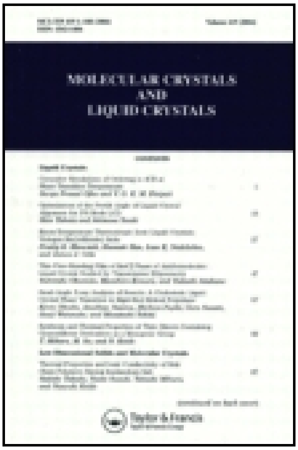

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: C. P. Landee & M. M. Turnbull (1999): Pyrazine-Bridged Copper Linear Chains: Molecular-Based One-Dimensional Quantum Antiferromagnets, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 193-200

To link to this article: http://dx.doi.org/10.1080/10587259908028863

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 193-200
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Printed in Malaysia

Pyrazine-Bridged Copper Linear Chains: Molecular-Based One-Dimensional Quantum Antiferromagnets

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Low-dimensional quantum antiferromagnets are among the best systems for studying effects of quantum fluctuations within interacting systems. The best 1D S=1/2 Heisenberg antiferromagnetic system is Cu(pyrazine)$(NO_3)_2$, or CuPzN, since it has excellent 1D isolation and an exchange constant ($2J/k_B = -10.5$ K) which permits available fields to saturate the magnetization. Replacing the pyrazine ligands with substituted pyrazines, such as methylpyrazine (mepz), 2,3-dimepz, and 2,5-dimepz, lowers the exchange strengths significantly. We are conducting an in-depth study of the static and dynamic properties of the CuPzN family, including high field magnetization studies and neutron scattering.

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

INTRODUCTION

Molecular-based magnetism (MbM) has yielded many novel magnets in the past fifteen years. Since the early days of this sub-discipline,[1] its techniques have been used to create increasingly sophisticated ordered bimetallic ferrimagnets in one-dimension,[2] two-dimensions,[3,4] and three-dimensions.[5,6] There have been many other successes in creating radical based magnets,[7,8] transition metal/radical hybrids,[9,10] and even a radical-based kagomé magnet.[11] In every case, materials were created which had no known predecessors.

MbM can also be used to "improve the breed", by beginning with a known compound and altering its properties by manipulating its structure and its exchange pathways with the goal of creating ever better manifestations of the desired magnet. For the past several years, we have been using this procedure to provide improved examples of some of the simplest extended quantum systems, the 1D and 2D S=1/2 (or quantum) Heisenberg antiferromagnets (1D QHAF and 2D QHAF). The 1D QHAF is a wonderfully rich system in which quantum fluctuations dominate its properties at all temperatures. It is a system strongly perturbed by external magnetic fields. While theorists have studied its behavior for nearly sixty years, many of their predictions have never been tested due to the lack of appropriate materials.

In this paper we will discuss our recent work on the 1D QHAF copper pyrazine nitrate (CuPzN) and its variations. Although known for many years,[12] it has been neglected, even though it has a nearly ideal combination of properties. It also lends itself to modification by MbM techniques. (Our recent work on new 2D QHAF is described elsewhere in these proceedings.)

STRUCTURAL INFORMATION

The original room temperature structural determination[12] has been confirmed[13] at a temperature of 150 K. The structure consists of chains of Cu(II) ions bridged by pyrazine molecules

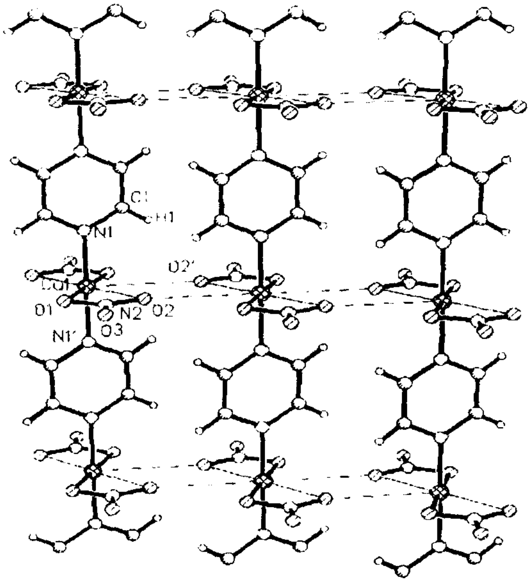

Figure 1 Crystal Structure of Cu(pz)(NO$_3$)$_2$

along the crystallographic *a*-axis (Cu1-N1 = 1.974(3) Å). The copper sites are also chelated by two nitrate ions with one short bond (Cu1-O1 = 2.004(3) Å) and one long bond (Cu1-O2 = 2.478(3) Å). The copper atoms and nitrate groups lie in mirror planes perpendicular to the two-fold *a*-axis. The O2 atoms also bridge the copper atoms to the copper sites on adjacent chains by a long pathway (3.264 Å, dashed lines). This long interaction may help stabilize the formation of the 3D lattice, but there is no evidence that it provides a superexchange pathway. The strength of the superexchange interactions through the pyrazine rings is presumed to be a function of the angle between the normal to the basal plane and the normal to the pyrazine molecules, 51°.

MAGNETIC PROPERTIES

The magnetic susceptibility of CuPzN was originally studied by the Hatfield group[14] who found the powder and single crystal data to be well described by the model of a 1D S=1/2 Heisenberg antiferromagnet with an exchange strength of $2J/k_B$ = -10.6(2) K. No anisotropy was found in the single crystal data. The specific heat of CuPzN was studied[15] down to 0.07 K and no evidence of a transition to a state of long-range order was found. The magnetic contribution to the specific heat was very well described by the same model with an exchange strength of $2J/k_B$ = -10.4(2) K. The degree of 1D isolation, as determined by the $T_N/2J$ ratio of less than 6.7×10^{-3}, is the lowest known for any 1D QHAF.

High field magnetization experiments have been carried out on CuPzN and a number of the substituted-pyrazine counterparts. The magnetization of CuPzN at 4.2 K and 1.82 K is shown as a function of field as the dotted and solid lines, respectively, Figure 2. The dot-dash curve corresponds to the theoretical T = 0 curve based upon the Bethe ansatz solution to this model.[16]

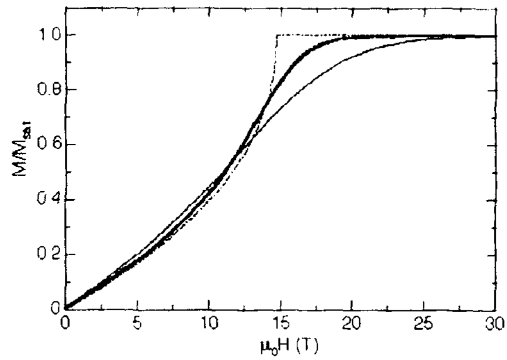

Figure 2 Relative magnetization M/M_{sat} of $Cu(pz)(NO_3)_2$. Dot-dashed line: calculated T = 0 magnetization of a 1D QHAF with $2J/k_B$ = 10.4 K. Dashed line: fit of T = 1.82 K data to theoretical model. The fit of the T = 4.2 K curve is indistinguishable from the data.

The distinctive upward curvature is a quantum effect due to the quenching of the quantum fluctuations in the ground state by the applied field. Both data sets have been fit simultaneously to a finite temperature solution for the magnetization. The fits are excellent with an exchange constant $2J/k_B$ = -10.4(1) K. This exchange strength corresponds to a T = 0 saturation field of 14.6 tesla, as determined by the molecular field result for S=1/2: $g\mu_B H_{sat} = 2zk_BJ$. It is this low value of the saturation field, along with the excellent 1D isolation and the absence of anisotropy, that makes CuPzN a suitable candidate for dynamics studies in applied fields. Similar high field magnetization experiments have been carried out at 2 K upon the methyl and 2,3-dimethyl analogues of CuPzN; these results are presented in Figure 3 along with the data from CuPzN. It is seen that the saturation fields for the substituted pyrazine compounds are both lower than that found for CuPzN. First approximations for the T = 0 saturation fields for the methyl and 2,3-

dimethyl compounds are 13.7(3) tesla and 11.3(4) tesla, respectively, corresponding to exchange strengths of 4.8(2) K and 4.0(2) K. More reliable values will be obtained upon fitting the data to the full temperature dependent theoretical prediction.

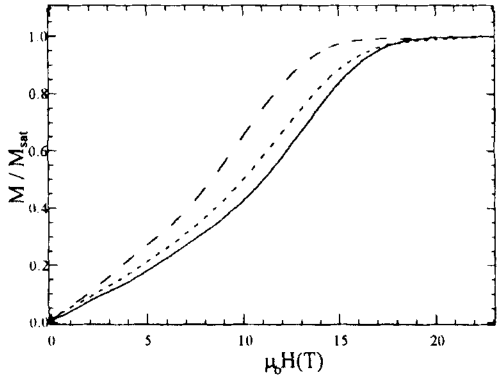

Figure 3 Relative magnetizations M/M_{sat} of long dashed line: Cu(2,3-dimepz)$(NO_3)_2$, short dashed line: Cu(mepz)$(NO_3)_2$, and solid line: Cu(pz)$(NO_3)_2$, determined at 2.0 K.

Powder susceptibility measurements have been made on the methyl, 2,3-dimethyl, and 2,5-dimethyl analogues of CuPzN; these results are presented in Figure 4. The 2,3-dimethyl analog is a new compound while the methyl and 2,5-dimethyl compounds have been studied previously.[17] The exchange strengths of these compounds were determined by comparing the temperature dependence of the susceptibilities to the theoretical predictions. The values of the exchange strengths determined from both the susceptibility studies and the magnetization studies described above are compared in Table 1.The values determined by our two sets of experiments are in good agreement, but some difference is noted between our values and those found previously.[17]

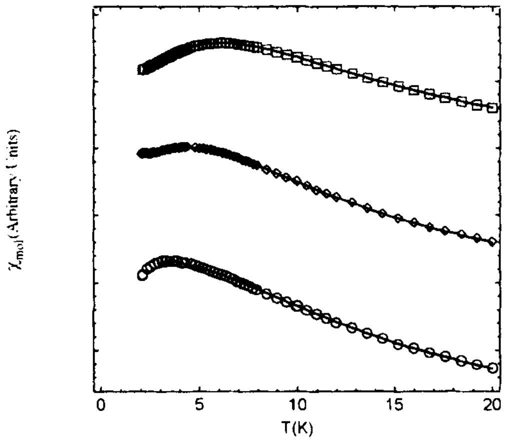

Figure 4 Powder susceptibility measurements on (□) Cu(mepz)(NO_3)$_2$, (◊) Cu(2,3-dimepz)(NO_3)$_2$, and (○) Cu(2,5-dimepz)(NO_3)$_2$. The solid lines correspond to results of the least square fits, with the exchange constants reported in Table 1.

Compound	H_{sat}(Tesla)	$-J_{mag}$(K)	$-J_{\chi}$(K)	$-J_{Hatfield}$(K)
Cu(pz)(NO_3)$_2$	14.7(1)	5.2(1)	~	5.3(2)
Cu(mepz)(NO_3)$_2$	13.7(2)	4.8(2)	4.8	4.5
Cu(2,3-dimepz)(NO_3)$_2$	11.3(4)	4.0(2)	4.1	~
Cu(2,5-dimepz)(NO_3)$_2$	~	~	4.6	5.0

Table 1

DISCUSSION

The CuPzN family is ideal for an extended examination of the properties of the 1D QHAF. The low saturation fields and availability of perdeuterated single crystals will allow the first extensive studies of the spin dynamics of such a magnet in an applied field. The dependence of the exchange strength upon the bridging group allows the possibility of studying the effect of random exchange in the 1D QHAF in materials with random mixtures of substituted pyrazines. These and other experiments are in progress.

Acknowledgments

This work has been supported in part by NSF grant DMR-9803813 and the Clark University Faculty Development fund. The high field magnetization studies were performed at the National High Magnetic Field Laboratory, which is supported by NSF cooperative agreement DMR-9527035 and the State of Florida. We thank Dan Reich and Colin Broholm for useful discussions. We thank Matt Woodward for his assistance in data collection and figure preparation as well as Melissa LaPierre for sample preparation.

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