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NOVEL ONE DIMENSIONAL MAGNETIC SYSTEMS BASED ON COPPER(II) HALIDE SALTS

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Abstract Copper(II) halides continued to provide examples of interesting low dimensional systems. In the cases discussed, inequivalent Cu-X-Cu linkages are the basis for the novel magnetic behavior. (N-methylphenethylammonium)$CuCl_3$ provides an example of chains with alternating FM interactions. The compound $(C_6N_2H_8)_2Cu_3Br_8$ contains chains of $Cu_3Br_8^{2-}$ trimers. Strong AFM coupling in the trimers lead to S=1/2 ground states, which are then coupled together to form FM chains. Cu(cyclam)$CuCl_4$ contains chains with alternating FM/AFM interactions, where $J_{FM} >> |J_{AFM}|$, so they should behave as S=1 Haldane chains at low T. The compound $(Et_3MeN)_3Cu_4Cl_{11}$ contains FM tetrametric units linked into chains by weak AFM coupling, defining a potential S=2 Haldane chain at low T.

INTRODUCTION

The very flexible stereochemistry of the copper(II) ion and the non-stereospecificity of the bridging halide ligand leads to a wide variety of bridging geometries in polymeric copper(II) halide complexes. This allows for the capability to finely tune the exchange coupling.

The source of the stereochemical variety is a combination of the Jahn-Teller effect coupled with strong halide-halide electrostatic repulsions. The Jahn-Teller effect destabilizes high symmetry geometries, while the extent of the resultant distortions depends on the effectiveness of the electrostatic repulsion. The latter can be tuned through electrostatic and hydrogen bonding interactions with other moieties in the lattice. The

concept of "charge compensation" has proved to be a useful mechanism to correlate the observed geometries in copper(II) halide salts.[1] Observed geometries include (a) four coordinate species with geometries ranging from square planar to distorted tetrahedral[2]; (b) five coordinate species where the dominate geometry is a folded 4+1 geometry[3] involving four nearly coplanar normal Cu-X bonds and one "semi-coordinate Cu-X bond, but with some square pyramidal or trigonal bipyramidal species existing; and (c) tetragonally elongated octahedral coordination with four normal Cu-X bonds and two semi-coordinate Cu-X bonds.[4]

The coordination polyhedra can be linked together through corner, edge, or face sharing. In each case, the Cu-X-Cu linkages are observed to contain either two normal Cu-X bonds (symmetric bridges) or one normal and one semi-coordinate bond (asymmetric bridge). The face-shared (tribridged) arrangement always supports ferromagnetic interaction with the J/k ~50K.[1] For the edge-shared arrangements with symmetric bridges, the exchange interaction can be turned from AFM to FM, depending on the coordination geometry. J/k values range from -30K to +30K (X=Cl) and -200K to +30K(Br).[5] Bibridged arrangements involving asymmetric bridges yield weaker couplings, with $|J/k|$ generally less than 5K.[6] Asymmetric monobridges (corner-sharing) are FM if linear (J/k ~15K to 30K),[7] but are AFM if bent.[8]

Several different coordination geometries and/or bridging geometries can exist within the same crystal structure.[9] The almost endless variety of organic cations which may be used to tune the electrostatic interactions as well to provide steric isolation, provide for a richness of opportunity for crystal engineering in these systems.

In the following section, we will examine several novel systems which have recently been synthesized in our

laboratory. The magnetic data in all cases is preliminary, and has been fit with simple models. Thus, exact values of the magnetic parameters may not be correct, but the basic underlying physics is certainly correct. The first two examples are 1d systems which potentially have a ground state with a permanent moment, while the last two examples are compounds which are potential Haldane-type systems.

AN ALTERNATING FM CHAIN.

The compound $(\phi CH_2NH_2Me)_2Cu_2Cl_6$ consists of well isolated chains of $Cu_2Cl_6^{2-}$ dimers (Fig. 1) with a symmetric bibridged arrangement within the dimers and asymmetric bibridged structures linking the dimer.[10] The Cu(II) coordination geometry is close to trigonal bipyramidal, which is expected to lead to a strong FM interaction within the dimer. The product $\chi_M T$ (Fig. 2) continues to

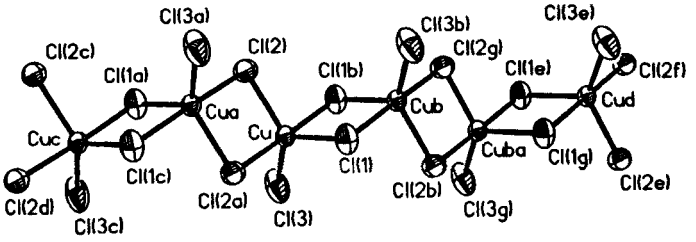

Fig. 1. Illustration of the dimer chain in $(NMPE)_2Cu_2Cl_6$.

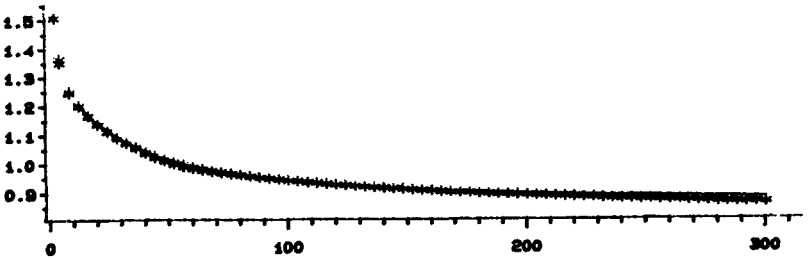

Fig. 2. Plot of $\chi_M T$ vs. T for $(NMPE)_2Cu_2Cl_6$.

increase down 2K, the lowest temperature measured. Fitting of the data above 10K to the mean-field corrected

dimer model yielded J/k = 27K and θ = 1K. The system thus contains the first example of alternating FM chains. The question of the nature of the interchain interaction is unresolved at this time, although indications lead one to speculate that the system may order as a 3d FM since no evidence of AFM interactions are observed in the $\chi_M T$ plot.

A FM CHAIN OF AFM COUPLED TRIMERS.

The compound $(1,2diMepyH)_2Cu_3Br_8$ contains chains of planar symmetric bibridged trimers.[11] The trimers are joined via simple asymmetric bibridged linkages, to form a linear chain system (Fig. 3). The planar symmetric bibridged arrangement yields, typically, strong AFM coupling in bromide salts.[5] This is exemplified in the $\chi_M T$ vs T plot in Fig. 4. At 300K, the $\chi_M T$ value of 0.84

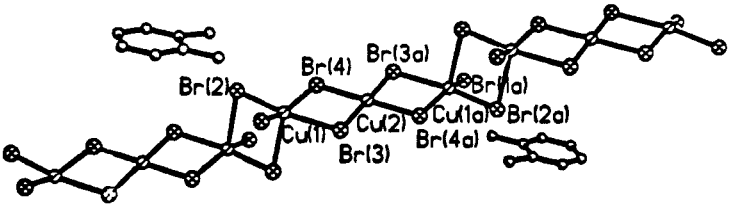

Fig. 3. Illustration of the trimer chain.

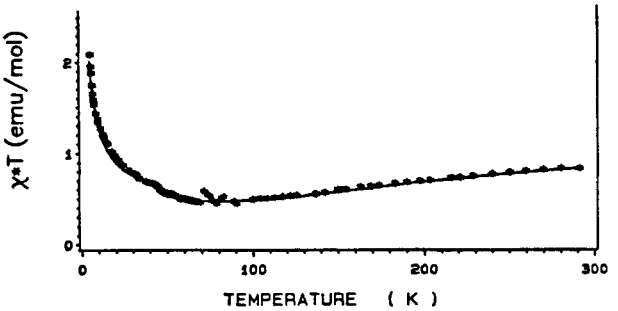

Fig. 4. Plot of $\chi_M T$ vs. T for $(1,2diMepyH)_2Cu_3Br_8$.

is already considerably reduced from the expected value of ~1.2 for three independent Cu(II) ions, and $\chi_M T$ continues to drop as T decreases. Fitting the data above

50K to the mean field corrected Heisenberg trimer model yields J/k = -150K. Thus, in the low T regime (T < 50K), the trimers are nearly completely depopulated into an S=1/2 ground state. Below T = 70K, the $\chi_M T$ value begins to rise, yielding behavior typical of a ferromagnetic system. The low T data has been analyzed in terms of a FM S=1/2 linear chain, which yields J'/k = 23K. Again, no evidence for AFM interchain coupling or the onset of long range order is observed so the existence of a ground state with a permanent moment is possible.

A PSEUDO S=1 HALDANE CHAIN.

We will next examine two systems where FM exchange pathways lead to even integer spin ground state segments which, in turn, are connected via weaker coupling into AFM chain. The compound $Cu(C_{14}H_{24}N_4)CuCl_4$ consists of $Cu(TIM)^{2+}$ units (TIM is the macrocycle 2,3,9,10-tetramethyl, 1,4,8,11-tetraazacyclo, 1,3,8,10-tetraminetetradecane) linked into infinite chains via $CuCl_4^{2-}$ anionic units (Fig. 5). Because the $Cu(TIM)^{2+}$ unit is cusped, the two independent $Cu(TIM)^{2+}\cdots Cu$-Cu linkages have different bond lengths and angles.[12] Hence, the system is correctly defined as an alternating site-alternating exchange linear chain. The $\chi_M T$ vs T

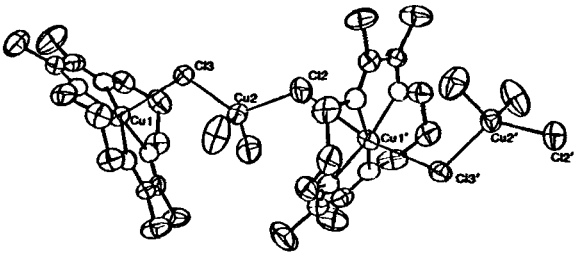

Fig. 5. Illustration of the chain structure for $Cu(TIM)CuCl_4$.

plot in Fig. 6 shows the existence of dominant FM interactions at high temperature. At lower temperature, an AFM interaction takes over, driving $\chi_M T$ steeply downward. No evidence for 3d ordering is observed.

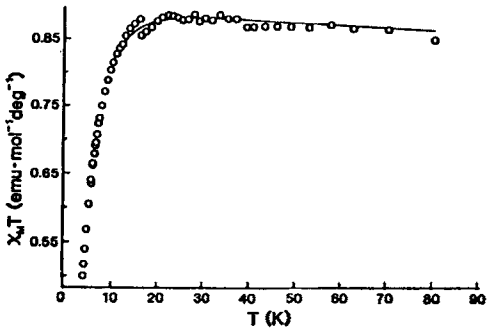

Fig. 6. Plot of $\chi_M T$ vs. T for $Cu(TIM)CuCl_4$.

Utilizing a mean field corrected Bleaney-Bowers dimer model, we obtain J_1/k = 13K and J_2/k = -2.6K.[13] Thus, the FM coupling effectively drives $Cu(TIM)^{2+}$ - $CuCl_4^{2-}$ spin units into S=1 ground states before the AFM coupling becomes effective. The AFM J_2 coupling which links these S=1 units thus defines an AFM S=1 linear chain. This system should have an energy gap, as predicted by Haldane. Excited states corresponding to the coupling of the S=0 components dimer unit into the S=1 chain should lie above the Haldane gap.

A PSEUDO S=2 HALDANE CHAIN.

The compound $(Et_2Me_2N)_3Cu_4Cl_{11}$ contains an unusual chain with four Cu(II) ions in the repeat unit[14] as seen in Fig. 7. The tribridged arrangement within the tetrameric unit is expected to lead to FM coupling. The bibridged geometry linking the tetrameric unit is close to the cross-over point from AFM to FM behavior, but experimentally it is observed to be weak but AFM. The chains assume a hexagonal packing arrangement with the cations located between the chains, much like the well studied $(Me_4N)CuCl_3$ salt (TMCuCu). In the latter the ratio of interchain to intrachain coupling is of the order of 10^{-4}.

The plot of $\chi_M T$ vs T (Fig. 8) gradually increases as the temperature is lowered from 100K to 40K. This is

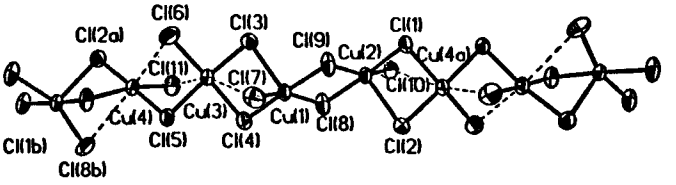

Fig. 7. Illustration of chain of tetramers.

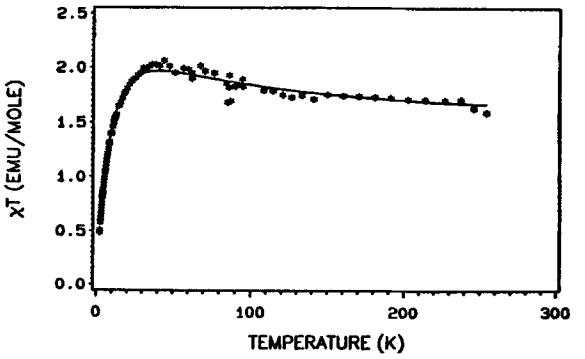

Fig. 8. Plot of $\chi_M T$ vs T for tetramer chain.

indicative of dominant FM coupling in the system. We associate this ferromagnetic coupling, J, within the tribridged (face sharing) tetrameric unit. Below 40K, the $\chi_M T$ value begins to drop, and the presence of this AFM coupling is associated with the bibridged (edge sharing) linkage. From analysis of $1/\chi_M$ vs T plots, we estimate the ratio of the intratetramer to intertetramer exchange coupling to be ~25. To model the system we assume all three face-shared linkages have the same exchange constant. We include the intertetramer coupling in a mean field approximation, so that

$$\chi_M = (\chi_{tetramer} T)/T-\theta).$$

A best fit is obtained with $J/k = 50K$ and $\theta/k = -10.5K$. For $T < 40K$, the tetrameric units are thus essentially completely depopulated into their S=2 ground state. With $\theta = S^2 J' z/k$, we have $J'/k = -1.3K$ for the intertetramer

coupling. The system is thus a reasonable model to test the Haldane hypothesis for S=2 AFM chains.

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