Polymorphism based on molecular stereoisomerism in tris(oxalato) Cr(III) salts of bedt-ttf [bis(ethylenedithio)tetrathiafulvalene]

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Polymorphs of the charge transfer salt (bedt-ttf)$_4$[(H$_3$O)-Cr^{III}(C$_2$O$_4$)$_3$]·PhCN [bedt-ttf = bis(ethylenedithio)tetrathiafulvalene] which are either superconducting or semiconducting differ in the spatial distribution of Δ and Λ enantiomers of [Cr(C$_2$O$_4$)$_3$]$^{3-}$ within the unit cell.

Solids built from molecules give chemists the ability to create materials with structural complexities not found in traditional continuous lattice materials. Subtle changes in structure may lead to large differences in collective physical properties such as electrical transport or magnetism. For example, molecular charge transfer salts of the donor bedt-ttf, bis(ethylenedithio)-tetrathiafulvalene, exhibit room temperature electronic ground states as diverse as metallic, wide band gap semiconducting and insulating. Some even display superconductivity.[1] Their transport properties vary with the acceptor anion and different structural modifications of bedt-ttf are possible with the same anion.[2–4] The collective electronic properties of such materials depend crucially on the charge distribution, distances and relative orientations of neighbouring donor molecules in the crystal, *i.e.* on the packing motif. Motifs can be controlled by organisation of the anions, *via* 'docking' of the terminal methylene H atoms of the bedt-ttf into cavities provided by the anions organisation.[5] Anion–cation atomic contacts provide further means of self assembly within the unit cell.

The series of compounds with general formula (bedt-ttf)$_4$ [AM^{III}(C$_2$O$_4$)$_3$]·PhCN (M = Fe, Cr; A = H$_3$O$^+$, K$^+$, NH$_4^+$) has been structurally characterised by room temperature and low temperature X-ray crystallography.[6–8] Their conducting and magnetic properties have been determined by single crystal resistivity measurements, SQUID magnetometry and variable temperature electron paramagnetic resonance. One polymorph of the compound with M = Cr and A = H$_3$O$^+$ (**I**)[8] has a metal to superconducting transition at T_c = 6.0(5) K. At high temperatures the bulk magnetic susceptibility is dominated by unpaired d electrons associated with the Cr(III) ion (S = 3/2). The Curie–Weiss law is obeyed from room temperature to just above T_c together with a small Pauli contribution as is usual for metallic salts. Below T_c the Meissner effect is observed and this is suppessed by an external field of 40 mT. The point symmetry about Cr is D_3 and so [Cr(C$_2$O$_4$)$_3$]$^{3-}$ exhibits optical isomerism although **I** is prepared from a racemic mixture of the tris(oxalato) starting material and crystallises in an achiral space group, *C*2/*c*. In contrast using enantiomerically pure [Cr(C$_2$O$_4$)$_3$]$^{3-}$ as a starting material we obtain another achiral phase (**II**) with identical stoichiometry to phase **I**† but with strikingly different physical properties. Transport measurements on **II** indicate semiconducting behaviour while no Meissner effect is seen and the magnetic susceptibility can be fitted to a Curie–Weiss law from ambient to low temperatures. The difference in physical properties between **I** and **II** arises from an unprecedented difference between their crystal structures namely a different spatial arrangement of the chiral enantiomers in the unit cell.

In both polymorphs‡ layers of cationic bedt-ttf molecules are interleaved by layers containing [Cr(C$_2$O$_4$)$_3$]$^{3-}$, H$_3$O$^+$ and PhCN. Each anionic layer forms a so-called 'honeycomb' lattice with alternate intralayer O (of H$_3$O$^+$) and Cr forming an approximately hexagonal network with benzonitrile molecules occupying the hexagonal cavities. The Cr atoms are octahedrally coordinated to three bidentate oxalate dianions, which confers the D_3 site symmetry about each transition metal. The uncoordinated O (oxalate) atoms surround a cavity occupied by H$_3$O$^+$. The area of the hexagonal cavities are almost identical and they are filled by a benzontrile molecule with little void space into which the terminal CH$_2$ groups of the bedt-ttf can 'dock'[5].

Despite identical stoichiometry, the organisation of the bedt-ttf layers is quite different in the two polymorphs: **I** has the so-called β'' packing motif (*C*2/*c* space group) whereas **II** presents a motif which we refer to as pseudo-κ (*Pbcn* space group). Analysis of the pseudo-κ C=C and C–S bond lengths[9] within the central ttf (tetrathiafulvalene) unit indicates that there are two different bedt-ttf molecules with charges close to 0 and +1. The +1 cations occur as face to face dimers and are surrounded by six neutral molecules. Neighbouring dimers are approximately orthogonal as in normal κ phases.[1] In the β'' phase the molecules are arranged into stacks with short S···S distances between them and bond length analysis reveals that all bedt-ttf molecules have similar but not identical positive charges close to +0.5. (Note that the sum of the bedt-ttf charges implies that in both polymorphs the water is present as H$_3$O$^+$). In **II** the centroids (centre of the ttf C=C bond) of the neutral molecules describe approximately hexagonal networks where the positively charged dimers lie close to oxalate anions, leading to H-bonding (2.51–3.05 Å) between the terminal ethylene hydrogens and oxygens (oxalate). The neutral bedt-ttf molecules are either positioned over H$_3$O$^+$ or close to the solvent.

The difference between the packing motifs of the donor cations in **I** and **II** must arise from the pattern of short atomic contacts, specifically H-bonds, between the organic and anionic layers. Evidence for such interactions between terminal CH$_2$ groups of bedt-ttf and the anion layer comes from translation of the [Cr(C$_2$O$_4$)$_3$]$^{3-}$ units within the plane of an anion layer on passing from one layer to the next. The displacement of the [Cr(C$_2$O$_4$)$_3$]$^{3-}$ matches the tilt of the long axis of the intervening bedt-ttf molecules, so that the contacts between H (CH$_2$) atoms and O (oxalate) are identical at both ends of the bedt-ttf.

The basic topography of the inorganic layers is very similar in both phases, so why should the packing of the organic donor molecules be so different? The answer lies in the distributions of enantiomeric [Cr(C$_2$O$_4$)$_3$]$^{3-}$. In **I** each anionic layer contains exclusively one enantiomer and the next layer contains the other giving a Δ-Λ-Δ-Λ-Δ-Λ . . . pattern. However, each anionic layer in **II** contains both Δ and Λ enantiomers arranged in rows. In adjacent layers the chiral centres are organised in an identical fashion, barring layer translation, which gives a $\Delta\Lambda$-$\Delta\Lambda$-$\Delta\Lambda$-$\Delta\Lambda$ . . . pattern. In neither polymorph does relative translation of the inorganic layer affect the bedt-ttf packing motif, but only the tilt angle of the long axis of these molecules. The arrangement of the enantiomers in a single anionic layer for **I** and **II** are shown in Fig. 1(*a*) and (*b*), respectively indicating two ways in which equal proportions of each enantiomer are accommodated in the lattice to give an achiral crystal structure. The different spatial distributions of enantiomers form the basis of the observed polymorphism and are responsible for self assembly into either pseudo κ or β″ bedt-ttf packing motifs, which determine the strikingly different electrical properties of the two phases.

The spatial relationship between the bedt-ttf packing motifs and a nearest neighbour anionic layer is given in Fig. 2(*a*) and (*b*). The bedt-ttf layer is in the foreground and superimposed, as the background, are the positions of the metal atoms and the H_3O^+ molecules (O atom is marked A) of the anion layer. The chiral environment about the metal atoms is shown as Δ or Λ, and the hexagonal honeycomb lattice marked with full lines. H-bonding interactions occur between the neighbouring O (oxalate) atoms and the H (CH_2) atoms on the extremity of each bedt-ttf. Fig. 2 shows that the two packing arrangements of the bedt-ttf are very closely related, the β″ phase being a more regular form of the pseudo-κ phase. If all enantiomers in alternate rows of **I** are changed to the other isomer then the inorganic layer topography is transformed to that of **II**. A corresponding rotation of the donor cations, maintaining the same number and disposition of H-bonds, transforms the pseudo κ phase into a phase almost identical to β″. In effect this gives a β″ phase, generated from the pseudo κ phase, which therefore contains dimers and the original pseudo-κ charge distribution.

In conclusion we have shown that there are two polymorphs of the molecular charge transfer salt (bedt-ttf)$_4$[(H$_3$O)Cr(C$_2$O$_4$)$_3$]·PhCN, with distinctly different, though related, packing arrangements of the bedt-ttf donor cations. The salts have either β″ or a pseudo-κ motif and they have contrasting physical properties, being superconducting or semiconducting respectively. The two modes of bedt-ttf packing are promoted by two different spatial distributions of the chiral enantiomers Δ- or Λ-$[Cr(C_2O_4)_3]^{3-}$ to give overall racemic lattices. It has been previously found that exposure to either racemic or enantiomer excess of components or additives in a crystallisation process can lead to different polymorphs of a solid.[12,13] However, to the best of our knowledge this is the first time that this specific source of polymorphism has been identified in any crystalline material. We are continuing our efforts to make related chiral compounds and to explore the supramolecular organisation in this family of organic conductors.

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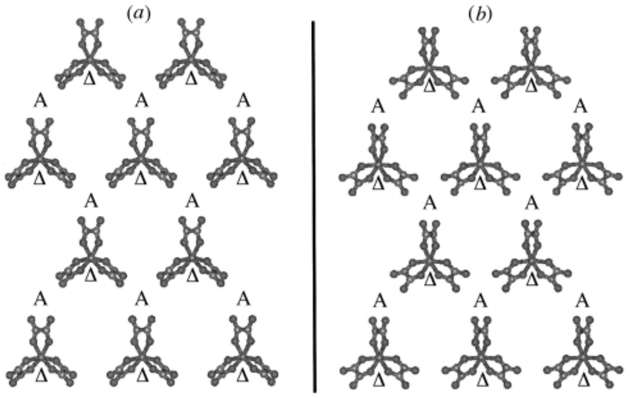

Fig. 1 Two different ways in which chiral $[Cr(C_2O_4)_3]^{3-}$ is accommodated in a single layer within (*a*) **I** and (*b*) **II**; A = H_3O^+.

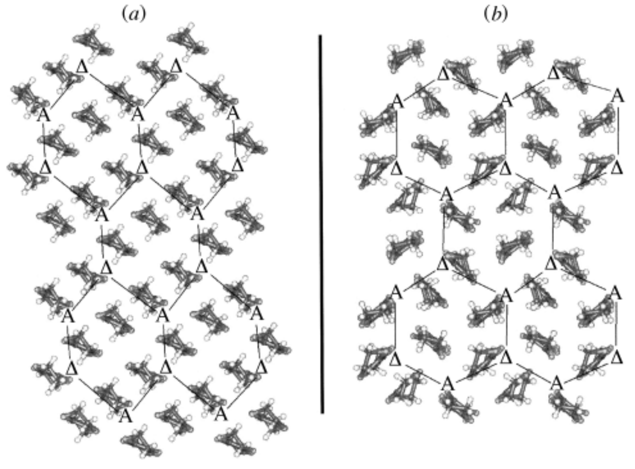

Fig. 2 The relationship between layers of bedt-ttf and $[Cr(C_2O_4)_3]^{3-}/H_3O^+$/PhCN in (*a*) **I** and (*b*) **II**.

Notes and references

† The salts were prepared by *in situ* electro-oxidation of neutral bedt-ttf at constant currents of between 0.05 and 0.2 μA, in the presence of the anion and relevant solvent. For **I** the anion source was racemic $(NH_4)_3[Cr(C_2O_4)_3]\cdot 3H_2O$.[10] The starting material used for **II** was either the pure Δ- or Λ-ammonium salt of $[Cr(C_2O_4)_3]^{3-}$, prepared by literature methods,[11] both of which gave identical products. In both syntheses the solvent was distilled and degassed just prior to use and then several drops of water were added to the electrochemical cell. All starting materials were purified by repeated crystallisation. It was noted that the crystals began to grow within two days when using racemic starting materials but only after two weeks when using a single enantiomer. The time delay confirms that at least partial racemisation must occur in the latter case prior to crystal formation.

‡ *Crystal data*: **I**: $C_{53}H_{39}CrNO_{13}S_{32}$, M = 1975.99, monoclinic, space group $C2/c$, a = 10.278(3), b = 20.130(4), c = 35.078(15) Å, β = 93.040(9)°, U = 7247.3(40) Å^3, T = 150(2) K, Z = 4, μ = 1.141 mm^{-1}, reflections collected = 8640, independent reflections = 4281, $R1$ = 0.0622, $wR2$ = 0.0945.

II: $C_{53}H_{39}CrNO_{13}S_{32}$, M = 1975.99, orthorhombic, space group $Pbcn$, a = 10.371(2), b = 19.518(3), c = 35.646(2) Å, U = 7216(2) Å^3, T = 150(2) K, Z = 4, μ = 1.146 mm^{-1}, reflections collected = 24400, independent reflections = 5599, $R1$ = 0.0655, $wR2$ = 0.1033.

CCDC 182/1170. See http://www.rsc.org/suppdata/cc/1999/513/ for crystallographic files in .cif format.

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