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Incommensurate Nature of the Multilayered Molecular Ferromagnetic Metals Based on Bis(ethylenedithio)tetrathiafulvalene and Bimetallic Oxalate Complexes

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The salt $[ET]_x[MnRh(ox)_3]\cdot CH_2Cl_2$ ($x = 2.526(1)$) has been obtained and characterized. This paramagnetic metal is essentially isostructural to the ferromagnetic metal $[ET]_y[MnCr(ox)_3]\cdot CH_2Cl_2$ ($y \approx 3$) and provides a definite answer on the origin of the structural disorder present on such systems. As in the ferromagnetic analogue, this material shows high electrical conductivity at room temperature ($13\ S\cdot cm^{-1}$) and metallic behavior.

In recent years, new functional materials have been designed using molecular building blocks that are able to mimic the technological properties of classic inorganic materials used in present technological applications.[1] A unique feature of molecule-based materials deals with the construction of hybrid two-network materials that mix in the solid different physical properties. This strategy has been particularly successful for the preparation of materials mixing conductivity and magnetism. Several magnetic conductors have been developed from tetrathiafulvalene (TTF) and derivatives,[2] and paramagnetic coordination complexes used as counterions. These compounds behave as semiconductors,[3] metals[4] and even superconductors.[5] But in all cases the paramagnetic complexes are well isolated from each other, and no bulk magnetism is observed, except at very low temperatures where antiferromagnetic ordering was observed in some exceptional cases.[6]

In 2000 we reported the final breakthrough in this area: the first molecular ferromagnetic metal as the salt $(ET)_3$-$[MnCr(ox)_3]$ (**1**).[7] In this case, the organic radical bis(ethylendithio)tetrathiafulvalene (ET) forms a two-dimensional network responsible for the metallic conductivity down to 0.3 K, alternating with polymeric bimetallic oxalate-bridged layers[8] responsible for the onset of ferromagnetic ordering below ca. 6 K. This same strategy has also been extended to other organic donors and metal ions.[9] Some important questions remain unsolved regarding the structure of these salts. In **1**, the inorganic network between the organic layers appeared as disordered, which was interpreted as due to the presence of stacking faults.[7,10] In the present work, we demonstrate that the apparent disorder of the inorganic layers is due to the incommensurate nature of these two-network materials. This important conclusion has been extracted from a structural study[11] on a salt analogous to **1** wherein Cr^{III} has been substituted by the heavier Rh^{III} ion (**2**).[12] Regarding the physical properties, this substitution is

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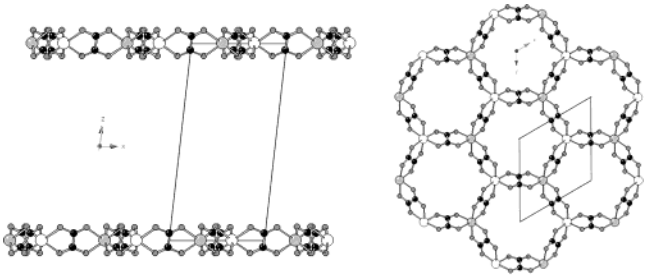

Figure 1. Side view (projection on the *ac* plane) and top view (projection on the *ab* plane) of the inorganic layer for **2**.

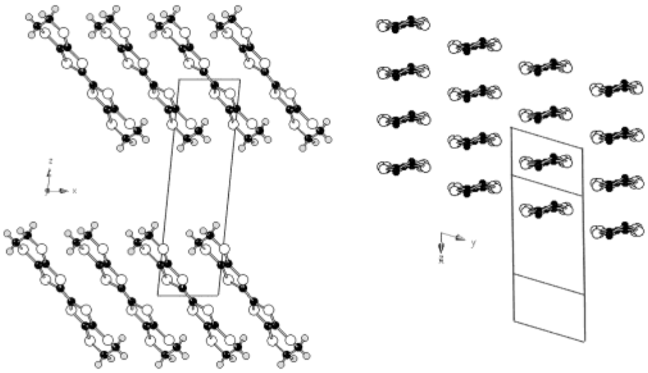

Figure 2. Side view (projection on the *ac* plane) and top view of the organic layer for **2** showing the β phase packing of the organic donors.

also of interest because low-spin Rh^{III}, being diamagnetic, suppresses the ferromagnetic transition in the inorganic network.

Most of the reflections observed in the X-ray data collection of **2** were indexed by a unit cell that led us to the determination of the crystal structure of the inorganic sublattice, but there were enough remaining intense reflections that could be indexed onto a second unit cell, isostructural to that obtained for **1**. The two unit cells are mutually incommensurate, which indicates that these materials belong to the class of incommensurate composite crystals.[13] One property of composite crystals is that if only the Bragg reflections of one sublattice are considered, the structure of the other sublattice appears disordered. This explains the apparent disorder of the inorganic sublattice of **1**[7] and other analogous derivatives,[9] where only Bragg reflections of the organic subsystem could be measured.

The solution for the first unit cell shows the typical honeycomb hexagonal 2D lattice (Figure 1). The hexagonal layers are stacked in an eclipsed way, indicating that a well ordered structure without stacking faults is present in regions of sufficient sizes to produce the Bragg reflections. This type of stacking has been observed in those salts having cations that do not penetrate into the holes of the honeycomb lattice.[14] A disordered solvent molecule occupies the hexagonal holes, which should correspond to dichloromethane, in agreement with elemental analysis. The position for the metal atoms is shared by Rh and Mn at half occupancy. Thus, although in a single layer the divalent and trivalent metals should be perfectly ordered,[15] adjacent layers do not maintain any given order in the distribution of the metal centers.

The solution for the second unit cell shows a typical β arrangement (Figure 2) made up from linear stacks along the *a* direction of coplanar ET molecules with close side contacts between the chains (S3$-$S4 = 3.51(5) Å), and with much longer intrachain S$-$S contacts (5.13(5) Å). The ET molecules show a canting with respect to the plane of the layers of 43°. This canting is just 2° smaller than that found in **1**. Apart from this, both structures can be considered essentially isostructural. Also, in both cases the terminal ethylenic groups of the ET molecules appear disordered between the two possible conformations that arise from the tetrahedral conformation of the $-CH_2-$ groups, that make them to be above or below the mean ET plane defined by the sulfur and the rest of the carbon atoms.

The c^* reciprocal lattice parameters of the two sublattices are found to be equal within the accuracy of the experiment, with the ratio c^*(inorganic)/c^*(organic) equal to 1.001. This relation is expected for a layered composite type crystal, because the layers cannot penetrate each other, leading to the requirement that the periodicity perpendicular to the layers is equal for the two subunit cells, and this periodicity is given by the c^* reciprocal lattice parameters. As found here, the periodicities parallel to the layers of the organic and inorganic subsystems do not match. The result is a nonstoichiometric compound with a stoichiometry that is directly obtained from the ratio of the volumes of the two unit cells, as $(ET)_x[MnRh(ox)_3]\cdot CH_2Cl_2$ (x = 2.526(1)). Unfortunately, the quality of the X-ray data is still not good enough to solve in more detail the relation between the two unit cells. A nonstoichiometric composition is not rare for organic conductors when the inorganic counterions are polymeric.[16]

Electrical conductivity measurements (Figure 3) performed on single crystals with the four probe method showed high

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(11) Crystal structure analysis: The data were collected with a Nonius KappaCCD diffractometer using graphite monochromatic Mo Kα radiation (λ = 0.71073) at 293 K. The structure was solved by direct method (SIR97) followed by Fourier synthesis, and refined on F^2 (SHELXL-97). The non-hydrogen atoms were refined anisotropically, except the disordered ones. Inorganic subsystem: $[ET]_{2.53}[MnRh(ox)_3]\cdot CH_2Cl_2$, M_w = 1479.99, triclinic, space group $P1$, a = 9.3480(11) Å, b = 9.4030(14) Å, c = 16.947(4) Å, α = 88.510(6)°, β = 85.137(4)°, γ = 119.617(5)°, V = 1286.4(4) Å^3, T = 293(2) K, Z = 1, ρ_{calcd} = 1.910 g$\cdot$cm^{-3}, $F(000)$ = 740, μ = 1.548 mm^{-1}, 5050 reflections, 2998 unique (R_{int} = 0.0824), $2\theta_{max}$ = 45.86. $R(F)$ = 0.1134 and $R_w(F^2)$ = 0.2620 for 1368 reflections [$I > 2\sigma$(I)]. Organic subsystem: $[ET]\{[MnRh(ox)_3]\cdot CH_2Cl_2\}_{0.40}$, M_w = 587.38.69, triclinic, space group $P\bar{1}$, a = 5.1330(5) Å, b = 6.3870(6) Å, c = 16.938(3) Å, α = 88.715(5)°, β = 84.201(5)°, γ = 67.230(5)°, V = 509.32(11) Å^3, T = 293(2) K, Z = 1, ρ_{calcd} = 1.915 g$\cdot$cm^{-3}, $F(000)$ = 294, μ = 1.553 mm^{-1}, 981 reflections, 560 unique (R_{int} = 0.0261), $2\theta_{max}$ = 45.98. $R(F)$ = 0.0884 and $R_w(F^2)$ = 0.2239 for 379 reflections [$I > 2\sigma$(I)].

(12) ET (10 mg, 0.03 mmol) was suspended in 40 mL of a methanol/dichloromethane/benzonitrile solution (1:1:1) of $[Rh (ox)_3]^{3-}$ (10 mM) and Mn^{2+} (15 mM). Through this suspension was passed a constant current of 0.1 μA for several weeks. Shiny platelike crystals of $[ET]_x[MnRh(ox)_3]\cdot CH_2Cl_2$ x = 2.526(1) (or $[ET]\{[MnRh(ox)_3]\cdot CH_2Cl_2\}_{1/x}$) were collected and washed with methanol and acetone and air-dried.

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(15) This is expected from the stability of the $[Rh(ox)_3]^{3-}$ as building block and clearly demonstrated by the magnetic measurements, which show no magnetic interactions between paramagnetic centers, when such a signature behavior would be expected from the oxalate-bridged Mn dimers present in a randomly disordered network.

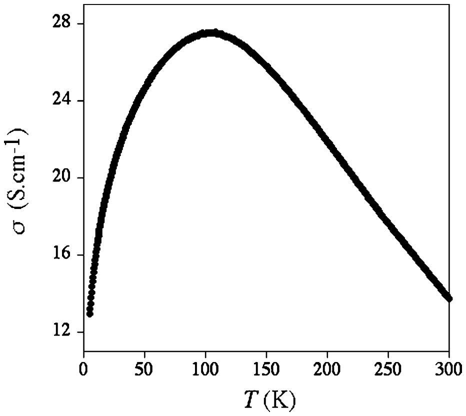

Figure 3. Temperature dependence of the electrical conductivity for the salt $[ET]_{2.53}[MnRh(ox)_3]\cdot CH_2Cl_2$ (**2**).

conductivity at room temperature (RT) (13 $S\cdot cm^{-1}$), that increases upon cooling the sample, as expected for a metal. Conductivity reaches a maximum at 103 K (28 $S\cdot cm^{-1}$) and starts to decrease. This behavior is probably related to charge localization (Anderson localization) in the organic lattice, and it is not a true transition into a semiconducting state, as proven by the fact that at 2 K conductivity is still as high as at room temperature. The reason this salt behaves differently from the Cr derivative is still not clear. Although essentially isostructural, the small differences in the orientation of the ET molecules and in band filling (the stoichiometry in both salts is close but not identical) could induce differences in the electrical conductivity. On the other hand, the behavior of the conductivity could be due to the quality of the crystals, which are brittle and probably multiple.

In conclusion, the structural characterization of the new hybrid magnetic conductor $(ET)_{2.53}[MnRh(ox)_3]\cdot CH_2Cl_2$, essentially isostructural to the metal ferromagnet $(ET)_y$-$[MnCr(ox)_3]\cdot CH_2Cl_2$ ($y < 3$), has allowed us to establish the incommensurate nature of these materials. The incommensurability allows these compounds to have fully ordered crystal structures, although stacking faults cannot be excluded. One important question raised by these molecular metal ferromagnets was the possibility of coexistence of ferromagnetism and superconductivity in the same crystal. In fact, in these materials, the lack of superconductivity might be attributed to the presence of an internal magnetic field below T_c coming from the inorganic network. From the studies on this new paramagnetic analogue, it is clear that ferromagnetism is not the only reason to explain the lack of superconductivity. Other reasons, for example the incommensurate nature, could be relevant in this respect.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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