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Superstructures of donor packing arrangements in a series of molecular charge transfer salts

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Three conducting BEDT-TTF charge-transfer salts with tris(oxalato)metallate anions have unit cells containing *both* α and β″ donor packing motifs.

The collective electronic ground states of conducting molecular charge transfer (CT) salts, (*e.g.* of tetrathiafulvalene, TTF or bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF), depends on the cation stacking motif. Diverse transport behaviour is observed in BEDT-TTF salts with the same mean donor charge but different stacking, designated by the conventional labels α, β, κ, θ *etc.*[1] The stacks are usually organised into layers, separated by layers of anions, which sometimes have cavities occupied by guest molecules (G). Varying G is an important means of correlating similar structures with the properties.

The series of (BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]·G salts provide an opportunity to study fine detail of structure with respect to the collective physical properties. The monocation (A), metal (M) and G can be varied, to give semiconductors, superconductors or metals.[2,3] The first paramagnetic superconductors with localised 3d moments (A = H_3O^+, NH_4^+; M = Cr, Fe, Ga; G = PhCN, PhNO$_2$)[3] were made in this way. They have β″-stacked donor layers[4] interleaved by anionic layers of near-hexagonal arrays of $[M(C_2O_4)_3]^{3-}$, with trigonally-distorted octahedral cavities that contain A cations. The phenyl (Ph) ring of G fits well inside an hexagonal cavity bounded by M$_3$A$_3$ and the –NO$_2$ or –CN groups lie wholly within the cavity. Here we report that including G having Ph rings with non-planar and more bulky substituents induces different donor stacking in alternate cation layers, giving an ordered superlattice.

α-β″-(BEDT-TTF)$_4$[(NH$_4$)M(C$_2$O$_4$)$_3$]·G with M/G = Ga/PhN(CH$_3$)COH (**1**), Ga/PhCH$_2$CN (**2**) and Fe/PhCOCH$_3$ (**3**) were synthesised,† and their structures determined by single crystal X-ray diffraction.‡ They have the layer structure but whereas the paramagnetic superconductors have donors in a β″ arrangement, in **1–3** this stacking alternates with the α-stacking mode. The asymmetric unit of each salt has four inequivalent BEDT-TTF molecules, two each from the different donor layers. The donor layer centered about $z = 0.0$ has BEDT-TTF cations with eclipsed ethylene groups and a β″ arrangement (Fig. 1). The layer centered at $z = 0.5$ consists of BEDT-TTF cations in the α-stacking motif with staggered ethylene groups (Fig. 1). Each layer has a network of S···S close contacts. In **1**, for example, contacts range from 3.33 to 3.60 Å (α-packed layer) and 3.38 to 3.60 Å (β″-packed layer). Cation charges were estimated using the empirical correlation between the donor bond lengths and charges of well known salts.[5] All have the same charge of +0.5(1), at 298(2) K as also found in the purely β″ superconducting phases. Also there is a linear relationship between the degree of CT and the Raman-active C=C stretching frequencies of BEDT-TTF.[6] Raman spectra of **1** and **2** show two overlapping bands at 300 K. For **1** the bands (1471.8 and 1492.6 cm^{-1}), correspond to a charge of +0.48 per cation and for **2** (1469.7, 1489.9 cm^{-1}) they indicate a single charge of +0.50 per cation.

SQUID magnetometry shows that **1–3** do not superconduct down to 2 K, whereas T_c's of the purely β″ compounds range from 8.3 to ~2 K.[2–4] Single crystal electrical transport†, parallel to the β″ stacks (210 direction), does not show metallic character. In this direction **1** has a conductivity at 300 K (σ_{300K}) of 0.44 to 0.60 S cm^{-1} and is non-metallic down to 2 K. Parallel to the side-to-side β″-packing ($1\bar{1}0$), **1** is also non-metallic with σ_{300K} = 0.26 to 0.41 S cm^{-1}. The resistivity in the $1\bar{1}0$ direction increases more steeply with decreasing temperature than in the 210 direction, although simple Arrhenius activated behaviour is not seen. **2** has similar behaviour; σ_{300K} = 0.24 to 1.34 S cm^{-1} (210) and 0.24 S cm^{-1} ($1\bar{1}0$). A suitable sample of **3** was not available for single crystal measurements. (BEDT-TTF)$_2$C(SO$_2$CF$_3$)$_3$,[7] the only other BEDT-TTF salt with α-β mixed layers, has a layer disordered between an α and β″-layer. This salt has almost temperature-independent resistivity to 240 K and non-metallic behaviour below this temperature.

The tight-binding extended Hückel band structures‡ exhibit bandwidths similar to other β″- and α-type salts, using the same computational methods. Thus, the activated conductivity of the salts is intriguing and stabilisation of the metallic state under pressure could occur. The calculated Fermi surfaces (FS's) of **2**, assuming identical CT for the two layers, are shown in Fig. 2. Both FS's contain an electron pocket (around Y for the α layers and X for the β″ layers) and a hole pocket (around X for the α layers and M for the β″ layers). In a given layer the two pockets have the same

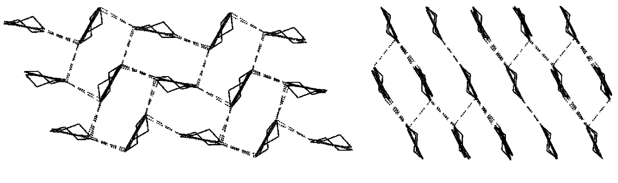

Fig. 1 Donor layers in **1** projected along the C=C molecular axis with α-packing (left) and β″-packing (right). Broken lines are S···S close contacts below sum of the Van der Waals radii.

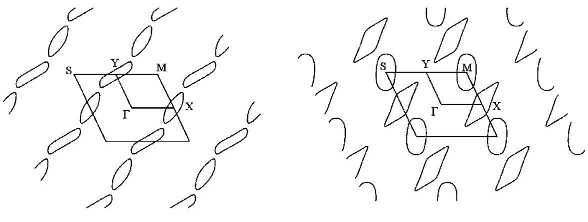

Fig. 2 Calculated FS's of BEDT-TTF α-stacked (left) and β″-stacked (right) layers in **2** assuming equivalent charge transfer in each layer.

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area but if the CT is not identical this is no longer true. In this case our calculations suggest donor charges of +0.57 (β″) and +0.43 (α). Since all pockets are closed, if the metallic state can be stabilized, magnetoresistance studies could be used to assess the CT. If both layers contribute to the conductivity, two Shubnikov-de Haas frequencies would be seen for identical CT and otherwise four frequencies. It should then be possible to derive the different CT between the two layers.

The dramatic contrast in properties between the β″ and α-β″ salts, raises the question of what supramolecular changes bring about this effect. Inspection of the α-β″ salts shows that the two sides of the anionic layer are not equivalent, as in the β″ compounds, due to the non-planar G molecules. The larger G requires that the planes of its Ph-rings be displaced towards one side of the layer (Fig. 3). The substituent groups are directed towards the opposite side and atoms in G (O from **1** or N of **2** and **3**) protrude marginally out of the plane formed by the oxalate O atoms. Therefore, one face of the anion layer presents a distinctly more ‘corrugated’ facade to the donor layer than the other. The β″-stacks lie next to the ‘corrugated’ faces and the α-stacks next to the ‘smoother’ faces (Fig. 4). A similar argument is valid for (BEDT-TTF)$_2$C(SO$_2$CF$_3$)$_3$ in which the anion presents a ‘corrugated’ face to the ordered β″-stacked layers and a ‘smooth’ one to the disordered α/β″ layer. There is no disorder in **1–3**, most likely due to the rigidity of the anionic layer.

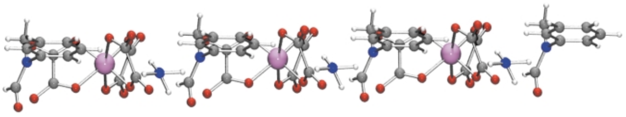

Fig. 3 The anion layer of **1** viewed along the *c* direction.

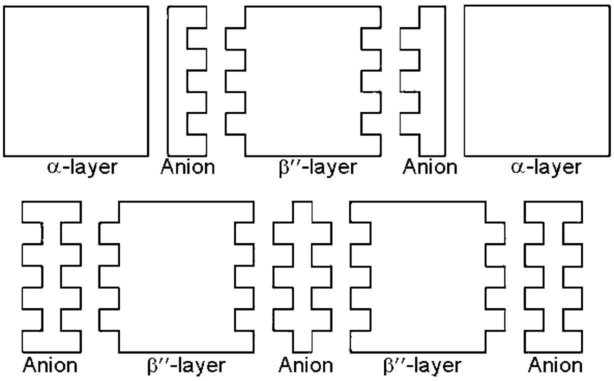

Fig. 4 Schematic diagram of the stacking cation layers in the present compounds (top) and purely β″ salts (bottom).

In the series of (BEDT-TTF)$_4$[AM(C$_2$O$_4$)$_3$]·G salts we have now identified three groups, with pure β″, pure ‘pseudo κ’ and now α-β″ phases. In each case an intimate correlation of the cationic and anionic layers is responsible for the different structures and physical properties. The α-β″ salts represent the first series with such packing, brought about by the supramolecular organisation of G.

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Notes and references

† **1–3** were synthesised in H-shaped electrochemical cells with two Pt electrodes. BEDT-TTF (10 mg) was placed in the anodic arm and a solution of (NH$_4$)$_3$[M(C$_2$O$_4$)$_3$]·3H$_2$O (100 mg) (M = Fe or Ga), with 18-crown-6 (200 mg) to aid dissolution, was added. Solvents were a 1 : 1 (v : v) mixture of PhN(CH$_3$)COH/CH$_3$CN (**1**), PhCH$_2$CN (**2**) or PhCOCH$_3$ (**3**), each with three drops of H$_2$O. 0.5 μA was applied to each cell for 8 to 10 days until crystals grew on the anode. Four probe DC electrical transport was measured to 2 K (15 μm diam. Au electrodes attached with Au paste) using a HUSO HECS 994C multi-channel conductometer. Single crystal X-ray diffraction was with a Rigaku quantum CCD system. Raman spectra were recorded on a Renishaw System 1000 Ramascope with He-Ne laser (λ = 632.8 nm), 10 μm slits and ×50 objective lens. Band structure calculations used an extended Hückel Hamiltonian[8] and double-ζ Slater-type orbitals for C and S, and single-ζ Slater-type orbitals for H.

‡ Crystal data for **1**: $C_{54}H_{45}GaN_2O_{13}S_{32}$, M = 2025.60, black plate, triclinic, a = 9.596(6), b = 11.179(5), c = 37.834(7) Å, α = 82.17(2), β = 84.53(2), γ = 65.400(13)°, U = 3652.3(25) Å^3, T = 298(2) K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo-K$_\alpha$) = 1.354 mm^{-1}, 14825 independent reflections with 10225 included in the refinement. $R1$ = 0.053, $wR2$ = 0.063 ($I > 3\sigma(I)$), $R1$ = 0.118, $wR2$ = 0.092 (all data) refined on F^2.

Crystal data for **2**: $C_{54}H_{43}GaN_2O_{12}S_{32}$, M = 2007.58, dark brown plates, triclinic, a = 9.824(1), b = 11.196(2), c = 37.88(1) Å, α = 81.469(5), β = 87.657(3), γ = 64.362(2)°, U = 3714(1) Å^3, T = 298(2) K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo-K$_\alpha$) = 1.330 mm^{-1}, 13242 reflections with 8548 included in the refinement. $R1$ = 0.084, $wR2$ = 0.067 ($I > 3\sigma(I)$), $R1$ = 0.138, $wR2$ = 0.104 (all data) refined on F.

Crystal data for **3**: $C_{54}H_{44}FeNO_{13}S_{32}$, M = 1996.71, dark brown plates, triclinic, a = 10.132(2), b = 11.261(1), c = 36.651(4) Å, α = 82.957(6), β = 86.413(3), γ = 63.477(1)°, U = 3713.3(8) Å^3, T = 298(2) K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo-K$_\alpha$) = 1.163 mm^{-1}, 15212 independent reflections with 6401 were included in the refinement. $R1$ = 0.088, $wR2$ = 0.075 ($I > 3\sigma(I)$), $R1$ = 0.2138, $wR2$ = 0.1529 (all data) refined on F.

Structures were solved by direct methods (G. M. Sheldrick, SHELX-97, University of Göttingen, Germany, 1997) and refined anisotropically, except for H atoms which were at ideal positions. Calculations were done using CRYSTALS (Chemical Crystallography Laboratory, Oxford, UK, 2001) and teXan v.1.06 for Windows (Molecular Structure Corporation, USA, 1999).

CCDC 213252–213254. See http://www.rsc.org/suppdata/cc/b3/b310683g/ for crystallographic data in .cif or other electronic format.

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