

Effect of Included Guest Molecules on the Normal State Conductivity and Superconductivity of β'' -(ET)₄[(H₃O)Ga(C₂O₄)₃]₂G (G = pyridine, nitrobenzene)

Hiroki Akutsu[†], Akane Akutsu-Sato[†], Scott S. Turner[†], Delphine Le Pevelen[†], Peter Day^{†*}, Vladimir Laukhin^{‡,§}, Anne-Katrin Klehe[‡], John Singleton[‡], Derek A. Tocher^{††}, Michael R. Probert^{†††} and Judith A.K. Howard^{†††}

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, UK, Clarendon Laboratory, Oxford University, Parks Road, Oxford OX1 3PU, UK, Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ, UK, Chemistry Department, University of Durham, South Road, Durham, DH1 3LE, UK, ICREA and ICMAB, Campus Universitari, 08193 Bellaterra, Catalunya, Spain

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Subtle variations in the supramolecular organization of donor molecules in molecular charge transfer salts of the organo-sulphur donor bis(ethylenedithio)tetrathiafulvalene (ET) have been found to promote most of the collective electronic groundstates known to condensed matter science. These appear as insulating, semiconducting, metallic, superconducting, charge density wave, spin density wave, spin-Peierls states etc.¹ This remarkable behavior stems from changes in intermolecular transfer integrals and band filling. Specific examples among ET salts that contain tris(oxalato)metallate(III) anions include a family of paramagnetic superconductors² and a ferromagnetic metal³. Structural subtlety in the former compounds is enhanced further by the presence of included guest molecules within cavities in the anion sublattice, which can modify the bulk physical properties. For instance in the salts β'' -(ET)₄[(H₃O)Fe(C₂O₄)₃]₂G the superconductivity critical temperature, T_c, is reduced from 8.3 K (G = C₆H₅CN) to 5.8 K (G = C₆H₅NO₂),² but when G = C₅H₅N there is an abrupt transition from metallic to semiconducting behaviour at 116 K⁴. Now we report that the C₆H₅NO₂ and C₅H₅N isomorphous analogues with diamagnetic Ga(III) are metallic from room temperature to 130-160 K, below which the resistance shows a marked upturn and at lower temperatures their transport properties differ dramatically. This occurs despite their unit cell constants and cell volumes being almost identical.

Crystals of β'' -(ET)₄[(H₃O)Ga(C₂O₄)₃]₂G (G = C₅H₅N and C₆H₅NO₂), hereafter called **I** and **II**, respectively, were obtained by analogous methods to those used for the Fe salts^{2,5}. Single crystal X-ray diffraction data were recorded at 290 K and additionally at 120 K for **I** and 100 K for **II**⁶. Their unit cell parameters and cell volumes are very similar. Both structures resemble the corresponding Fe and Cr²⁺ salts, consisting of alternate layers of ET cations arranged in the β'' -stacking mode and layers containing [(H₃O)Ga(C₂O₄)₃]₂G (Figure 1 and 2). The anionic layer is a pseudo-hexagonal array of [Ga(C₂O₄)₃]³⁻ and H₃O⁺ in the ab-plane with the guest molecules, G, occupying cavities bounded by the O atoms of the oxalato ligands. At 290K **I** and **II** have considerable positional disorder in a terminal ethylene group of one of the two independent ET molecules, which corresponds to inversion of the twisted conformation.

At low temperatures this disorder is suppressed in **II** but remains fully present in **I**, strongly suggesting that in the former it is thermal in origin while in the latter it is static. In addition, the C₅H₅N molecule in **I** exhibits disorder over two orientations within the molecular plane, which makes an angle of 36.1° to the plane defined by Ga atoms. Again, the lower temperature structure determination shows that this disorder is static in nature. In **II** the plane of the phenyl ring of the ordered C₆H₅NO₂ makes an angle of 31° to the same 'Ga plane', with the C-N bond aligned along the Ga...O(H₃O⁺) axis of the pseudo-hexagonal cavity.

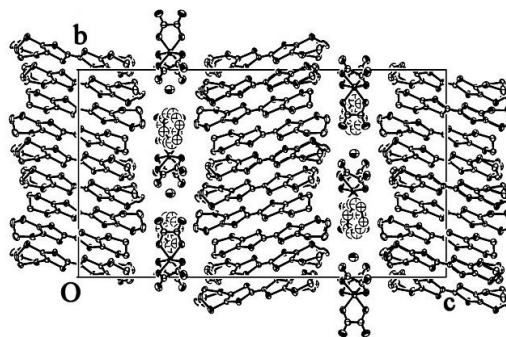


Figure 1. Crystal structure of **I** at 290 K, projected on the bc plane.

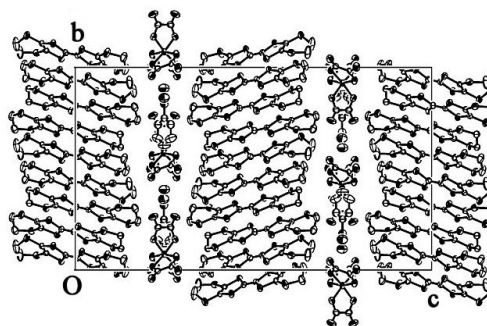


Figure 2. Crystal structure of **II** at 290 K, projected on the bc plane.

The resistance profiles of **I** and **II** are shown in Figure 3 normalized to their 300K values. Both **I** and **II** are metallic at room temperature, with conductivities of 10.4 and 20.2 Scm⁻¹, respectively, parallel to the conducting plane. The resistance values fall with decreasing temperature, reaching minima in the region 130-140 and 160-180 K respectively.⁹ However, at lower temperatures the transport behaviour of the two compounds

* To whom correspondence should be addressed. E-mail pday@ri.ac.uk

[†] Royal Institution of Great Britain

[‡] Clarendon Laboratory

^{††} University College

^{†††} University of Durham

[§] ICREA and ICMAB

differs radically. For **I**, the resistance rises to a maximum at about 50 K for current flow parallel to the conducting layers and 60 K perpendicular to the layers. It then falls again, before exhibiting a further much smaller maximum at about 2 K in both directions (Figure 4). Below 2 K there is evidence for the onset of superconductivity, in that application of a magnetic field of 0.16 T causes a marked increase in resistance. In contrast, the electrical resistance of **II** rises as the temperature is reduced below 170 K, but it does not pass through a broad maximum. Rather, after a shoulder at about 20 K, it continues to rise until there is an abrupt transition to superconductivity at 7.5 K. The superconductivity of **II** is further indicated by the zero field cooled magnetic susceptibility measurement at 3.0 Oe (Figure 5), where the volume fraction at 1.8 K is estimated at 31%, a high value for a polycrystalline sample.¹⁰

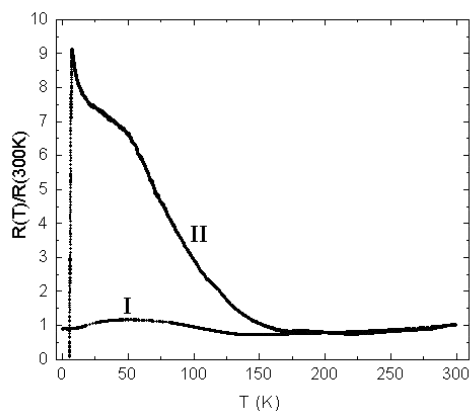


Figure 3. Temperature dependent resistance for **I** and **II** normalized to 300K, with current flow parallel to the conducting layers.

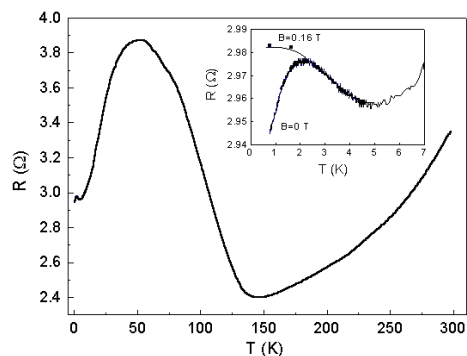


Figure 4. Temperature dependence of resistance for compound **I** with current flow parallel to the ET layers. Inset shows the lowest temperature region with the effect of magnetic field $B = 0.16$ T

The magnetic susceptibilities of both compounds measured at a higher field (3000 Oe) after zero field cooling have only a weak temperature dependence between 300 and 10 K except for shallow minima corresponding to the resistance minima above 100 K. However, the absolute value of the susceptibility of **II** ($4.3\text{--}5.0 \times 10^{-4}$ emu mol⁻¹) is twice as large as that of **I** ($1.5\text{--}2.5 \times 10^{-4}$ emu mol⁻¹), suggesting that **I** is a wider conduction band metal.

In summary, we have discovered dramatic divergences between the low temperature transport properties of two new ET charge transfer salts that have the same donor-packing motif and near identical cell constants and volumes, simply by changing an organic guest molecule. Further detailed physical studies are in progress to identify the origin of the difference but our results serve to emphasize the extreme sensitivity of the collective

electronic behavior of such materials to very small changes in the supramolecular organization.

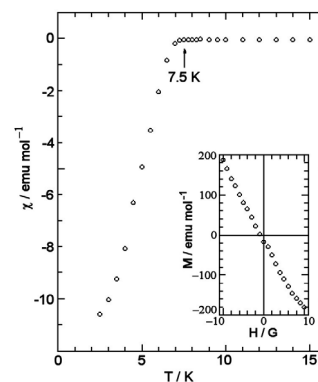
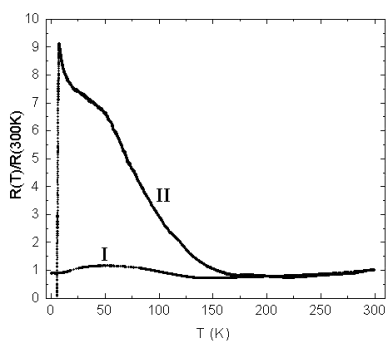


Figure 5. Zero field cooled magnetic susceptibility of **II** at 3.0 Oe. Inset shows the low field magnetization at 1.8 K.

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Supporting Information Available: Table S1 and CIF files with crystal data for **I** and **II** at each temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

- See, for example, Williams, J.M. *et al Organic Superconductors (including Fullerenes) Synthesis, Structure, Properties and Theory*, Prentice-Hall, New York, NY, 1992
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- 100mg (NH₄)[Ga(C₂O₄)₃].5H₂O, 200mg 18-crown-6 ether, and 10mg of ET were placed in an electrochemical cell with 40ml of distilled pyridine and 5 drops of water for **I**, and 30ml of distilled PhNO₂ with no water for **II**. A current of 0.5μA was applied across each cell and good quality crystals resulted after 10 days.
- X-ray data sets at 290K and that for **II** at 100K were collected on a Bruker SMART-CCD diffractometer with MoK α radiation. Frames were integrated using the SAINT⁷ package and corrected with SADABS⁷. Structures were solved using SHELXTL⁷. Data for **I** at 120K were collected on an Enraf Nonius κ -CCD diffractometer also with MoK α radiation. The structure was solved using direct methods with CRYSTALS 2000.⁸ X-ray data for **I**: 290K, C2/c, $a = 10.3605(9)$ Å, $b = 19.9645(17)$ Å, $c = 35.428(3)$ Å, $\beta = 92.760(2)^\circ$, $V = 7319.6(11)$ Å³, $R_w = 0.1185$, $R = 0.0498$; 120K, C2, $a = 10.2588(1)$ Å, $b = 19.7015(1)$ Å, $c = 34.9512(3)$ Å, $\beta = 93.3665(4)^\circ$, $V = 7051.9(5)$ Å³, $R_w = 0.0506$, $R = 0.0550$. X-ray data for **II**: 290K, C2/c, $a = 10.3547(4)$ Å, $b = 20.1508(7)$ Å, $c = 35.5424(12)$ Å, $\beta = 92.5710(10)^\circ$, $V = 7408.7(5)$ Å³, $R_w = 0.1319$, $R = 0.0636$; 100K, C2/c, $a = 10.2782(3)$ Å, $b = 19.8733(6)$ Å, $c = 35.0431(10)$ Å, $\beta = 93.4230(10)^\circ$, $V = 7145.2(5)$ Å³, $R_w = 0.0811$, $R = 0.0414$ (See supporting information for further details).
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- AC electrical transport measurements to 0.6K were measured at 77 Hz with four-probes using Pt wires (20μm diameter) attached to the crystals by graphite paste and using a homemade conductivity rig.
- Magnetic measurements were made on polycrystalline samples (3.8 mg for compound **I** and 4.3 mg for **II**) wrapped in Al foil with a Quantum Design MPMS-7 SQUID magnetometer.



Normal state conductivity and superconductivity together with bulk magnetic susceptibility and magnetization measurements have been measured for two molecular charge transfer salts: β'' -(ET)₄[(H₂O)Ga(C₂O₄)₃]G (ET = bis-ethylenedithio-tetrathiafulvalene, G = pyridine for compound **I** and nitrobenzene for compound **II**). Excepting the included guest molecules (G) the crystal structures are almost identical. Both show minima in their electrical transport at 130 K for **I** and at 160 K for **II**, but at lower temperatures their behavior differs markedly. The resistance of **I** reaches a maximum at 50 K with a further small peak at 2 K and possible superconductivity only below 2 K whereas that of **II** increases continuously down to 7.5 K, where an abrupt transition to a superconducting state occurs.
