J|A|C|S
COMMUNICATIONS

A Chiral Ferromagnetic Molecular Metal

José R. Galán-Mascarós,[*,†] Eugenio Coronado,[*,‡] Paul A. Goddard,[§] John Singleton,[‖]
Amalia I. Coldea,[§,⊥] John D. Wallis,[#] Simon J. Coles,[∇] and Antonio Alberola[‡]

Institute of Chemical Research of Catalonia (ICIQ), Av. Paisos Catalans 16, 43007 Tarragona, Spain, Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán 2, 46980 Valencia, Spain, Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, U.K., National High Magnetic Field Laboratory (MST-NHMFL), Los Alamos National Laboratory, Los Alamos, New Mexico 87545, H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, U.K., School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, U.K., and U.K. National Crystallography Service, Department of Chemistry, University of Southhampton, Highfield, Southampton SO17 1BJ, U.K.

Received April 14, 2010; E-mail: jrgalan@iciq.es; eugenio.coronado@uv.es

Abstract: The first molecular material with the coexistence of ferromagnetism, metal-like conductivity, and chirality has been prepared using an organic/inorganic approach. In this case, a two-dimensional packing of chiral organic radical cations (responsible for both the electrical conductivity and optical activity) was assembled with a layered bimetallic oxalate-based anionic network (responsible for the magnetic properties). Shubnikov–de Haas oscillations confirmed the presence of a Fermi surface even when the transport properties suggested "insulating"-type behavior at very low temperatures.

Molecular materials offer unparalleled possibilities in the search for novel combinations of multiple properties in a single material. Several dual-function molecular materials have been reported, including ferromagnetic metals,[1] magnetic (super)conductors,[2] chiral magnets,[3] chiral conductors,[4] and switching magnets.[5]

The first ferromagnetic organic metal was discovered in 2000.[1] Its structure consists of alternating layers of the organic donor bis(ethylenedithio)tetrathiafulvalene (ET), which is responsible for the transport properties, and a polymeric bimetallic oxalate (ox)-bridged complex, $[MnCr(ox)_3]^-$, which is responsible for the appearance of ferromagnetic ordering. Interestingly, the metallic regime is maintained down to 0.3 K[6] and is apparently unaffected by the onset of ferromagnetic ordering at $T_c = 5.5$ K. With this strategy, the structurally analogous materials $D_x[M^{II}M^{III}(ox)_3]\cdot CH_2Cl_2$ (D = ET-type derivative; M^{II} = Mn, Co; M^{III} = Cr, Rh)[7] were prepared. The T_c for magnetic ordering was increased up to 13 K, but the transport properties could not be improved. One possible reason may be connected with the intrinsic disorder of these hybrid materials, which possess an incommensurate structure[8] in addition to the local disorder generated by the terminal ethylenic groups of the ET molecules in the organic layers. Following this strategy, we tested the use of a chiral ET derivative, (*S*,*S*,*S*,*S*)-tetramethyl-ET (TM-ET),[9] for the preparation of a ferromagnetic molecular conductor, with the double goal of increasing the functionality of the system and avoiding the disorder of the ethylenic groups in the organic layer.

$[TM\text{-}ET]_x[MnCr(ox)_3]\cdot CH_2Cl_2$ (**1**) was successfully prepared by electro-oxidation of the organic donor in the presence of the building blocks for the inorganic oxalate-based polymeric network. This multilayered material shows an organic layer with typical β packing (Figure 1) in which the mean planes of all the ET derivatives are parallel to each other, forming stacks along the *a* direction. The similar range of close S···S contacts along the stack [3.579(3)···3.777(3) Å] and between stacks [3.654(3)···3.795(3) Å] clearly indicate its two-dimensional nature. The stoichiometry was estimated to be $x \approx 2.6$ using elemental analysis. This is in good agreement with the mean oxidation state of +0.39 for the TM-ET molecules, as extracted from the bond-length analysis.[10]

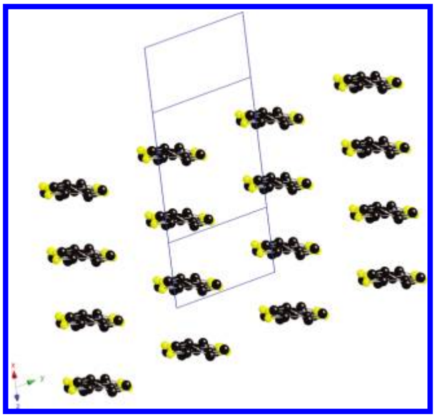

Figure 1. β-Packing of the organic layers in the crystal structure of $(TM\text{-}ET)_x[MnCr(ox)_3]\cdot CH_2Cl_2$.

In this case, as in all other structurally characterized ferromagnetic conductors,[1,7a] the structure of the inorganic bimetallic oxalate-bridged honeycomb network cannot be determined from X-ray diffraction experiments. As already mentioned, these materials are incommensurate composites because of the noninteger match between the charge distribution in the two sublattices. As previously shown, this could only be discovered by inclusion of a heavy-metal atom in the inorganic lattice.[8] Nevertheless, the presence of the $[MnCr(ox)_3]^-$ honeycomb network can conveniently be proved beyond any reasonable doubt on the basis of magnetic data. Thus, as the sample was cooled, the $\chi_m T$ product first showed a linear decrease from 9.60 emu K mol^{-1} at room temperature due to the presence of temperature-independent paramagnetism (TIP) of the Pauli type (coming from the conducting electrons). Second, $\chi_m T$ changed slope below 150 K and started to increase as a result of the expected ferromagnetic interactions between the oxalate-bridged Mn^{II} and Cr^{III} metal centers. Third, a sudden increase in χ_m below 10 K was observed (Figure S1a in the Supporting Information); χ_m reached saturation at very low temperatures, indicating the appear-

---

[†] Institute of Chemical Research of Catalonia.
[‡] Universidad de Valencia.
[§] University of Oxford.
[‖] Los Alamos National Laboratory.
[⊥] University of Bristol.
[#] Nottingham Trent University.
[∇] University of Southhampton.

10.1021/ja103147k

ance of ferromagnetic ordering. The ac magnetic susceptibility measurements (Figure S1b) showed a maximum in the in-phase signal (χ') and the appearance of an out-of-phase signal (χ'') that confirmed the onset of magnetic ordering with a T_c of 5.5 K. This critical temperature for ferromagnetic ordering is the signature of the $[MnCr(ox)_3]^-$ honeycomb network, since it cannot be reached by any other structural type in an oxalate-bridged bimetallic coordination network. The field dependence of the magnetization at 2 K showed a rapid increase in the magnetization for small fields, with M reaching a saturation value of 7.73μ_B. This value corresponds to the parallel alignment of all spins, again confirming the ferromagnetic ordering and the structural presence of the $[MnCr(ox)_3]^-$ network between the organic layers. No hysteresis was observed, as in soft ferromagnets.

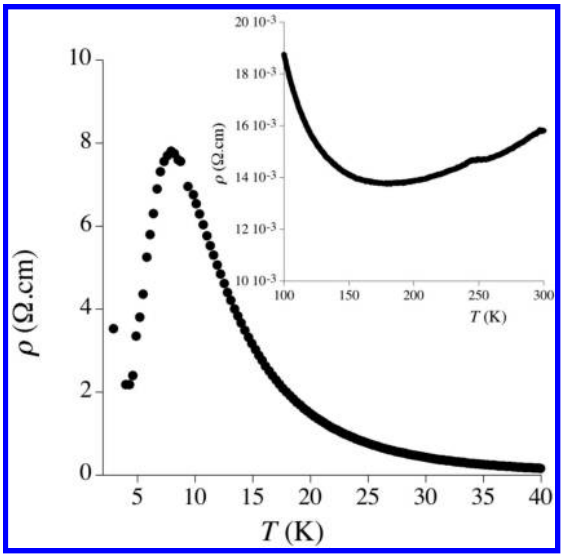

Figure 2. Typical thermal dependence of the in-plane resistivity for crystals of the title compound.

The transport properties (Figure 2) were measured on platelike single crystals using the standard four-contact dc method, with the current applied and voltage measured parallel to the highly conducting layers. The conductivity at room temperature was as high as 65 S cm^{-1}, and the temperature dependence of the resistance showed metal-like behavior down to ~190 K, where a minimum was reached. This change in slope was not abrupt, suggesting that no phase transition into a semiconducting state was reached but that a charge localization process appeared. Below 10 K, re-entrance into a metal-like regime occurred. The position and magnitude of this feature was sample-dependent, with some of them showing only a small bump. Near 5 K, at the onset of ferromagnetic ordering, a second minimum was reached, and the resistivity increased again very rapidly.

In the interlayer magnetoresistance measurements on single crystals of **1** (Figure 3a), the resistivity increased rather smoothly with decreasing temperature, suggesting “insulating”-type behavior. However, weak Shubnikov−de Haas quantum oscillations were observed, suggesting the presence of small metallic regions exhibiting Fermi liquid-like behavior in coexistence with insulating domains at very low temperatures (Figure 3b). The inverse-field positions of the oscillations for **1** (Figure 3c) allowed us to determine a frequency of 215 ± 10 T at $\theta = 0°$, where θ is the angle between the magnetic field and the normal to the highly conducting layers. When the sample was tilted to $\theta = 38.8°$, an additional lower-frequency set of oscillations became visible (Figure S3), probably as a result of the angle-dependent intensity of the quantum oscillations caused by the spin-damping term of the Lifshitz−Kosevich formula. This set of oscillations had a frequency of 31 ± 3 T. Thus, the metallic regions of these crystals seem to possess a Fermi surface comprising (at least) two small quasi-two-dimensional pockets. No evidence of the so-called magnetochiral anisotropy[11] was observed, perhaps because the interlayer transport is incoherent.

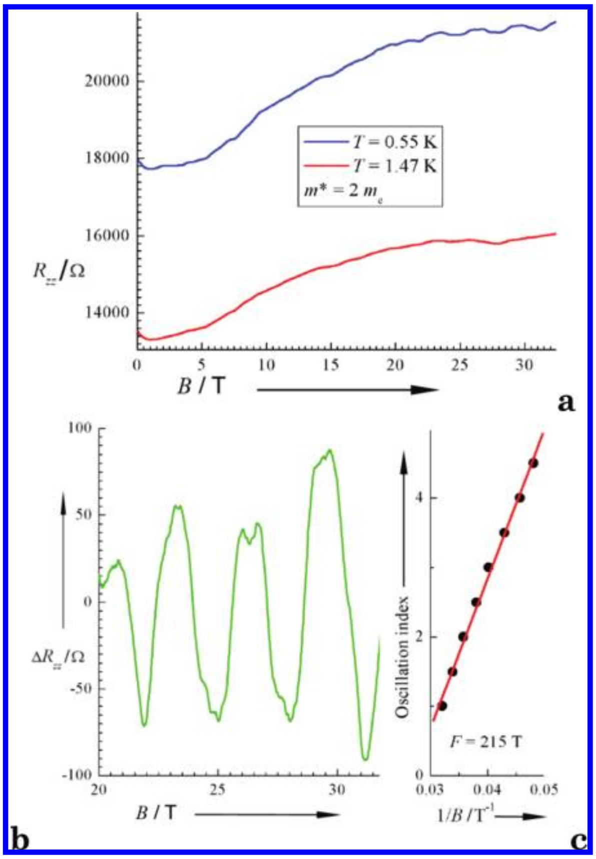

Figure 3. (a) Interlayer resistance (R_{zz}, proportional to ρ_{zz}) of a single crystal of $(TM\text{-}ET)_x[MnCr(ox)_3]\cdot CH_2Cl_2$ as a function of magnetic field (tilt angle $\theta = 0$). (b) Shubnikov−de Haas oscillations at $T = 550$ mK. (c) Plot of the oscillation index vs inverse field position, whose slope gives the frequency (i.e., cross-sectional area of the Fermi surface).

In summary, we have designed and obtained the first molecular material with the coexistence of metallic conductivity, ferromagnetism, and chirality. The disorder encountered in the organic layer of the previously reported ferromagnetic molecular metals has been suppressed. Although there is no clear evidence that chirality does indeed affect the transport properties, the data reported shows Shubnikov−de Haas oscillations for the first time in such a multifunctional material, indicating the presence of a Fermi surface, very similar in all respects to what was found in an analogous series of paramagnetic superconductors.[12]

Acknowledgment. We are grateful for the financial support from the European Union (ERC Advanced Grant SPINMOL to E.C.), the Spanish Ministerio de Ciencia e Innovación, with FEDER cofinancing (Project Consolider-Ingenio in Molecular Nanoscience and Projects MAT2007-61584 and CTQ-2008-03197/BQU), and the Generalitat Valenciana (Prometeo Program). Work carried out at the NHMFL was supported by the U.S. Department of Energy (partly through Grant LDRD-DR 20070013) and by NSF and the State of Florida. J.D.W. thanks Nottingham Trent University for support and the EPRSC X-ray Crystallography Service for a data set and acknowledges the EPSRC's Chemical Database Service at Daresbury for access to the Cambridge Structural Database. P.A.G. acknowledges the support of the UK EPSRC.

Supporting Information Available: Experimental details; structural data, including a CIF file for the organic sublattice; magnetic data; and additional transport data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447. (b) Galán-Mascarós, J. R.; Coronado, E. *C. R. Chim.* **2008**, *11*, 1110.

(2) (a) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caufield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209. (b) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368. (c) Yamamura, S.; Sugawara, Y.; Suzuki, K.; Sugawara, T. *J. Am. Chem. Soc.* **2010**, *132*, 4528.

(3) (a) Mito, M.; Iriguchi, K.; Deguchi, H.; Kishine, J.; Kikuchi, K.; Ohsumi, H.; Yoshida, Y.; Inoue, K. *Phys. Rev. B* **2009**, *79*, 012406. (b) Train, C.; Gheorghe, R.; Krstic, V.; Chamoreau, L. M.; Ovanesyan, N. S.; Rikken, G. L. J. A.; Gruselle, M.; Verdaguer, M. *Nat. Mater.* **2008**, *7*, 729.

(4) Avarvari, N.; Wallis, J. D. *J. Mater. Chem.* **2009**, *19*, 4061.

(5) (a) Arimoto, Y.; Ohkoshi, S.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 9240. (b) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (c) Dei, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1160.

(6) Klehe, A.-K.; Laukhin, V.; Goddard, P. A.; Symington, J. A.; Aghassi, J.; Singleton, J.; Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Giménez-Saiz, C. *Synth. Met.* **2003**, *133*−*134*, 549.

(7) (a) Alberola, A.; Coronado, E.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 10774. (b) Coronado, E.; Forment-Aliaga, A.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J.; Martínez-Ferrero, E.; Nuez, A.; Romero, F. M. *Solid State Sci.* **2003**, *5*, 917.

(8) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Martínez-Ferrero, E.; van Smaalen, W. *Inorg. Chem.* **2004**, *43*, 4808.

(9) (a) Wallis, J. D.; Karrer, A.; Dunitz, J. D. *Helv. Chim. Acta* **1986**, *69*, 69. (b) Karrer, A.; Wallis, J. D.; Dunitz, J. D.; Hilti, B.; Mayer, C. W.; Bürkle, M.; Pfeiffer, J. *Helv. Chim. Acta* **1987**, *70*, 942.

(10) Guionneau, P.; Kepert, C. J.; Bravis, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. *Synth. Met.* **1997**, *86*, 1973.

(11) Rikken, G. L. J. A.; Folling, J.; Wyder, P. *Phys. Rev. Lett.* **2001**, *87*, 236602.

(12) (a) Coldea, A. I.; Bangura, F.; Singleton, J.; Ardavan, A.; Akutsu-Sato, A.; Akutsu, H.; Turner, S. S.; Day, P. *Phys. Rev. B* **2004**, *69*, 085112. (b) Bangura, A. F.; Coldea, A. I.; Singleton, J.; Ardavan, A.; Akutsu-Sato, A.; Akutsu, H.; Turner, S. S.; Day, P.; Yamamoto, T.; Yakushi, K. *Phys. Rev. B* **2005**, *72*, 014543.

JA103147K