Effect of Included Guest Molecules on the Normal State Conductivity and Superconductivity of \( \beta'^{-}(ET)\left[(H_3O)Fe(C_2O_4)_3\right]G \) (G = pyridine, nitrobenzene)

Hiroki Akutsu\(^1\), Akane Akutsu-Sato\(^1\), Scott S. Turner\(^1\), Delphine Le Pevelen\(^1\), Peter Day\(^*\), Vladimir Laukhin\(^\dagger\), Anne-Katrin Klehe\(^\dagger\), John Singleton\(^\ddagger\), Derek A. Tocher\(^\ddagger\), Michael R. Probert\(^\ddagger\ddagger\) and Judith A.K. Howard\(^\ddagger\ddagger\ddagger\)

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 ICMA, Campus Universitari, 08193 Bellaterra, Catalunya, Spain

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 superconductors\(^2\) and a ferromagnetic metal\(^3\). 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 \( \beta'^{-}(ET)\left[(H_3O)Fe(C_2O_4)_3\right]G \) the superconductivity critical temperature, \( T_c \), is reduced from 8.3 K (G = C\(_6\)H\(_5\)CN) to 5.8 K (G = C\(_6\)H\(_5\)NO\(_2\))\(^2\) but when G = C\(_6\)H\(_3\)N there is a marked transition from metallic to semiconducting behaviour at 116 K\(^4\). Now we report that the C\(_6\)H\(_3\)NO\(_2\) and C\(_6\)H\(_5\)N isomorphous analogues with diamagnetic Ga(III) are metallic from room temperature to 120-160 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 \( \beta'^{-}(ET)\left[(H_3O)Ga(C_2O_4)_3\right]G \) (G = C\(_6\)H\(_3\)N and C\(_6\)H\(_5\)NO\(_2\)), hereafter called I and II, respectively, were obtained by analogous methods to those used for the Fe salts\(^5\). Single crystal X-ray diffraction data were recorded at 290 K and additionally at 120 K for I and 100 K for II. Their unit cell parameters and cell volumes are very similar. Both structures resemble the corresponding Fe and Cr\(^4\) salts, consisting of alternate layers of ET cations arranged in the \( \beta'^{-}\)-stacking mode and layers containing \( [(H_3O)Ga(C_2O_4)_3]G \) (Figure 1 and 2). The anionic layer is a pseudo-hexagonal array of \( [Ga(C_2O_4)_3]^+ \) and \( H_2O \) 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 C\(_6\)H\(_3\)N 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 C\(_6\)H\(_5\)NO\(_2\), makes an angle of 31° to the same ‘Ga plane’, with the C-N bond aligned along the Ga...O(H\(_2\)O) axis of the pseudo-hexagonal cavity.

![Figure 1. Crystal structure of I at 290 K, projected on the bc plane.](image1)

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.\(^6\) However, at lower temperatures the transport behaviour of the two compounds
differences 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 below 170 K, but it does not pass through a broad maximum.

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 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 (4.3–5.0 \times 10^{-4} \text{emu mol}^{-1}) is twice as large as that of I (1.5–2.5 \times 10^{-5} \text{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.

Acknowledgement. We thank the UK EPSRC for funding. H.A. and A.A.-S. wish to thank the Japanese Society for Promotion of Science (JSPS) for postdoctoral fellowships. V.L. thanks the Royal Society for study visit grants. D.L.P. was supported by the EC TMR Network on Molecular Magnets and J.A.K.H. thanks the EPSRC for a Senior Research Fellow award.

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.

(5) 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 PhNO2 with no water for II. A current of 0.5µA was applied across each cell and good quality crystals resulted after 10 days.
(6) X-ray data sets at 290K and that for II at 100K were collected on a Bruker SMART-CCD diffractometer with MoKα radiation. Frames were integrated using the SAINT package and corrected with SADABS. Structures were solved using SHELXTL. Data for I at 120K were collected on an Enraf Nonius κ-CCD diffractometer also with MoKα radiation. The structure was solved using direct methods with CRYSTALS 2000. X-ray data for I, 290K, C2/a, a = 10.3605(9) Å, b = 19.9645(17) Å, c = 35.432(3) Å, β = 92.760(2°), V = 7319.6(11) Å³, R = 0.1185, R = 0.0498; 120K, C2/a, a = 10.2588(1) Å, b = 19.701(5) Å, c = 34.951(2) Å, β = 93.3685(4)°, V = 7051.95(5) Å³, R = 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, β = 92.5710(10)°, V = 7409.75(7) Å³, R = 0.1139, R = 0.0636; 100K, C2/c, a = 10.2783(2) Å, b = 19.8733(6) Å, c = 35.0431(10) Å, β = 93.4238(10)°, V = 7145.2(5) Å³, R = 0.0811, R = 0.0414 (See supporting information for further details).
(7) SAINT 5.0 data reduction software and SHELXTL 5.1, Bruker Analytical X-Ray Instruments Inc, Madison, Wisconsin, USA. SADABS empirical absorption correction program, Shelldick, G.M., University of Gottingen, Germany 1998.
(9) AC electrical transport measurements to 0.6 K 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 ring.
(10) 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: \( \beta^\text{+}(\text{ET})_4[(\text{H}_3\text{O})\text{Ga(C}_2\text{O}_4)_3]\) \( G \) (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.