

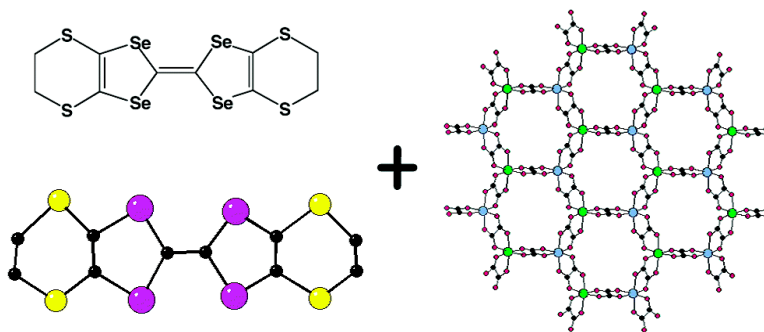
Communication

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A Molecular Metal Ferromagnet from the Organic Donor Bis(ethylenedithio)tetraselenafulvalene and Bimetallic Oxalate Complexes

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The field of functional molecular materials has witnessed rapid progress since the discovery of a variety of cooperative solid-state properties such as conductivity and superconductivity, nonlinear optics, and ferromagnetism.¹ Currently, one of the most appealing aims is to create hybrid molecular materials that combine in the same crystal lattice two of these bulk properties. In this context, an attractive approach for obtaining multifunctional molecular materials combining magnetism with conductivity is to make two-network solids containing stacks of π -electron donor or acceptor molecules, with magnetic transition metal complexes which act as counterions. Several of these hybrid salts have been reported, with transport properties ranging from semiconducting² to metallic³ and even superconducting.⁴ These materials, however, are usually paramagnets that only in exceptional cases order antiferromagnetically.⁵ To obtain bulk ferromagnetism combined with conductivity, polymeric inorganic networks are a better choice, since they ensure the presence of long-range ferromagnetic coupling. Recently, we reported a breakthrough in this area, with the synthesis of the salt $(\text{ET})_3[\text{MnCr}(\text{ox})_3] \cdot (\text{CH}_2\text{Cl}_2)$ (**1**), the first synthetic ferromagnetic metal.⁶ In this case, conducting layers of the bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) (or ET) organic donor responsible for the metallic conductivity down to 0.3 K are alternating with bimetallic oxalate-based honeycomb layers responsible for the appearance of ferromagnetic ordering below 5.5 K.

One of the key difficulties encountered in the search for such materials is the preparation of high-quality single crystals. The two layers self-assembled from solution tend to impose their own rigidity and registry. Actually, only the organic sublattice could be structurally fully characterized for **1**. The presence of the inorganic network was determined by indirect methods since it showed an untractable crystallographic disorder.⁷ Now we report the successful extension of the synthesis of single crystals of ferromagnetic conductors to the selenium-substituted ET derivative BEDT-TSF (or BETS).

Single crystals of $[\text{BETS}]_x[\text{MnCr}(\text{ox})_3] \cdot (\text{CH}_2\text{Cl}_2)$ (**2**) ($x \approx 3$) were obtained.⁸ X-ray diffraction experiments revealed that this material is formed by alternating layers of partially oxidized molecules of the organic donor BETS (Figure 1). As observed for **1**, the electron density between the organic layers appears to be heavily disordered, which prevents location of the atomic positions that should correspond to the well-known bimetallic hexagonal oxalate-based lattice. The presence of this bimetallic lattice was confirmed by elemental analysis and also by the magnetic measurements, as will be discussed later. This crystallographic disorder could be translational, as is common in these layered compounds due to the presence of stacking faults.⁹ The fact that this disorder does not affect the organic layers is surprising. One plausible explanation is the possibility of this compound being an incommensurate phase. Indeed, other examples of incommensurate charge-transfer salts with polymeric anionic networks are known.¹⁰

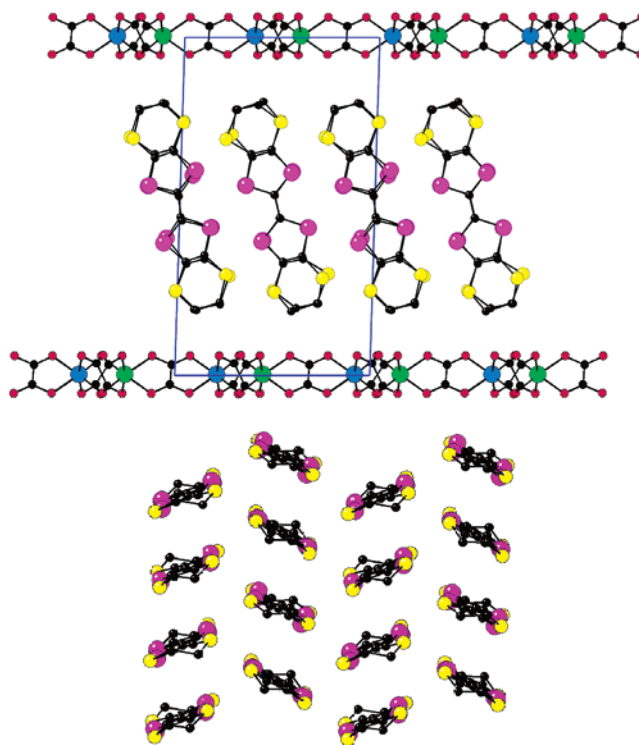


Figure 1. Representation of the structure of $[\text{BETS}]_x[\text{MnCr}(\text{ox})_3] \cdot (\text{CH}_2\text{Cl}_2)$ (**2**): idealized side view of the alternating layers (up) and top view of the organic layer (down).

The crystallographic solution for the organic sublattice¹¹ reveals that **2** presents a packing motif close to the so-called α -phases (Figure 1), whereas the ET derivative crystallized as a β -phase. This difference will have a tremendous effect on the physical properties. In this case, the chains of parallel BETS molecules are not parallel to each other, with a dihedral angle between BETS molecules of adjacent chains of 131° . The adjacent chains are connected through short interchain contacts (3.571 \AA S1–S4) when the intrachain contacts are slightly longer (3.955 \AA Se1–C1). It is also surprising to observe a larger interlayer separation (20.09 vs 16.61 \AA), mostly due to a different orientation of the organic molecules. The mean planes of BETS molecules are almost perpendicular to the mean plane of the oxalate layer, whereas in **1**, the plane of the ET molecules showed a canting of 41° . The BETS molecules are side-tilted at an angle of 15° from the plane normal to the layers.

From the stoichiometry,⁸ it is obvious that the charge residing on the BETS molecules is close to $1/3$. This is an unusual charge for this donor, imposed by the geometry and size of the inorganic layer.

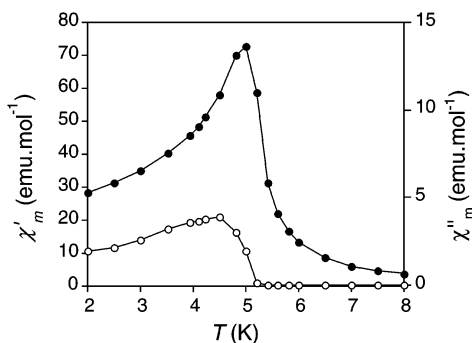


Figure 2. Temperature dependence of the in-phase (full circles) and out-of-phase (empty circles) AC magnetic susceptibility for $[\text{BETS}]_x[\text{MnCr}(\text{ox})_3] \cdot (\text{CH}_2\text{Cl}_2)$ (**2**).

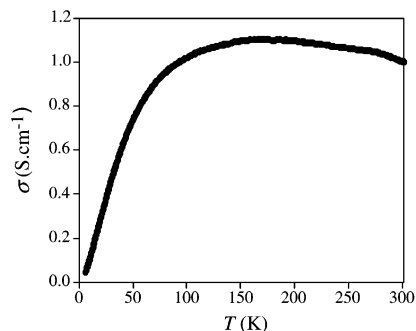


Figure 3. Thermal dependence of the electrical conductivity for $[\text{BETS}]_x[\text{MnCr}(\text{ox})_3] \cdot (\text{CH}_2\text{Cl}_2)$ (**2**).

Magnetic measurements confirm the presence of the bimetallic oxalate-bridged 2D network. The $\chi_m T$ product at room temperature ($7.36 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$) corresponds to the expected value for the bimetallic oxalate network with no contribution from the organic layer. The $\chi_m T$ product increases below 50 K due to the ferromagnetic interactions between metal centers. AC magnetic measurements confirmed the presence of magnetic ordering, showing a peak in the in-phase signal and an out-of-phase signal that is nonzero below 5.3 K, defining T_c for this magnet (Figure 2). There is no frequency dependence of peak position. The ferromagnetic nature of the magnetic ordering was also confirmed by the field dependence of the magnetization. At 2 K the magnetization shows a rapid increase at small fields and reaches a value very close to saturation above 1 T. The saturation value at 5 T ($7.69 \mu_B$) is slightly lower than the expected value for parallel alignment of the spins ($8 \mu_B$). This common feature has been observed for other 2D oxalate-based magnets and is attributed to the presence of magnetic canting between spins.¹²

Electrical conductivity measurements were performed on single crystals with four contacts (Figure 3). The room temperature conductivity along the organic layers is relatively high ($1 \text{ S} \cdot \text{cm}^{-1}$), and upon cooling the sample the response shows metal-like behavior down to 150 K. Below 150 K, the conductivity decreases, which is a signature of semiconducting behavior, in contrast with the ET salt, which is metallic down to 0.3 K. This result was expected since it is well-known that β -type phases are, in general, better conductors than α -phases because they offer closer and more effective contacts between the organic donors. Electrical conductivity measurements under pressure and under magnetic fields are in progress to probe the interplay between conductivity and ferromagnetism in this material.

In conclusion, we have shown how the molecular approach allowed for the preparation of a new hybrid molecular material that exhibits ferromagnetic ordering below 5.3 K and metal-like conductivity. This is only the second example of such a dual-function material and the first example based on the selenium derivative BETS. In this case, the change in the organic radical generates a new structural phase and therefore different conducting properties. It is also important to note that the magnetic properties remain unchanged, even when the interlayer separation is much larger (20.09 vs $9\text{--}10 \text{ \AA}$ in other known analogous magnets).¹³ This confirms that the magnetic ordering in these systems is essentially bi-dimensional.

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Supporting Information Available: Crystallographic data for the organic sublattice, including main bond distances and angles, and complete magnetic data (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Very recently we have confirmed the incommensurate nature of these materials by completely solving the two subunit cells for the $(\text{ET})_x[\text{MnRh}(\text{ox})_3] \cdot (\text{CH}_2\text{Cl}_2)$ analogue. Manuscript in preparation.
- (8) $[\text{BETS}]_x[\text{MnCr}(\text{ox})_3] \cdot (\text{CH}_2\text{Cl}_2)$ (**2**): 10 mg of the organic radical BEDT-TSF were suspended in 40 mL of a methanol/dichloromethane/benzonitrile (1:1:1) solution of $[\text{Cr}(\text{ox})_3]^{3-}$ (0.010 M) and Mn^{2+} (0.015 M). Through this suspension, a constant current of $0.1 \mu\text{A}$ was passed for several weeks. Shiny platelike crystals of **2** were collected and washed with methanol and acetone and air-dried. For $x = 3$, $\text{C}_{37}\text{H}_{26}\text{Cl}_2\text{CrMnO}_{12}\text{S}_{12}\text{Se}_{12}$: Calcd C, 20.45; H, 1.21; Cl, 3.26; S, 17.71. Found C, 20.16; H, 1.10; Cl, 2.98; S, 17.22.
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- (11) Crystallographic data for the organic sublattice: $a = 4.356(2)$, $b = 11.575(3)$, and $c = 20.090(4) \text{ \AA}$, $\alpha = 91.71(3)$, $\beta = 92.90(3)$, and $\gamma = 90.04(3)^\circ$, $V = 1011.2 \text{ \AA}^3$, $P1$. The structure was solved using direct methods (SIR97; Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115) and refined by full-matrix least-squares calculations on F^2 (Sheldrick, G. M. *SHELXL-97*; University of Göttingen, 1997). Final refinement for 114 parameters with 997 reflections ($I > 4\sigma$) gives $R_1 = 0.1060$ and $R_2 = 0.2533$.
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