A Molecular-Based Magnet with a Fully Interlocked Three-Dimensional Structure

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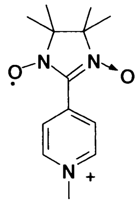
A compound has been synthesized with the formula $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2.2H_2O$, where rad^+ is 2-(4-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, opba is orthophenylenebis(oxamato), and DMSO is dimethyl sulfoxide. It consists of two nearly perpendicular graphite-like networks with edge-sharing $Mn(II)_6Cu(II)_6$ hexagons. The two networks are fully interlocked with the same topological relationship as that between adjacent rings of a necklace. The compound has three kinds of spin carriers: Mn(II) and Cu(II) ions, antiferromagnetically coupled through oxamato bridges, and rad^+ radical cations, bridging the Cu(II) ions through the nitronyl nitroxide groups and forming Cu-rad chains. The temperature dependence of the magnetization reveals that below 22.5 K, the compound behaves as a magnet.

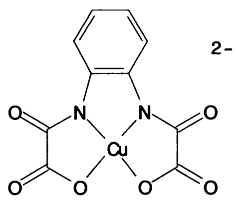
One of the main challenges in the field of molecular materials is the design of compounds exhibiting a spontaneous magnetization below a critical temperature T_c (*1*). The first molecular-based magnets were reported in 1986 (*2, 3*). Since then, several other systems of this kind have been described with critical temperatures ranging from 0.6 to 450 K (*4–18*). However, in quite a few cases, the crystal structures of the compounds are not known, and it is difficult to analyze the mechanism leading to a magnetically ordered state. Most of the molecular-based magnets whose structures have been determined are one-dimensional systems (*4–6, 16*). In these materials, the interchain interactions are very weak compared with the intrachain interaction, and $T_c < 10$ K.

Up to now, our strategy for the design of molecular-based magnets consisted of assembling Mn(II)Cu(II) ferrimagnetic chains within the crystal lattice in a ferromagnetic fashion (*5, 7*). Because there is no magnetic ordering for a purely one-dimensional system, except at absolute zero, it is necessary to increase the dimensionality of the compounds in order to raise T_c.

We synthesized a molecular-based magnet with a three-dimensional structure resulting from the interlocking of two two-dimensional networks. This compound contains three kinds of spin carriers: Mn(II) and Cu(II) ions and rad^+, the organic radical cation 2-(4-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (*18*)



The formula of the compound is $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2.2H_2O$, where $[Cu(opba)]^{2-}$, with opba standing for orthophenylenebis(oxamato), is the Cu(II) dianionic precursor



We synthesized the compound by reacting the rad^+ salt of $[Cu(opba)]^{2-}$ with $MnCl_2$ in DMSO (*19*).

The x-ray crystal structure of the compound (*20*) revealed the two two-dimensional networks. Each network is made up of layers stacked on each other, as in graphite, with a mean interplane separation of 14.8 Å. A layer consists of edge-sharing, nearly planar hexagons with a Mn(II) ion in a distorted octahedral position at each corner and a Cu(II) ion in an elongated tetragonal position at the middle of each edge (Fig. 1). The Mn(II) ions present a perfect alternation of Λ and Δ chiral sites (Λ and Δ define the absolute configuration for the two possible arrangements of the bidentate ligands $[Cu(opba)]^{2-}$ around the Mn atom). Nearest neighbor Mn(II) and Cu(II) ions are bridged by oxamato groups, which efficiently transmit an antiferromagnetic interaction between spin carriers (*21*). The mean length of an edge is 10.9 Å, and the mean separation between opposite corners is 21.5 Å. Within each hexagon, two opposite Cu(II) ions have DMSO molecules in

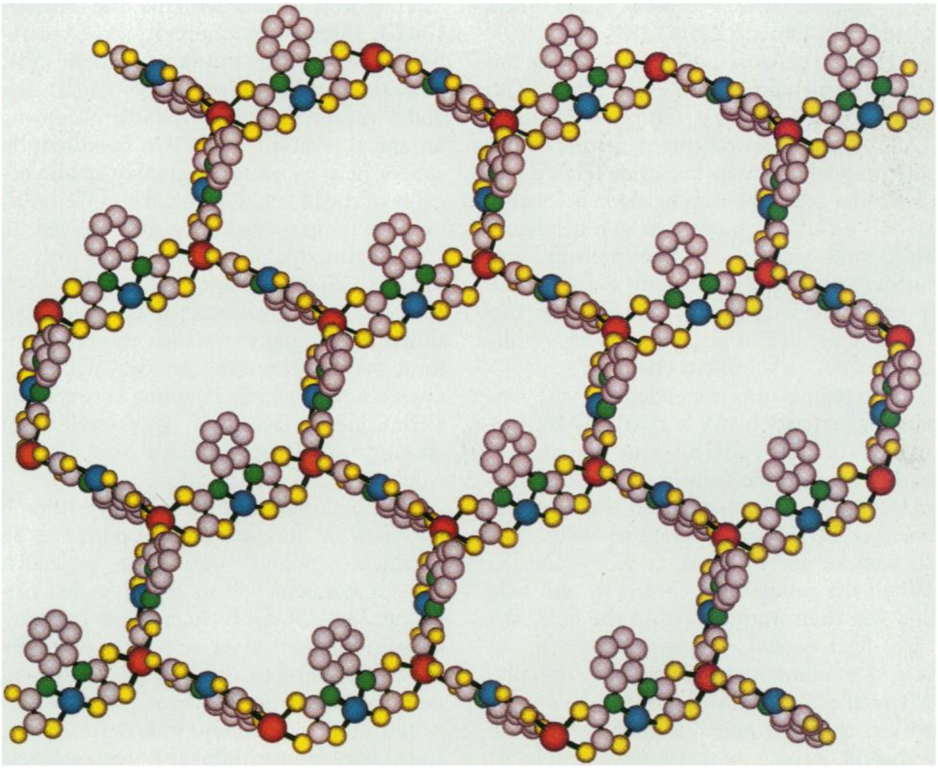


Fig. 1. View of a layer showing the $Mn(II)_6Cu(II)_6$ hexagons. The Mn(II) ions are represented in red, the Cu(II) ions in blue, the nitgrogen atoms in green, the oxygen atoms in yellow, and the carbon atoms in gray.

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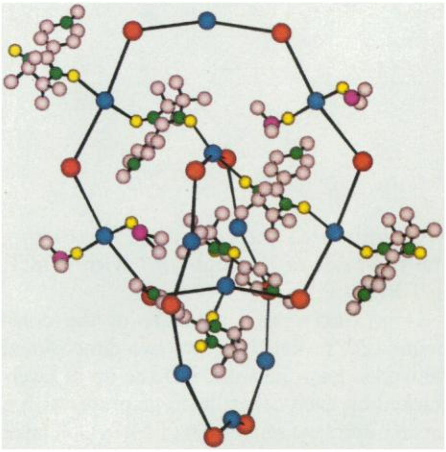

Fig. 2. Interlocking of two hexagons, one from each network, and the CuA-rad-CuB-rad chains. The DMSO molecules are in the coordination sphere of two opposite Cu(II) ions, and the nitronyl nitroxide groups of the radical cations are in the coordination sphere of the other four Cu(II) ions. For clarity, the opba ligands have been omitted, as have the rad$^+$ cations around one of the Cu(II) ions belonging to the hexagon parallel to the plane of the paper. Only the metal ions of the second hexagon have been represented. In addition to the colors used in Fig. 1, the sulfur atoms of the DMSO molecules are violet.

their coordination spheres, and the other four Cu(II) ions have nitronyl nitroxide groups of the radical cations in their coordination spheres, all occupying the apical positions with, in both cases, very weak Cu-O apical interactions (around 2.8 Å) (Fig. 2).

The two networks, denoted A and B, are nearly perpendicular to each other: The dihedral angle between the mean planes is 72.7°. These networks interpenetrate with a full interlocking of the hexagons (Figs. 2 and 3). In the center of each hexagon belonging to A is a Cu(II) ion of a hexagon belonging to B and vice versa. The networks are further connected by the nitronyl nitroxide groups of the rad$^+$ cations, which bridge two Cu(II) ions, one from each network, resulting in CuA-rad-CuB-rad chains (Fig. 2).

The temperature dependence of the molar magnetization M for $(rad)_2Mn_2[Cu(opba)]_3(DMSO)_2 \cdot 2H_2O$ was investigated within a magnetic field H of 1 Oe. When the sample was cooled within the field, the "field-cooled" magnetization (Fig. 4) showed an abrupt break at T_c = 22.5 K. When the sample was cooled in zero field and was then warmed within the field, the "zero-field–cooled" magnetization (Fig. 4) had a maximum just below T_c. Finally, when the sample was cooled below T_c within the field and was then warmed in zero field, a remnant magnetization (Fig. 4) was observed that vanished at T_c. All of these features are characteristic of a magnetically ordered state existing below 22.5 K. The zero-field susceptibility $(dM/dH)_{H=0}$ at 10 K is extremely large, as expected for a magnet, and a magnetization of ~4 bohr magnetons per mole is obtained within a field of a few tens of oersted (Fig. 5). As the field is increased further, the magnetization increases smoothly, which could be a result of the decoupling of the radical spin.

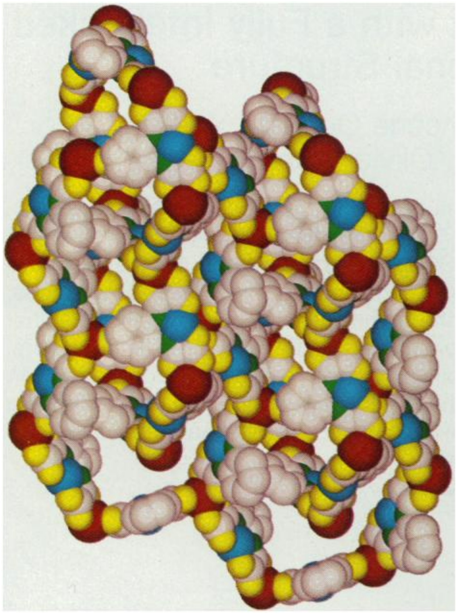

Fig. 3. Space-filling representation of the structure emphasizing the interlocking of the honeycomb networks.

It is well established that the Mn(II)-Cu(II) interaction through an oxamato bridge is strongly antiferromagnetic (*5*). The interaction between the Cu(II) ion and a nitronyl nitroxide radical occupying an apical position in the Cu coordination sphere may be either negligibly small, because of the long Cu-O apical bond lengths, or weakly ferromagnetic, as observed in Cu(II)-nitroxide molecular species with related structures (*22*). It follows that both networks can be considered as two-dimensional ferrimagnets in which the rad$^+$ cations, which connect the two networks, favor a ferromagnetic coupling between the ferrimagnetic layers. It is possible that stronger Cu(II)-rad$^+$ apical interactions would give a T_c > 22.5 K.

Interlocking of supramolecular rings is an area of fundamental importance in chemical topology. Interlacing molecular threads are achieved in the so-called catenanes (*23–25*). Of the many two- or three-dimensional molecular structures, very few present a complete interlocking of independent infinite networks. Examples of interpenetrating two-dimensional networks are silver tricyanomethide (*26*), trimesic acid (*27*), and diaquabis-(4,4′-bipyridine)zinc hexafluorosilicate (*28*). The structure described here, however, has some additional subtleties, such as the presence of the three kinds of interacting spin carriers, the imbrication of Mn_6Cu_6 interlocked hexagons, and the formation of Cu-rad chains, in addition to the chirality of the Mn(II) sites.

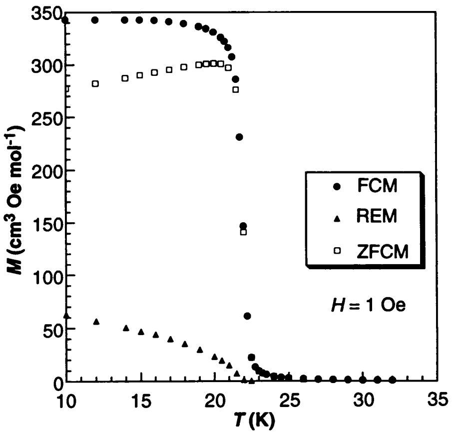

Fig. 4. Temperature dependence of the magnetization within a field of 1 Oe. The field-cooled magnetization (FCM) was measured upon cooling within the field. The zero-field–cooled magnetization (ZFCM) was measured after cooling in zero field and then warming within the field. The remnant magnetization (REM) was measured after cooling within the field and then warming in zero field.

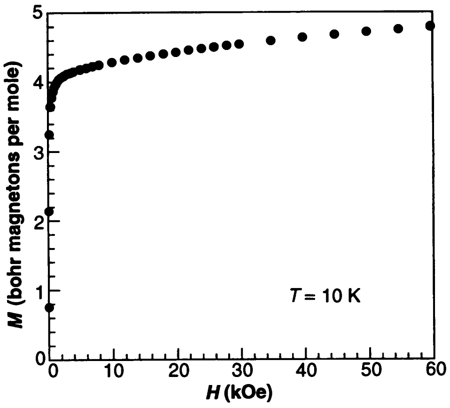

Fig. 5. Field dependence of the magnetization at 10 K.

The interlocking is a result of several factors. The large fraction of empty space in the network, because of the size of the Mn_6Cu_6 hexagons, is part of the reason. The Cu(II)-rad$^+$ interactions, even if they are weak, should also contribute to the interpenetration of the two networks. Indeed, the size and the shape of the radical cation fit the free space within the rings. Further explanation of the mechanism of interlocking and investigation of the properties arising from the structure is needed.

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19. We obtained the diethyl ester Et_2H_2opba (Et, ethyl) of orthophenylenebis(oxamic acid) by adding 0.06 mol of ethyloxalylchloride to a solution of 0.03 mol of orthophenylenediamine dissolved in 150 ml of tetrahydrofurane. The *n*-tetrabutylammonium salt $(NBu_4)_2$[Cu(opba)] (Bu, butyl) was prepared by the successive addition of 0.137 mol of NBu_4OH (40% in water) and 50 ml of an aqueous solution containing 0.0325 mol of $CuCl_2.2H_2O$ to a suspension of 0.0325 mol of Et_2H_2opba in 250 ml of a 4:1 water-ethanol mixture. Then, $(NBu_4)_2$[Cu(opba)] was extracted with CH_2Cl_2. The rad$^+$I$^-$ was prepared as previously described (*18*). We prepared (rad)$_2$[Cu(opba)].H_2O by adding 5×10^{-3} mol of $(NBu_4)_2$[Cu(opba)] in 90 ml of dichloromethane to a solution of 10^{-2} mol of rad$^+$I$^-$ in 250 ml of dichloromethane. After a few minutes, a precipitate of (rad)$_2$[Cu(opba)].H_2O appeared. Finally, we synthesized (rad)$_2$Mn$_2$-[Cu(opba)]$_3$(DMSO)$_2$.2H_2O by adding 5×10^{-5} mol of $MnCl_2$ to a solution of 5×10^{-4} mol of (rad)$_2$[Cu(opba)].H_2O in 25 ml of DMSO. The mixture was stirred, and then 25 ml of water were slowly added. Well-shaped single crystals of (rad)$_2$Mn$_2$[Cu(opba)]$_3$(DMSO)$_2$.2H_2O appeared within a few days.
20. The compound (rad)$_2$Mn$_2$[Cu(opba)]$_3$(DMSO)$_2$.-2H_2O crystallizes in the monoclinic system, space group *Cc*, with a = 25.379(8) Å, b = 25.146(8) Å, c = 18.845(4) Å, and β = 131.52(4)°, where the number in parentheses is the error in the last digit, and V = 9004 Å^3, Z = 4, and d_{calc} = 1.280 g cm^{-3}. Analysis was done at wavelength λ (Mo-Kα) = 0.71073 Å. The structure was solved by direct methods and successive Fourier difference syntheses. The refinements by full-matrix least squares gave final R = 0.091 and R_w = 0.104 from 2642 reflections with intensity $I \geq 2\sigma(I)$ for 485 variables. Because of the small number of observed reflections, only the Mn and Cu atoms were refined anisotropically. The DMSO and water molecules are disordered.
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Strained-Layer van der Waals Epitaxy in a Langmuir-Blodgett Film

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Atomic force microscope images of Langmuir-Blodgett films of lead and manganese fatty acid salts show that these monolayers have long-range order and are oriented with respect to the mica substrate, although the lattice symmetries of the monolayers and substrate are dramatically different. The surface lattice of sequentially thicker films evolves toward the bulk structure while retaining the substrate alignment. This behavior is in distinct contrast to films of cadmium fatty acid salts on mica, or all films on amorphous silicon oxide, in which the monolayer structure is disordered and a three-layer-thick film displays the bulk structure.

Langmuir-Blodgett (LB) films have been widely studied because of their applications in the areas of molecular electronics, nonlinear optics, cell membrane models, and biosensors (*1*). Most of the potential applications of LB films are based on the premise of perfect molecular layering and orientation. The technique of atomic force microscopy (AFM) (*2*), which probes only the outermost layer of the film, is ideal for the study of LB films (*3*). Although in many ways LB films demonstrate behavior analogous to thin solid films such as having long-range positional order (*4–7*), grain boundaries (*4*), and surface reconstructions (*6, 7*), both interlayer and intralayer interactions in the films can be quite important (*6, 7*); the presence of these interactions makes LB films relevant to the study of biomembranes, vesicles, and microemulsions.

In the experiments reported here we demonstrate that the growth of certain LB films proceeds by a type of epitaxy which we call "strained-layer van der Waals epitaxy" because it represents a compromise between the well-known strained-layer epitaxy and the recently reported van der Waals epitaxy (*8*). In contrast with previous work on cadmium arachidate (CdA) (*4–6*), and barium arachidate (BaA) (*7*), monolayers of lead stearate (PbSt) on mica substrates have long-range positional and orientational order that differs significantly from both that of multilayer films of PbSt and that of mica. However, the lattice is oriented with respect to the substrate. Monolayers of manganese arachidate (MnA) have short-range positional order, but long-range orientational order, and are also oriented with respect to the mica substrate. Monolayers of both materials on amorphous silicon surfaces were completely disordered. These results show that coupling between the substrate and the monolayer and the nature of the counterion have a significant effect on the molecular packing in LB films. The differences between cadmium- and lead-containing films on mica are all the more surprising given that the structures of thick films (>10 layers) of these materials are nearly identical.

The concept of strained-layer epitaxy is familiar from semiconductor systems. In these systems the first monolayer of an adsorbed film, which has a bulk lattice constant no more than a few percent different from that of the substrate, replicates the in-plane structure of the substrate exactly, and subsequent layers gradually relax to the bulk structure of the adsorbate. For PbSt and MnA films on mica, however, the bulk crystal structure has a significant mismatch with the substrate in both lattice constants and lattice symmetry. We show here that centered-rectangular PbSt monolayers are deposited on the hexagonal mica substrate in a well-defined orientation such that there is a close match between one set of lattice rows of monolayer and substrate. However, the other lattice constants of the monolayer are far from commensurate with the substrate. In spite of this large mismatch, PbSt monolayers have long range positional and orientational order. In this regard, the PbSt monolayers are analogous to films of transition metal dichalcogenides

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