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A SYSTEMATIC STUDY OF THE RELATIONSHIP BETWEEN CRYSTAL STRUCTURE, ESR CHARACTERISTICS AND ELECTRICAL PROPERTIES IN BEDT-TTF SYNTHETIC METALS

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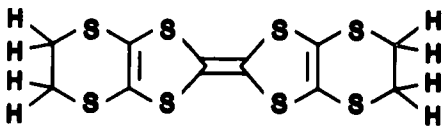
Abstract The crystal packing motifs exhibited by the BEDT-TTF (or "ET") donor molecules in the various ET:X charge-transfer salts are summarized. In spite of the variable stoichiometries and crystal symmetries found for these synthetic metals, the number of different crystal packing motifs is limited -- two interstack (L- and Z-modes) and three intrastack modes (a-, b- and c-modes). Of these, superconductivity has been observed only in the 2:1 (BEDT-TTF:X) salts which adopt a combination of the L- and a-modes of inter- and intrastack packing, respectively. ESR linewidth measurements provide a means of separating different crystal phases within a given donor-acceptor system and are especially useful in differentiating the non-superconducting α-$(ET)_2X$ phases, $X = I_3^-$ and IBr_2^-, from the ambient pressure superconducting β-$(ET)_2X$ phases, $X = I_3^-$ and IBr_2^- (T_c's = 1.4 K and 2.7 K, respectively).

INTRODUCTION

The charge-transfer salts of BEDT-TTF (bis-ethylelene-dithiotetrathiafulvalene, $C_{10}S_8H_8$, also known hereafter as "ET"), form a new class of S-based organic conductors with novel electrical properties including superconductivity.

The recent discovery of superconductivity in $(ET)_2ReO_4$ with $T_c \simeq 2$ K ($P > 4$ kbar) constituted the first observation of this phenomenon in a sulfur-based organic metal[1]. The subsequent finding of superconductivity at ambient pressure in the two related compounds, β-$(ET)_2I_3$ ($T_c \simeq 1.4$ K)[2-4] and β-$(ET)_2IBr_2$ ($T_c \simeq 2.7$ K)[5,6] presents new opportunities for the synthesis of novel materials with possibly even higher T_c's. Ever since the first discovery[7] of metallic conductivity to 1.4 K in $(ET)_2ClO_4(TCE)_{0.5}$, numerous $(ET)_2X$, X = monovalent anion, synthetic metals have been synthesized. These have included materials containing various monovalent anions and, in some cases, different solvent molecules. Often, solvent-free materials of the type $(ET)_n(X)_m$ have also been prepared. A wide variation in the electrical properties of these materials has been reported. In the present study, a summary of the known ET charge-transfer salts is reported which relates the crystal structures and basic room-temperature ESR data of these materials to their electrical properties.



BEDT-TTF or "ET"

THE CRYSTAL STRUCTURES OF THE CHARGE TRANSFER SALTS OF ET

While the more familiar TMTSF and TMTTF charge-transfer salts have similar stoichiometries and crystal structures -- $(TMTSF)_2X$ or $(TMTTF)_2X$ (X = ClO_4^-, BF_4^-, ReO_4^-, PF_6^-, AsF_6^-, etc.)[8] which are isostructural (space group P1), the crystal chemistry of the charge transfer salts of ET

is quite varied. Electrocrystallization reactions, using the same anion during crystal growth and under identical conditions, often produce several different crystal phases. For example, there are at least three such phases in the ET:ReO_4 system viz., $(ET)_2(ReO_4)$, $(ET)_3(ReO_4)_2$ and$(ET)_2(ReO_4)(THF)_{0.5}$ with vastly different electrical properties[1,9]. They also have different ESR linewidths at room temperature and have vastly different temperature dependent ESR signals (see Table 1)[9]. These different phases are observed to co-crystallize during a single electrocrystallization reaction. Depending on the conditions of crystal growth, the relative abundance of these phases may also vary. However, only one of these phases, $(ET)_2ReO_4$, is observed to be superconducting at $\simeq$ 2 K ($P > 4$ kbar)[1]. Even though some derivatives may even have identical stoichiometries, these charge-transfer salts often have different electrical properties and crystal structures. For example, $(ET)_2I_3$, crystallizes in two different forms designated as the α- and β-forms, respectively[10,11]. While both of these materials are metallic near room temperature, α-$(ET)_2I_3$ undergoes a metal-insulator (MI) transition at $\sim$ 135 K[10]. On the other hand β-$(ET)_2I_3$ remains metallic to 1.4-1.5 K, at which temperature the onset of superconductivity at ambient pressure occurs[2-4]. Superconducting β-$(ET)_2I_3$ is particularly interesting because of the occurence of an incommensurate phase transition at $\sim$ 195 K which is attributed to a displacive structural modulation[12]. Clearly, the electrical properties of these charge transfer salts are very dependent on their compositions and, as we shall demonstrate, the crystal packing motifs. A summary of

crystallographic, ESR, and electrical data of the known ET salts is given in Table 1. ESR measurements were performed on a Varian E-9 spectrometer at 9.14 GHz with 100 KHz field modulation. The modulation amplitude was kept well below the linewidth and the microwave power of 10mW was well below saturation. The first derivative peak to peak linewidths are reported with much of the standard deviation due to linewidth anisotropy. The great virtue of this method is that even very tiny (< 0.1 mm) crystals can be examined[21].

Although the space group symmetries and the stoichiometries of these ET salts appear to vary widely, the modes of crystal packing of the ET molecules appear limited (vide infra). In general, there are two different types of packing along the interstack directions (see Figure 1), designated as L- and Z-modes for "linear" and "zigzag", respectively.

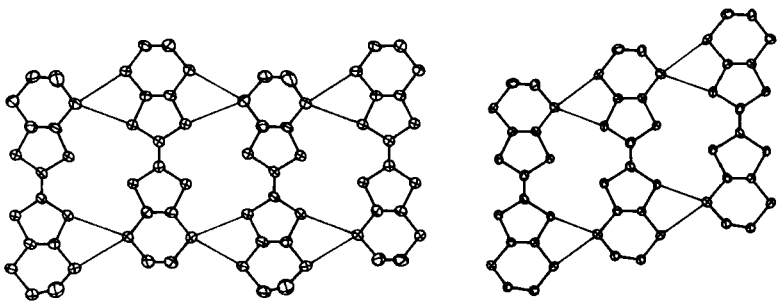
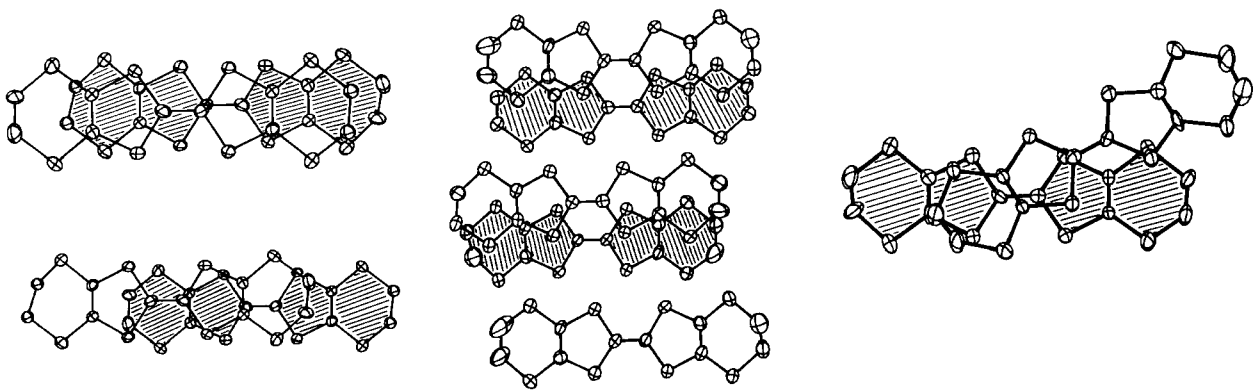


Figure 1. Illustration of two distinct types of interstack packing of the ET molecules in ET:X salts: zigzag or Z-mode (left) and linear or L-mode (right). The hydrogen atoms are omitted for clarity.

As opposed to the TMTSF and TMTTF systems[8], in which the intermolecular Se···Se and S···S interactions, respectively, are more important in the intrastack direction, short S···S contacts always occur mainly along the interstack directions in the ET:X systems. In fact, these short S···S contacts are often significantly shorter than the sum of their van der Waals radii (3.6 Å) generally indicating strong intermolecular interactions. Regardless of the type of interstack packing, many of these materials exhibit metallic properties (see Table 1).

Along the loosely packed ($d_{S\cdots S} > 3.60$ Å) intrastack direction, there appear to be three different packing modes exhibited by the ET molecules in the known ET:X systems. For convenience, these intrastack-packing modes are designated as a-, b-, and c-modes (see Figure 2). In the a-mode, the ET molecules pack in a face-to-face manner. As shown in Figure 2, quantitative differences in the intermolecular overlaps can occur due to the relative molecular displacements along the long in-plane axes of the organic molecules. This displacement, designated "D" by Mori et al.[13], is a very important factor in determining the overlap integrals between adjacent ET molecules. It is noteworthy that all the known superconducting phases of the ET salts adopt the a-type packing mode.

In cases of the b-mode, there is no distinct stacking direction. Each ET molecule overlaps with two others along a direction perpendicular to the ET sheets. All known ET salts which adopt this packing mode are metallic, but superconductivity has never been observed in these systems. For example, $(ET)_2ClO_4(TCE)_{0.5}$ remains metallic



a-mode b-mode c-mode

Figure 2: Illustration of the three distinct intrastack packing motifs of the ET molecules in ET:X systems. The ET molecules in the bottom layer are shaded.

to 1.4 K but is never superconducting.[7] A theoretical calculation by Mori et al.[13] indicates tremendous variations in the intermolecular overlap integrals as a function of ϕ, the angle between the molecular planes of two adjacent ET molecules. The values of ϕ are 0° and 90° for the side-by-side and face-to-face (both are within the a-mode) interactions, respectively. The b-mode has ϕ values which are intermediate between these two values.

Interestingly, those ET salts which adopt the c-mode of intrastack packing are all semi-conductors[14-16]. In the c-mode, often designated as the "herring-bone" configuration, overlaps between the ET sheets along the stacking axis are thought to be small, as suggested by the large differences in the anisotropic conductivities. In β-$(ET)_2PF_6$, for example[14], the room temperature conductivities along the inter- and intrastack axes differ by almost a factor of 100.

RELATIONSHIP OF CRYSTAL STRUCTURES AND ELECTRICAL PROPERTIES

Clearly, the differences in crystal packing of the ET molecules can significantly affect the band structures of these materials. As shown above, some of the crystal packing modes are characteristic of a structure that exhibits superconductivity at low temperature, while the other modes offer less favorable intermolecular S···S overlaps and are not associated with the superconducting state.

In general, a two-dimensional packing of the ET molecules appears necessary in order to suppress low temperature MI transitions which are very common in low-

dimensional conductors. Indeed, the extended exocyclic (non-TTF S-atom framework) rings in the ET molecules offer an opportunity for two-dimensional interactions. These exterior S-atoms are absent in the related TMTTF and TMTSF systems. However, the significant interstack interactions in the ET salts always appear to involve such exterior sulfur atoms. The importance of the 2-D S•••S interactions can be seen in the modulated structure of β-$(ET)_2I_3$ in which the displacive structural modulation causes large local modifications of the intermolecular (S•••S) contacts[12]. Yet, the variation in the resistivity of this material is smooth throughout this incommensurate transition at 195 K[22].

It appears that the detailed crystal packing of ET molecules in these materials depends not only on the intermolecular interactions between the ET molecules, but also on the interactions between the counterions. In addition, the packing energy of the different modes of interacting ET molecules appear to be nearly degenerate since they often co-crystallize during the same synthesis. Hence, substitution of different anions can cause substantial changes in the anion-cation interactions which can be very significant in the overall crystal packing. A systematic study of this inter-play between cation-cation and cation-anion interactions is expected to be very fruitful in terms of future synthetic strategies aimed at the development of new materials.

TABLE 1 Summary of Crystallographic, ESR and Conductivity Data on BEDT-TTF Salts

Compound	Space Group	Unit Cell Vol. ($Å^3$) (298 K)	Z	Inter-stack Mode (Fig. 1)	Intra-stack Mode (Fig. 2)	ESR linewidth (Gauss) (Avg. ± esd)	Comment	T(MI)	Ref.
β-$(ET)_2I_3$	$P\bar{1}$	856	1	L	a	21±4	T_c = 1.4 K	—	2-4,11,12
α-$(ET)_2I_3$	$P\bar{1}$	1717	2	–	–	94±15	metallic	135 K	10
β-$(ET)_2IBr_2$	$P\bar{1}$	828	1	L	a	21±2	T_c = 2.7 K	—	5,6
$(ET)_2ReO_4$	$P\bar{1}$	1565	2	L	a	16±3	T_c = 2 K (P > 4 kbar)	81 K	1,9
$(ET)_2ReO_4(THF)_{0.5}$	—	—	–	–	–	15±3	semiconductor(?)		1,9
$(ET)_3(ReO_4)_2$	$P2_1/n$	2418	2	–	–	35±4	metallic(?)		1,9
$(ET)_3(BrO_4)_2$	$P\bar{1}$	1213	1	L	a	–	metallic	50 K	19
$(ET)_2(BrO_4)(TCE)_{0.5}$	$P\bar{1}$	1668	2	Z	b	31±6	---	—	19
$(ET)_2BrO_4$	$P\bar{1}$	1589	2	L	a	–	metallic	—	18
$(ET)_2InBr_4$	$P\bar{1}$	1820	2	L	a	9±1	semiconductor	—	20
$(ET)_2(ClO_4)(TCE)_{0.5}$	$P\bar{1}$	1684	2	Z	b	30±3	metallic	none	7
$(ET)_3(ClO_4)_2$	$P\bar{1}$	1182	1	Z	b	–	metallic	170 K	16
$(ET)_2(ClO_4)(C_4H_8O_2)$	P2/c	1814	2	L	c	–	semiconductor	—	16
$(ET)_2AsF_6$	A2/a	3274	4	L	c	13±5	semiconductor	—	15
α-$(ET)_2PF_6$	$P\bar{1}$	794	1	L	a	–	semiconductor	—	17
β-$(ET)_2PF_6$	Pnna	3255	4	L	c	–	semiconductor	—	14

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