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Effect of Included Guest Molecules on the Normal State Conductivity and Superconductivity of β''-$(ET)_4[(H_3O)Ga(C_2O_4)_3]\cdot G$ (G = Pyridine, Nitrobenzene)

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Subtle variations in the supramolecular organization of donor molecules in molecular charge-transfer salts of the organo−sulfur donor bis(ethylenedithio)tetrathiafulvalene (ET) have been found to promote most of the collective electronic ground states known to condensed matter science. These appear as insulating, semiconducting, metallic, superconducting, charge density wave, spin density wave, spin-Peierls states, and so forth.[1] This remarkable behavior stems from changes in intermolecular transfer integrals and band filling. Specific examples among ET salts that contain tris(oxalato)metalate(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 β''-$(ET)_4[(H_3O)Fe(C_2O_4)_3]G$ the superconductivity critical temperature, T_c, is reduced from 8.3 K ($G = C_6H_5CN$) to 5.8 K ($G = C_6H_5NO_2$),[2] but when $G = C_5H_5N$, there is an abrupt transition from metallic to semiconducting behavior at 116 K.[4] Now we report that the $C_6H_5NO_2$ and C_5H_5N 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''-$(ET)_4[(H_3O)Ga(C_2O_4)_3]G$ ($G = C_5H_5N$ and $C_6H_5NO_2$), hereafter called **I** and **II**, respectively, were obtained by methods analogous 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 at 100 K for **II**.[6] Their unit cell parameters and cell volumes are very similar. Both structures resemble the corresponding structures for the Fe and Cr[2,4] salts, consisting of alternate layers of ET cations arranged in the β''-stacking mode and layers containing $[(H_3O)Ga(C_2O_4)_3]G$ (Figures 1 and 2). The anionic layer is a pseudohexagonal array of $[Ga(C_2O_4)_3]^{3-}$ and H_3O^+ in the *ab*-plane with the guest molecules, G, occupying cavities bounded by the O atoms of the oxalato ligands. At 290 K **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.

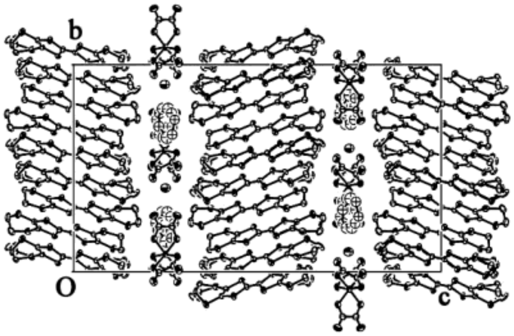

Figure 1. Crystal structure of **I** at 290 K, projected on the *bc* plane.

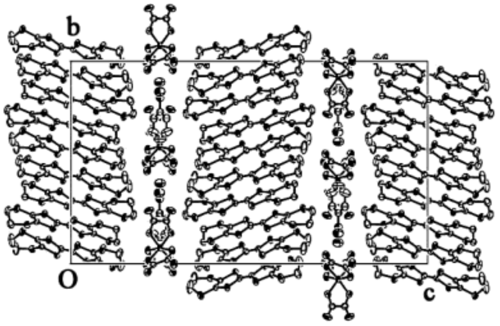

Figure 2. Crystal structure of **II** at 290 K, projected on the *bc* plane.

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_5H_5N 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 $C_6H_5NO_2$ makes an angle of 31° to the same "Ga plane", with the C−N bond aligned along the Ga···O(H_3O^+) axis of the pseudohexagonal cavity.

The resistance profiles of **I** and **II** are shown in Figure 3 normalized to their 300 K values. Both **I** and **II** are metallic at room temperature, with conductivities of 10.4 and 20.2 S cm^{-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 behavior of the two compounds differs

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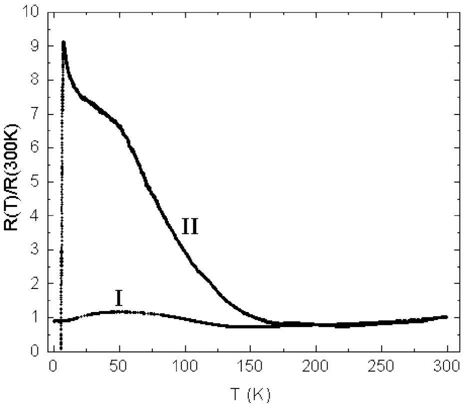

Figure 3. Temperature-dependent resistance for **I** and **II** normalized to 300 K, with current flow parallel to the conducting layers.

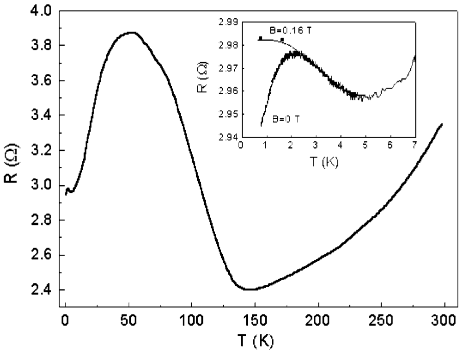

Figure 4. Temperature dependence of resistance for compound **I** with current flow parallel to the ET layers. Inset shows the lowest-temperature region with the effect of magnetic field $B = 0.16$ T.

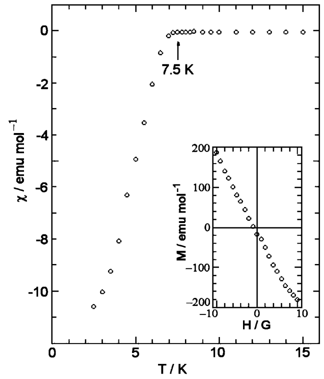

Figure 5. Zero-field-cooled magnetic susceptibility of **II** at 3.0 Oe. Inset shows the low-field magnetization at 1.8 K.

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]

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

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Supporting Information Available: Table S1 (PDF) 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.

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(5) 100 mg of $(NH_4)[Ga(C_2O_4)_3]\cdot 5H_2O$, 200 mg of 18-crown-6 ether, and 10 mg of ET were placed in an electrochemical cell with 40 mL of distilled pyridine and 5 drops of water for **I**, and 30 mL of distilled $PhNO_2$ with no water for **II**. A current of 0.5 μA was applied across each cell, and good-quality crystals resulted after 10 days.

(6) X-ray data sets at 290 K and at 100 K for **II** were collected on a Bruker SMART-CCD diffractometer with Mo Kα radiation. Frames were integrated using the SAINT[7] package and corrected with SADABS.[7] Structures were solved using SHELXTL.[7] Data for **I** at 120 K were collected on an Enraf Nonius κ-CCD diffractometer also with Mo Kα radiation. The structure was solved using direct methods with CRYSTALS 2000.[8] X-ray data for **I**: 290 K, $C2/c$, $a = 10.3605(9)$ Å, $b = 19.9645(17)$ Å, $c = 35.428(3)$ Å, $\beta = 92.760(2)°$, $V = 7319.6(11)$ Å^3, $R_w = 0.1185$, $R = 0.0498$; 120 K, $C2$, $a = 10.2588(1)$ Å, $b = 19.7015(1)$ Å, $c = 34.9512(3)$ Å, $\beta = 93.3665(4)°$, $V = 7051.9(5)$ Å^3, $R_w = 0.0506$, $R = 0.0550$. X-ray data for **II**: 290 K, $C2/c$, $a = 10.3547(4)$ Å, $b = 20.1508(7)$ Å, $c = 35.5424(12)$ Å, $\beta = 92.5710(10)°$, $V = 7408.7(5)$ Å^3, $R_w = 0.1319$, $R = 0.0636$; 100 K, $C2/c$, $a = 10.2782(3)$ Å, $b = 19.8733(6)$ Å, $c = 35.0431(10)$ Å, $\beta = 93.4230(10)°$, $V = 7145.2(5)$ Å^3, $R_w = 0.0811$, $R = 0.0414$ (See Supporting Information for further details).

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(9) AC electrical transport measurements to 0.6 K were measured at 77 Hz with four probes using Pt wires (20 μm diameter) attached to the crystals by graphite paste and using a homemade conductivity rig.

(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.

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