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Structural and Magnetic Properties of the Topologically Novel 2-D Material $Cu_9F_2cpa)_6$: A Triangulated Kagome - Like Hexagonal Network of Cu(II) Trimers Interconnected by Cu(II) Monomers

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STRUCTURAL AND MAGNETIC PROPERTIES OF THE TOPOLOGICALLY NOVEL 2-D MATERIAL $Cu_9F_2(cpa)_6$: A TRIANGULATED KAGOME - LIKE HEXAGONAL NETWORK OF Cu(II) TRIMERS INTERCONNECTED BY Cu(II) MONOMERS

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Abstract $Cu_9F_2(cpa)_6 \cdot xH_2O$ (cpa = carboxypentonic acid) has been synthesized, and characterized by x-ray diffraction. It is isomorphous with the Cl and Br congeners. Two coordinatively different Cu(II) ions comprise the unit cell: six Cu_{trimer} (square pyramidal) and three $Cu_{monomer}$ (elongated octahedra). The six Cu_t ions form two exchange coupled trimeric clusters. Each of these trimers is bridged to three Cu_m sites; each Cu_m is connected to two trimers. The extended lattice is a hexagonal network with trimers at the vertices and Cu_m ions along the edges. Magnetic field-dependent magnetic susceptibility studies in the range 1.7 - 300 K demonstrate that the compound has a magnetic ground state which is highly field dependent at lower temperatures (<20K). The interconnected triangulation suggests spin frustation. Theoretical results for this type of lattice are unknown, but analogies can be drawn to the Kagomé lattice.

INTRODUCTION

The connectivity patterns which define magnetic lattices represent a common meeting ground for chemists and physicists interested in molecular-based magnetic materials.[1] This arises because novel interconnection patterns ultimately lead to new insight concerning the fundamental nature of extended interaction mechanisms, as well as suggesting technologically advantageous magnetic structure types and applications. Magnetic lattices are described in terms of their topology: namely, what types of magnetic sites are involved (organic, inorganic, mono- *vs.* polynuclear, total spin value per site, spin anisotropy, etc.) and what is the nature of the pairwise interactions that interconnect the magnetic sites (number and type of nearest- or next-nearest neighbors, whether antiferro- or ferromagnetic, relative magnitudes, and the presence of exchange anisotropy - Ising, XY or Heisenberg). Indeed, designing extended magnetic lattices with prescribed topologies and properties is the challenge at hand.

In our lab, efforts have been aimed at using framework structures as candidates for investigating novel magnetic phenomena and particularly as magneto-optical

materials based on organic/inorganic 'composites' at the molecular level. Part of this strategy is based on the use of ligands that are rich in the number of ligating donor atoms. In the present paper, we report preliminary magnetic studies and structural data for the fluoride congener of a series of isomorphous compounds given by the formula $Cu_9X_2(cpa)_6 \cdot xH_2O$[2], a triangulated hexagonal layer which represents a unique extension of the interconnection exhibited by the idealized Kagomé lattice. It is particularly interesting from the viewpoint of cyclic exchange and spin frustration.

EXPERIMENTAL

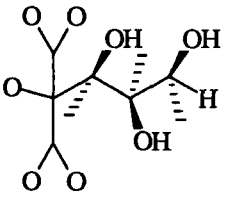
Synthesis of $Cu_9F_2(cpa)_6 \cdot xH_2O$. $CuCl_2 \cdot 2H_2O$ was reacted with ascorbic acid (2:1 mol ratio). The mixture was heated and allowed to stir until the precipitation of CuCl was complete (*ca.* 0.5 h), after which the CuCl was filtered off. CuF_2 (1 mmol) was added to the clear solution followed by the addition 0.10 M NaOH to raise the pH to a value of 6. Blue hexagonal prisms were collected after 2-3 days. *Caution: HF is produced!*

Crystal Structure Determination. A blue hexagonal crystal (0.10 x 0.25 x 0.28) was mounted in a capillary with mother liquor and sealed. Crystal data were collected at room temperature on a R3m/V Nicolet four circle diffractometer with graphite monochromated MoKα radiation; λ = 0.71073 Å. Unit cell parameters and standard deviations were obtained by least squares fit to 25 reflections randomly distributed in reciprocal space and lying in the range 15 - 30°. The structure was solved by full matrix least squares refinement using Shelextl-Plus on a Microvax II. It is isomorphous with the Cl and Br derivatives.[2] *Crystal Data:* $C_{36}H_{50}F_2Cu_9O_{51} \cdot xH_2O$ (unit cell contents), trigonal, P321, a = b = 21.297(11), c = 7.965(10) Å, V= 3128.6(4.9) Å^3, channels of disordered water (solvent) occupy ca. 40% of the unit cell.

Magnetic susceptibility measurements. Magnetic susceptibility data were collected in the temperature range 1.7 - 250 K using a Quantum Design SQUID-based magnetometer utilizing modifications and procedures described elsewhere.[3] Data were corrected for temperature independent magnetism (-556 x 10^{-6}/mol) using Pascal's constants[4] for the diamagnetic components and a T.I.P./Cu(II) of 60 x 10^{-6}. Figures in this paper are based on a molecular weight of 2603.1 g/mol (9 Cu(II)/unit cell).

RESULTS

Structural Description of $Cu_9F_2(cpa)_6 \cdot xH_2O$. 2-Carboxypentonic acid (cpa) is a poly-hydroxypolycarboxylic acid obtained from the decomposition of ascorbic acid in the presence of Cu(II).[5] Its structure lends itself to a multitude of ligating possibilities in



which interconnected high-nuclearity species are readily envisaged. Two environments are found for the Cu(II) ions. The copper designated Cu_{trimer} (Cu_t) is near a crystallographic three fold axis and generates the trimeric unit shown in Figure 1. The

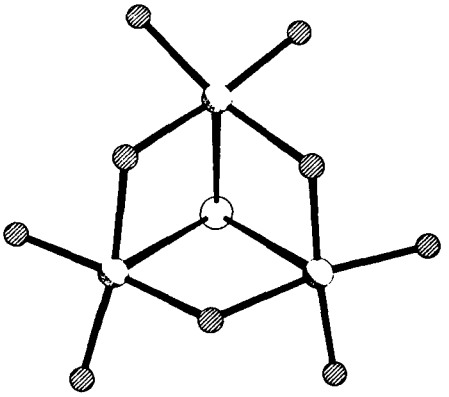


FIGURE 1 Trimeric cluster of three square pyramidal Cu_t ions.

ion has a square-pyramidal coordination sphere in which the basal sites are oxygen atoms from two different cpa anions, and the apical site is filled by a common μ_3-fluoride ion located on the 3-fold axis. The Cu-O bridging network within the trimer is an alternating Cu_3O_3 'ring'; the Cu-O distances (2-hydroxy) are 1.92(2) - 1.94(2) Å.

$Cu_{monomer}$ (Cu_m) is located on a crystallographic two-fold axis. It has four short Cu-O equatorial bonds and two longer Cu-O axial bonds; see Figure 2. Two carboxylate groups (of a single cpa) bridge the Cu_m site to two Cu_t sites; all relevent Cu-O distances are in the range 1.91(3) - 1.97(3). As shown in Figure 2, three such Cu_m sites are connected to every Cu_t based trimer; two trimers are connected to each Cu_m. The axial positions of the six coordinate Cu_m sites are occupied by the 3-hydroxy groups of two different cpa anions; these Cu-O distances are 2.29(4) Å.

To further develop the extended lattice structure, the fragment shown in Figure 2 is repeated so as to form a polymeric sheet which grows in the ab-plane. Figure 3 emphatically demonstrates that the sheet is a result of Cu-O, C-O and C-C bonding. The layer shown in Figure 3 stacks in the c direction; the layers are held together by

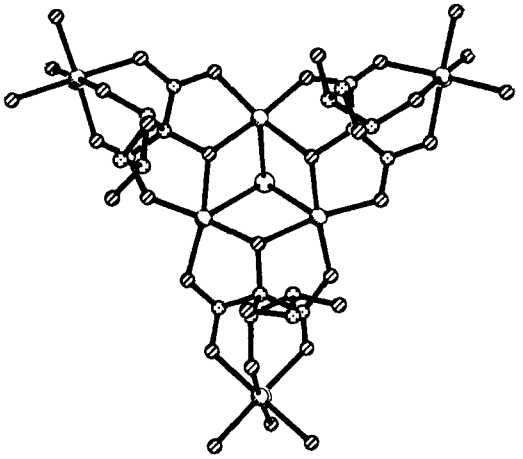


FIGURE 2 The trimeric cluster (of Figure 1) bridged to three Cu_m.

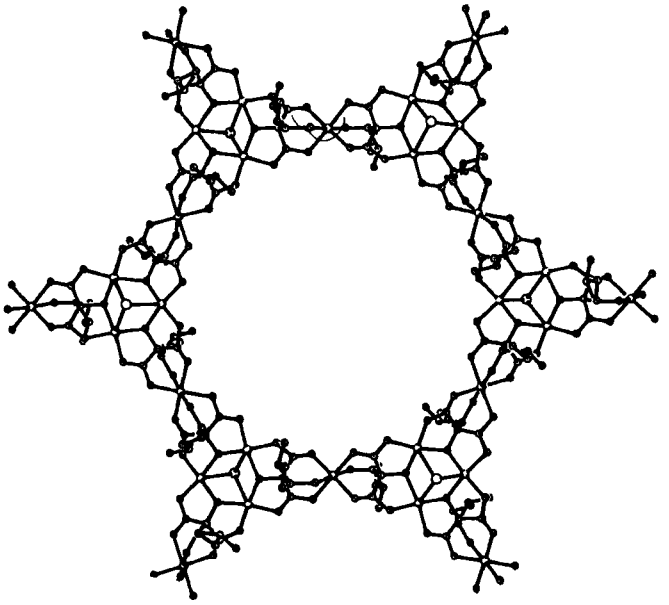


FIGURE 3 The infinite layer structure and hexagonal columnar channels.

interactions involving extensive hydrogen bonding. The vertical stacking of the layers results in channels that pass through the crystals. These channels are *ca.* 20 Å in diameter and are occupied by water; channel volume is nearly 40% of the unit cell.

Magnetic Susceptibility. Susceptibility data were collected with applied magnetic fields in the range 1.0 G to 10 kG in the temperature range 1.7 to 300 K. The data are plotted in Figures 4 and 5 as χ_m, $1/\chi_m$, and $\mu_{eff} = 2.828(\chi_m T)^{1/2}$; the molar basis is per

unit cell ($Cu_9F_2(cpa)_6 \cdot xH_2O$). Several dominant features are noteworthy. In Figure 4, it is clearly seen that χ_m diverges at low temperatures; it does not exhibit a maximum as a function of temperature. Although μ_{eff} = 3.8 B.M. at 300 K, it reaches a minimum (2.8 B.M.) near 60 K and a maximum (4.7 B.M.) near 6.8 K.

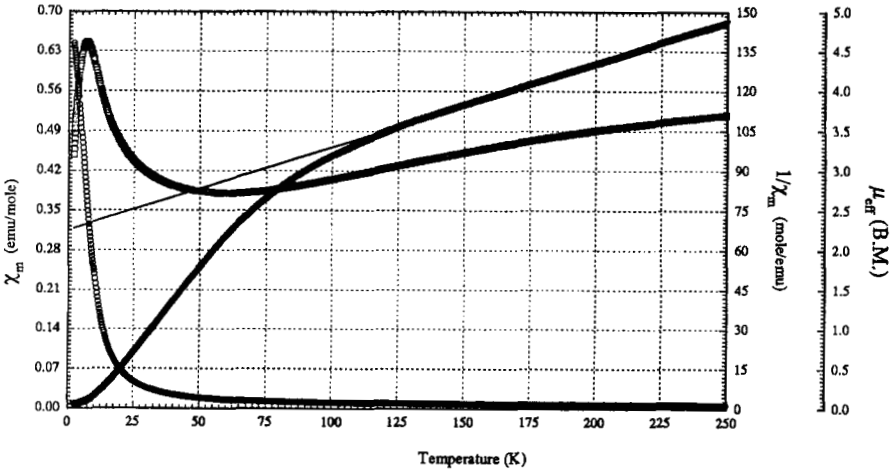


FIGURE 4 Magnetic data (o – χ_m, ∇ – $1/\chi_m$, □ - μ_{eff}); H = 10,000 G.

The $1/\chi_m$ plot exhibits three distinct regions: for T > 150 K, the data are linear as a function of temperature and can be fit by the Curie Weiss law, $\chi_m = C/(T-\theta)$, with parameters C = 3.193 and θ = -215.8 K; for 50 < T < 150 K, the slope of the $1/\chi_m$ curve changes continuously and it is not appropriate to use a Curie Weiss fit; for

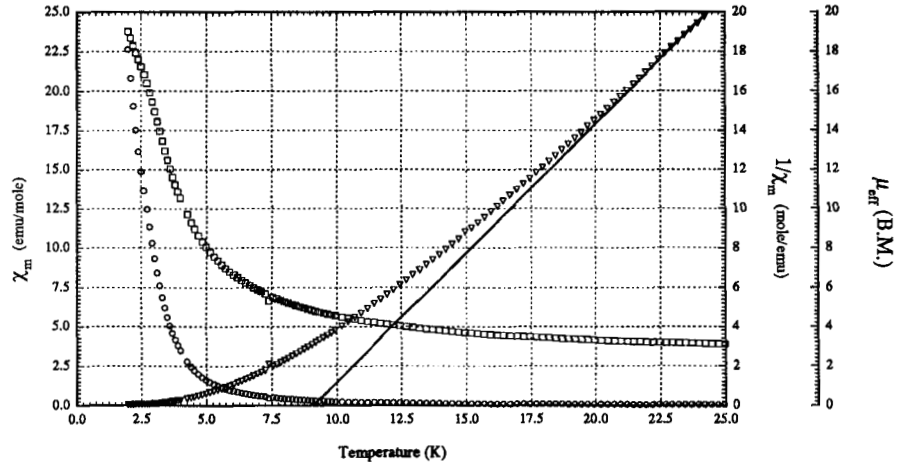


FIGURE 5 Magnetic data (o – χ_m, ∇ – $1/\chi_m$, □ - μ_{eff}); H = 10 G.

$20 < T < 50$ K, the $1/\chi_m$ curve is again nearly linear and the best-fit Curie-Weiss parameters are $C = 0.7618$ and $\theta = +9.3$ K (this is the best-fit that is compared to the low-field data in Figure 5). Below 20 K the data become increasingly field dependent and exhibit a marked increase in the susceptibility and moment values.

For $T > 125$ K, and using an average g-value of 2.1 for Cu(II), the S value per unit cell formula is clearly reduced with respect to the value expected for nine moles of noninteracting paramagnetic $S = 1/2$ ions.[4] Such a reduction in S value is in agreement with the decreasing value of μ_{eff} and is indicative of the very strong antiferromagnetic exchange interactions that are suggested by $\theta = -215.8$ K. At high fields, the μ_{eff} plot clearly indicates that a minimum spin value is reached before a rounded maximum occurs upon further cooling. The temperature at which such a rounded maximum occurs in μ_{eff} is highly dependent on the applied field; the maximum shifts to lower temperatures with smaller applied fields. The low-field data in Figure 5 clearly demonstrate this feature - μ_{eff} reaches a maximum value of over 19 B.M. at 1.7 K whilst it is clear that a maximum has yet to be realized, perhaps at lower temperatures.

DISCUSSION

The extended structure of $Cu_9X_2(cpa)_6 \cdot xH_2O$ is clearly unique, particularly among layered magnetic materials. This stems from several reasons. *First*, it is quite clear that the chemical lattice shown in Figure 3 must correspond to the magnetic network, or

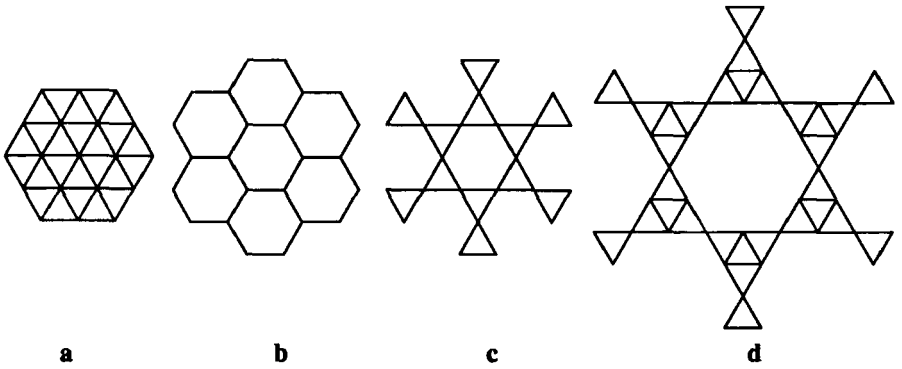


FIGURE 6 a) triangular, b) honeycomb, c) Kagomé, d) $Cu_9F_2(cpa)_6 \cdot xH_2O$

connectivity pattern, displayed in Figure 6d, where the solid lines represent possible superexchange pathways and the points of intersection are spins. Careful comparison to other triangulated lattices currently of interest (Figures 6a-c) emphasizes a number of topological similarities and differences.[6] *Second*, triangulated spin systems are

notable for the spin frustration they may exhibit. A large number of triangular clusters are already known.[7] More to the point however, extended lattices which consist of interconnected, possibly frustrated, triangulated units have heretofore not been reported for molecular-based magnetic materials. In fact, the $Cu_9X_2(cpa)_6 \cdot xH_2O$ lattice suggests a new direction for the design and synthesis of novel magnetic materials. *Third*, triangulated magnetic lattices are of particular interest as experimental testing grounds for the physics associated with degenerate ground states and finite entropies (at T = 0).

Chemically, the $Cu_9X_2(cpa)_6 \cdot xH_2O$ magnetic lattice consists of two different spin sites and two exchange parameters. There are twice as many Cu_t sites as there are Cu_m sites. Each Cu_t site is connected by superexchange pathways to two other Cu_t sites within the same trimeric unit. Each Cu_t site is also connected by two separate but crystallographically equivalent superexchange pathways to two Cu_m sites. Each Cu_m site is connected by four such pathways to four equivalent Cu_t sites (alternately speaking, two trimers). Topologically, the pairwise exchange interactions between Cu_t sites is equal in value and we refer to it as the *intra*trimer exchange parameter. The trimeric units are interconnected to one another by way of four pairwise exchange interactions inbetween four Cu_t sites on two trimers and the Cu_m site that interconnects the two trimers. We refer to each of these exchange interactions as the *inter*trimer parameter. The intratrimer exchange parameter is likely to be large in magnitude and antiferromagnetic in nature because of the alkoxy bridging oxygens in the Cu_3O_3 ring and, to a much lesser extent, the tri-bridging fluoride.[8] (To the best of our knowledge, tri-bridging fluorides are extremely rare in Cu(II) systems.) The intratrimer exchange is likely responsible for the large θ value observed in the high temperature data. With a large antiferromagnetic intratrimer/intertrimer exchange ratio, the trimers could in principle behave as effective S = 1/2 magnetic entities, resulting in *five* S = 1/2 sites per $Cu_9X_2(cpa)_6 \cdot xH_2O$ unit cell. This is in agreement with the gradually increasing μ_{eff} value of 3.8 - 4.0 B.M. (calculated for five moles of noninteracting S = 1/2 sites per MW unit). Such a model is more accurately depicted by the network schematic shown in Figure 7, where the magnetic lattice could be treated as a honeycomb-type lattice in which effective S =1/2 spin sites are located at the vertices *and along the edges*.

There is presently a great deal of interest in topologically frustrated systems.[9] On the theoretical side, this stems in part from Anderson's resonating valence bond structure for superconductivity in doped cuprates.[10] One feature of the liquidlike RVB state is the absence of long-range order in the ground state. Similar results for cooperative spins on frustrating lattices can also be obtained. Although good experimental examples of either have not yet been found in real magnetic materials, a few compounds have been found to exhibit a number of novel low-temperature states

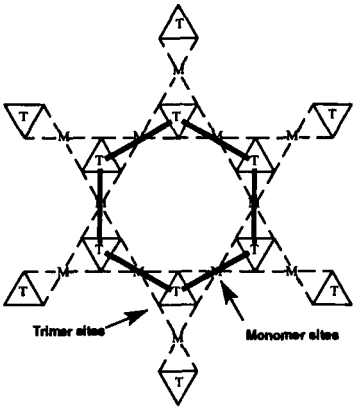


FIGURE 7 Alternate schematic in which strongly antiferromagnetic trimers are a single site.

that may be associated with frustration. The Kagome lattice, in particular, can display 'order from disorder' -- the order being spin nematic. The KL has been proposed[6] as a model for ^{3}He adsorbed on graphite (S = 1/2) and for the insulating layered compound $SrCr_8Ga_4O_{19}$ (S = 3/2). Given the possibility that such novel states may also occur in other triangulated lattices, further study of the $Cu_9X_2(cpa)_6$ compounds is certainly warranted. Additional synthetic work and magnetic characterization is in progress.

ACKNOWLEDGMENTS

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