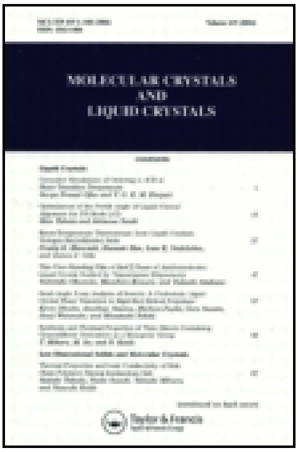

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Synthesis, Structure and Physical Properties of the Molecular Magnetic Semiconductor (BEDT-TTF)$_4$KF$_e$(C$_2$O$_4$)$_3$.C$_6$H$_5$CN(BEDT-TTF═BIS(ethylenedithio) Tetrathiafulvalene)

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SYNTHESIS, STRUCTURE AND PHYSICAL PROPERTIES OF THE MOLECULAR MAGNETIC SEMICONDUCTOR (BEDT-TTF)$_4$KFe(C$_2$O$_4$)$_3$.C$_6$H$_5$CN (BEDT-TTF = BIS(ETHYLENEDITHIO) TETRATHIAFULVALENE)

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Abstract We report the synthesis and physical properties of compounds of BEDT-TTF with transition metal tris-oxalate anions. The crystal structure of one such compound, (BEDT-TTF)$_4$KFe(C$_2$O$_4$)$_3$.C$_6$H$_5$CN (**1**) has been determined. The structure consists of alternating layers of BEDT-TTF and a hexagonal network of K$^+$ and Fe(C$_2$O$_4$)$_3{}^{3-}$. This material is a semiconductor with an activation energy of 0.14eV. Magnetic data obey the Curie-Weiss law with C= 4.44 (S=5/2) and θ= -0.25K.

INTRODUCTION

Charge transfer salts of the organic donor molecule bis (ethylenedithio)tetrathiafulvalene (BEDT-TTF) have been of interest to solid state scientists for the last decade, due to the wide range of physical properties which they exhibit. By varying the charge compensating anion, a multitude of properties have been observed, notably, superconductivity in over 20 of its salts[1]. The incorporation of different shapes of anion can lead to a change in the packing of the BEDT-TTF molecules, which results in marked variations in the physical properties.

The structures of the large majority of these materials consist of segregated layers of anions and cations between which there is little (if any) electronic interaction. Band structure calculations indicate that the electrical conduction takes place principally through the overlap of the sulfur orbitals on the BEDT-TTF molecules. It may therefore be possible to observe superconductivity in the donor layer and magnetic interaction in the acceptor layer. Attempts to achieve this goal have been reported, notably in $(BEDT\text{-}TTF)_3CuCl_4.H_2O$ which remains metallic to 400mK [2]. It has been suggested that it is weak ferromagnetic interactions between the Cu(II) ions in this compound that supresses the superconducting transition. The focus of the work reported in the present note is to determine the effect of magnetic anions on the conducting properties of the layers of organic cations and ultimately to investigate whether superconductivity and magnetism may co-exist in charge transfer salts.

EXPERIMENTAL

BEDT-TTF [3] and $K_3Fe(C_2O_4)_3.3H_20$ [4] were prepared according to literature methods. The corresponding Na and NH_4 salts were prepared by replacing the potassium oxalate in the synthesis with sodium and ammonium oxalate respectively. The Co analogues were similarly prepared. 18-crown-6 ether (Aldrich) was recrystallised from acetonitrile. Benzonitrile was dried over $CaCl_2$ and freshly distilled before use. The crystals were grown by electrocrystallisation in a H-cell, applying a current of 0.3μA between Pt electrodes for a period of 21 days.

Single crystal X-ray diffraction data were collected at the EPSRC service facility at the University of Cardiff. Two probe dc conductivity measurements were performed along the three crystallographic axes, Pt paint being used to make contact to the crystals. Magnetic susceptibility was measured on a polycrystalline sample using a Quantum Design MPMS 7 SQUID magnetometer in an applied field of 1T.

RESULTS AND DISCUSSION

The results of the crystal growth experiments are summarised in Table 1. All but one of the phases isolated are semiconductors. For the purpose of discussion in this note we concentrate on the one phase whose structure has been determined to date.

The X-ray data show this compound to have the formula

$(BEDT\text{-}TTF)_4KFe(C_2O_4)_3.C_6H_5CN$. The asymmetric unit consists of 2 independent BEDT-TTF molecules, BEDT-TTF* and BEDT-TTF', and half of $KFe(C_2O_4)_3.C_6H_5CN$. The structure consists of segregated layers of the organic cation and the inorganic anion, as is customary in these charge transfer salts [5]. It can be described roughly as a herring bone like structure. The conformations of the terminal ethylene groups differ in the two independent BEDT-TTF molecules: those of BEDT-TTF* are staggered with respect to each other whereas on BEDT-TTF' they are eclipsed.

The two independent BEDT-TTF molecules are distinguished from each other by having different central C=C bond lengths (1.38Å and 1.33Å), which are associated with neutral and monopositive charge states respectively. The projection of the organic donor layer along the long axes of the BEDT-TTF molecules shows how the monopositve BEDT-TTF molecules form face-to-face dimers and are surrounded by six monomers of neutral BEDT-TTF molecules (Fig. 1). Co-existence between different charge types of BEDT-TTF has been reported before [6], however, this is the first time that this arrangement of BEDT-TTF molecules has been observed.

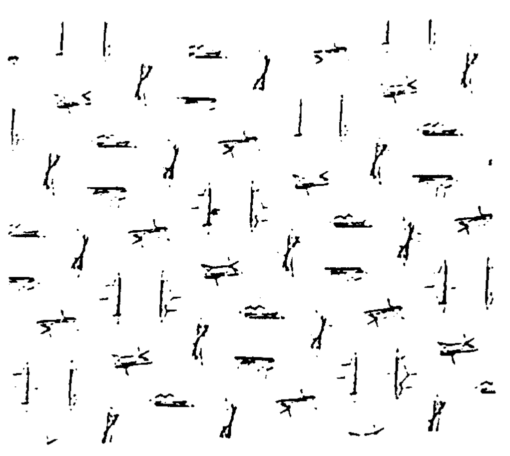

Fig. 1. The BEDT-TTF layer of $(BEDT\text{-}TTF)_4KFe(C_2O_4)_3.C_6H_5CN$

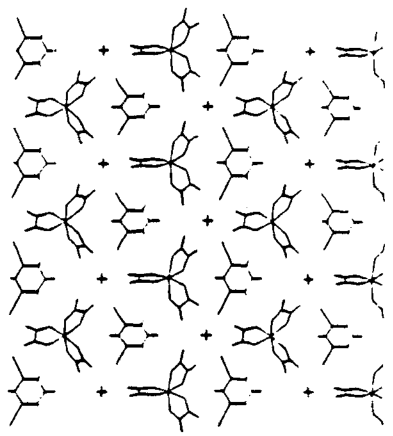

Fig. 2. The anion layer

The anion layer is arranged in a honeycomb lattice, similar to that seen in previously reported M, M' oxalate salts [7] (Fig. 2). The hexagons are formed from the oxalate oxygen atoms co-ordinating on either side to K^+ and Fe^{3+}. Thus the alkali metal replaces the divalent transition metal ions found in the previous examples [7].

As a result, there is no magnetic interaction between the trivalent metal ions, in contrast to the ferrimagnetism observed in (for example) the Fe^{3+} Fe^{2+} complexes [8]. The solvent molecule resides in the centre of the honeycomb so that the K is co-ordinated by six oxygen atoms from the oxalate and two nitrogen atoms from benzonitrile. The K, Fe and benzonitrile are all in the same plane.

The cavities in the honeycomb of the BEDT-TTF layer are slipped with respect to those in the oxalate layer. Therefore, the charged BEDT-TTF molecules are positioned above the oxalate anion, giving rise to short hydrogen - oxygen distances, ranging between 2.51Å to 3.05Å. Short S-S contact distances are observed between the BEDT-TTF molecules which form the dimers, ranging between 3.47Å and 3.77Å. Consequently, there is substantial overlap between the S orbitals on adjacent molecules, which is a pre-requisite for electrical conduction. Short S-S distances are also observed between the charged and neutral BEDT-TTF molecules, ranging between 3.28Å - 4.45Å. However, as the charged BEDT-TTF molecules form dimers, it is not surprising that the compound is a semiconductor. Figure 3 shows the resistance along the three crystal axes. The data correspond to an activation energy of 0.14eV. Single crystal conductivity data of related compounds are listed in table 1.

The crystal structures of these compounds are currently under investigation and a more detailed treatment will be published elsewhere.

The temperature dependent magnetic susceptibility is shown in Figure 4. The data have been fitted to the Curie-Weiss law assuming g=2. This gives a Curie constant of 4.44 (S=5/2) and θ=-0.25K, indicating very little interaction between Fe^{3+} moments. If there was a spin contribution from the monopositive BEDT-TTF molecules, a Curie constant of 6 would be expected. As the spin value is as predicted for a high spin Fe^{3+} complex, this would suggest that there is no contribution from the BEDT-TTF molecules. Such a result is to be anticipated because the neutral closed shell BEDT-TTF molecules form cages around the charged BEDT-TTF molecules, which, having dimerised, also have no net spin.

CONCLUDING REMARKS

New phases of BEDT-TTF have been synthesised using highly symmetric $M(C_2O_4)_3$ (M= Co or Fe) as the charge compensating anion. The structure of one such phase reveals alternating layers of BEDT-TTF molecules and K^+, $Fe(C_2O_4)_3{}^{3-}$. It is postulated that the hydrogen bonding interactions between the donor and acceptor molecules result in the BEDT-TTF layer mirroring the honeycomb structure of the metal oxalate layer. In this compound neutral BEDT-TTF molecules form closed shells around charged dimers and therefore the material behaves as a semiconductor, with an activation energy of 0.14eV. There is no spin contribution to the total susceptibility from the BEDT-TTF molecules.

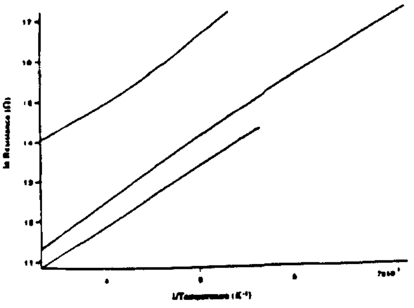

Fig. 3. Temperature dependence of the resistance single crystal of (**1**) along three axes.

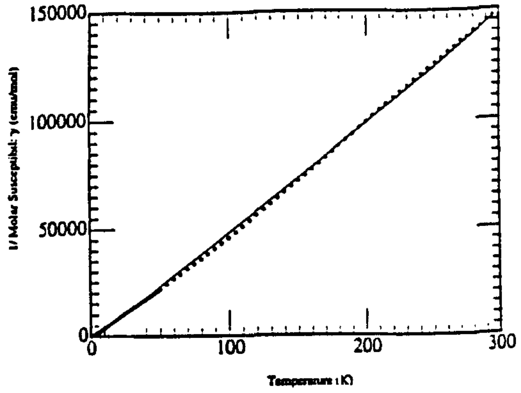

Fig. 4. Temperature dependence of inverse magnetic susceptibility of (**1**).

Table 1. Crystal growth and properties of charge transfer salts of BEDT-TTF with tris (oxalato) metallate anions.

Electrolyte	Solvent	Morphology	Activation Energy (eV)
$K_3Fe(C_2O_4)_3$	C_6H_5CN	Diamond	0.14
$(NH_4)_3Fe(C_2O_4)_3$	C_6H_5CN	Diamond	0.14
$Na_3Fe(C_2O_4)_3$	C_6H_5CN	Hexagon	0.08
$Na_3Fe(C_2O_4)_3$	C_6H_5CN	Spear	0.23
$(NH_4)_3Fe(C_2O_4)_3$	$C_6H_5CN+H_2O$	Plate	0.18
$(NH_4)_3Fe(C_2O_4)_3$	$C_6H_5CN+H_2O$	Needle	Metal
$K_3Co(C_2O_4)_3$	C_6H_5CN	Spear	0.11
$(NH_4)_3Co(C_2O_4)_3$	C_6H_5CN	Diamond	0.21

* +18-crown-6 ether

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REFERENCES

1. Organic Superconductors (including Fullerenes) J.M. Williams *et al*, Prentice-Hall (1992)
2. P. Day, M. Kurmoo, I. Marsden, M. Allan, R. H. Friend, F. L. Pratt, W. Hayes, D. Chasseau, G. Bravic, and L. Ducasse, *J. Am. Chem. Soc.* **114**, 10722 (1992)
3. J. Larsen and C. Lenoir, *Synthesis* **2,** 134 (1988)
4. J.C. Bailar and E. M. Jones, *Inorganic Synthesis*, **1**, 35 (1939)
5. P. Day, *Physica Scripta* , **T49**, 726 (1993)
6. T. Mori and H. Inokuchi *Bull. Chem. Soc. Jpn* , **61**, 591 (1988)
7. S. Decurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. Ensling, P. Gütlich and A. Hauser, *Inorg. Chim. Acta.*, **216** p.65-73. (1993)
8. C. Mathoniere, S.G. Carling, D. Yusheng, P.Day, *J.C.S., Chem. Commun.* 1551 (1994).