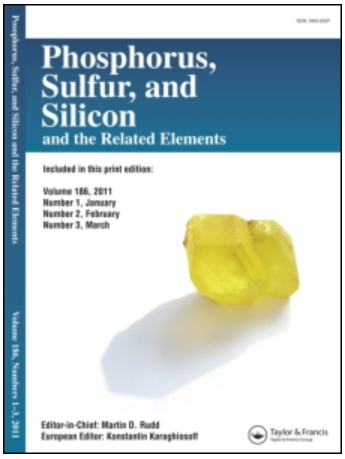

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RECENT PROGRESS IN BEDT-TTF BASED SYNTHETIC METALS

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Abstract BEDT-TTF based organic metals with tetrahedral and linear anions are reviewed. New $(ET)_2MX_4$ complexes, their electrical and ESR properties are reported (M = Ga, In, Tl, and X is halides). A novel solid state phase transformation from semiconducting α to superconducting β-$(ET)_2IBr_2$ is presented.

INTRODUCTION

Synthetic metals have been studied since the early seventies. These materials consist of donors and acceptors, e.g., TTF-TCNQ,[1,2] or radical cations and charge balancing anions, e.g. $(TMTSF)_2X$[3,4] where the acronyms stand for tetrathiofulvalene, tetracyanoquinonedimethane and tetramethyltetraselenafulvalene, respectively. Radical anions with simple cations have also been reported.[5] The electrical properties of synthetic metals vary from semiconducting for the major portion of them, metallic for a good number of compounds, to even superconducting for a handful of new materials. Compared to pure metals where the highest superconducting transition temperature (T_c) is 9 K in Nb, the organics has reached 8 K in β*-$(BEDT\text{-}TTF)_2I_3$.[6-9] BEDT-TTF is bis(ethylenedithio)-tetrathiofulvalene, $C_{10}S_8H_8$, or abbreviated as "ET". We are interested in the syntheses, solid state structures, transport properties as well as high and low

temperature phase transitions. The ET based synthetic metals have been extensively reviewed previously.[10-12] In this article we briefly summarize the results and report the current findings in the field.

ET SALTS WITH TETRAHEDRAL ANIONS

Most of the ET containing materials have been prepared by electrocrystallization techniques while chemical oxidation can be performed with iodine as an oxidant along with anions formed in situ such as I_3^-, I_5^-, I_8^{2-}.[13] Electrocrystallization has many advantages because a large variety of anions can be used and crystal growth rate is better controlled. There are some limitations to both techniques, i.e., the stoichiometries and phases are difficult to control. When small tetrahedral anions are used (FSO_3^-, HSO_4^-, BF_4^-), only $(ET)_3X_2$ complexes are reported.[14,15] When large anions are applied ($InBr_4^-$, InI_4^-), 2:1 complexes, $(ET)_2X$, are formed exclusively.[16] In order to understand this observation we estimated the anion volume by the following equation,

$$Vol = (R_i + 2\ R_o)^3$$

where R_i and R_o are the ionic radii of the inner and outer atom.[17] While this is only an estimation, the relative anion volume should be accurate. In Figure 1, the estimated anion volumes are plotted against a series of isostructural $(ET)_3X_2$ unit cell volumes. A reasonably linear correlation is observed.

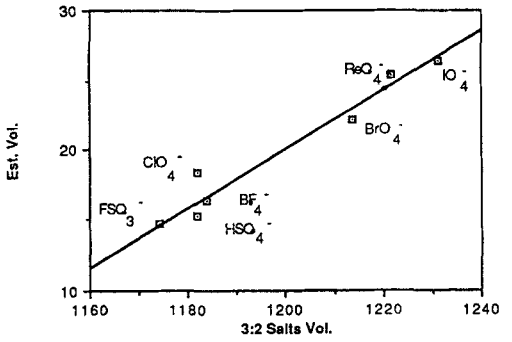

FIGURE 1 Estimated anion volumes against $(ET)_3X_2$ unit cell volumes ($Å^3$).

In Figure 2 the estimated anion volumes are plotted with known stoichiometries which are established by single crystal structural studies. It is evident that small anions favor 3:2 packing while large anions form 2:1 structure.

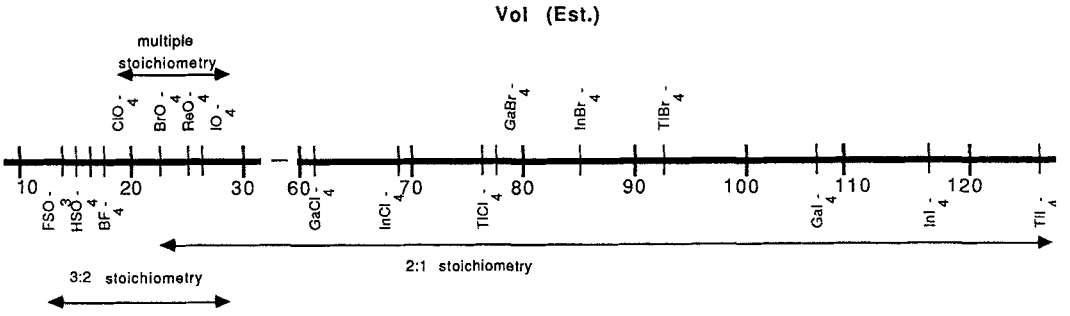

FIGURE 2 Estimated anion volumes vs. known stoichiometries

In the area where ClO_4^-, BrO_4^-, ReO_4^-, and IO_4^- are located, it is labelled as multiple stoichiometry.[18-21] Up to five different stoichiometries have been reported. These medium size anions all form isostructural 3:2 phases and tend to trap solvent molecules in the crystal lattices to give $(ET)_2X(Sol)_{0.5}$ or $(ET)X(Sol)_{0.5}$ stoichiometries. $(ET)_2X$ phases are reported for BrO_4^- and ReO_4^- anions. The physical properties of these materials include superconductivity under pressure and metallic behavior.[19,20] For large anions MX_4^-

(M = Ga, In, Tl; X = Cl, Br, I) only two structures are known, i.e., $(ET)_2InBr_4$[16] and $(ET)_2InI_4$.[22] For the single stoichiometry region (3:2 or 2:1), crystal packing requirements dominate the resulting stoichiometries. However, in the multiple stoichiometry region, kinetic effects are also involved since the product distribution often varies from cell to cell.

The room temperature ESR peak-to-peak linewidth (G), conductivity (S/cm), and activation energy (eV) of recently prepared $(ET)_2MX_4$ compounds are listed in Table I.

TABLE I Room temperature ESR linewidth, conductivity, and activation energy of $(ET)_2MX_4$.

Anion	Linewidth(G)	σ_{300}(S/cm)	E_a(eV)
$GaCl_4$	9-10, 14[a]	0.05	0.19
$InCl_4$	8-10	1.1	0.09
$TlCl_4$	8-10	0.27	0.07
$InBr_4$[16]	8-10, 42-47[a]	0.05-0.5	0.15
$TlBr_4$	8-11	0.5	0.07
GaI_4	14-16, 39-51[a]	9.2×10^{-6}	0.07
InI_4[b]	14-19	1.1×10^{-3}	0.12
TlI_4[b]	17-21	5.8×10^{-4}	0.09

[a]Different phase and the conductivity was not measured.
[b]Anions are susceptible to decomposition. α and β-$(ET)_2I_3$ phases have been observed for InI_4 cell and $(ET)_2(TlI_4)(I_3)$ has been reported.[13]

For M = Ga, In, Tl and X = Cl, Br, all five compounds are thin long needles. They show the same ESR linewidth (8-10 G) and

are expected to have similar structures and physical properties. Compounds which give 14-19 G linewidth belong to a different structure type and one of them, $(ET)_2InI_4$, has been characterized. Conductivity measurements on a few of these compounds indicate that they are all semiconductors with E_a = 0.07-0.19 eV. Variable temperature ESR experiments have been carried out on $InCl_4$ and $TlBr_4$ salts (Figure 3). Monotonic linewidth decrease from 300 to 100 K are observed in both cases. Although the region below 100 K is yet to be investigated, preliminary results are similar to that of β'-$(ET)_2X$, X = ICl_2, $AuCl_2$, which undergo antiferromagnetic coupling at 22 and 32 K, respectively.[23,24]

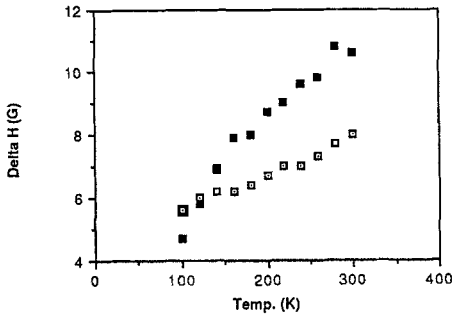

FIGURE 3 Single crystal ESR linewidth against temperature for $(ET)_2TlBr_4$ (solid) and $(ET)_2InCl_4$ (hollow).

ET SALTS WITH LINEAR ANIONS

There are two types of linear anions, i.e., polyhalides and MX_2^- where M is a transition metal at +1 oxidation state and X is either a halide or pseudohalide. Care must be taken to exclude moisture and oxygen for AuX_2^- anions in order to grow high quality crystals. All ET salts containing linear anions exhibit 2:1 stoichiometry. However, among ET_2X complexes there are many different types of crystal packing motifs which result in totally different physical properties. We designate β phase as a unit cell which is ~800 $Å^3$ and contains one

formula unit (z = 1) and α phase as 1600 $Å^3$ and z = 2. Various anions following decreasing anion length are listed in Table II along with known $(ET)_2X$ phases, unit cell volume and physical properties for the β phase.

Table II Summary of $(ET)_2X$ salts with linear anions.[10,12]

Anion	Length(Å)	$(ET)_2X$ phase with ESR linewidth(G)	Unit cell volume ($Å^3$)[a]	Electrical property[b]
I_3^-	10.14	α(90), β(20-25)	855.9	T_c = 1.4K
AuI_2^-	9.42	β(18-20)	845.2	T_c = 4.98K
I_2Br^-	9.72	α, β(20-25)	842.3	Metallic to 0.4K
IBr_2^-	9.30	α(50), β(20-25)	828.7	T_c = 2.8K
$BrICl^-$	9.01	α(50), β'(10)	821.3	Semiconductor
$IAuBr^-$	8.98	β''	826.3	
ICl_2^-	8.72	β'(6-10)	814.3	T_N = 22 K
$AuBr_2^-$	8.70	α'(~40), β''(~40)	811.8	Metallic to 1.4K
$AuCl_2^-$	8.14	β'(6-10)	800.7	T_N = 32K

[a]β-phase at 298 K [b]β-phase

All α-$(ET)_2X$ compounds are semiconductors. They grow simultaneously with the β phase and the multiple phase phenomenon is due to a kinetic effect (vide infra). When I_3^- and I_2Br^- are used as anions, with proper choice of solvents (e.g. dried THF) and under slow growth conditions, the β phase is grown exclusively. Most of the linear anions adopt the β-like structure along with other phases except for $Ag(CN)_2^-$ and $Au(CN)_2^-$ where only α' structures are reported.[25] There are three types of β structures, i.e., β, β'[23-24] and β''[26-28] (Figure 4) and the angle between the "stacking axis" and the short in-plane axis of ET for these three β phases are 90, 90-60, and 60, respectively.

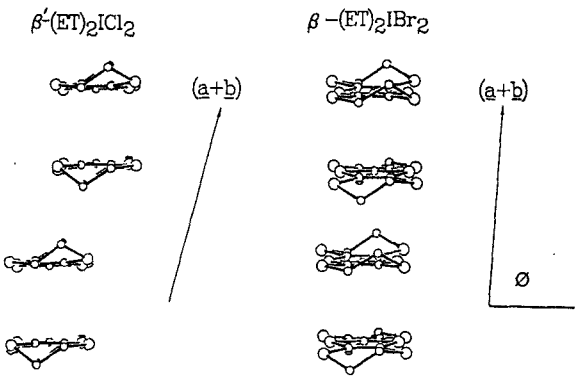

FIGURE 4 Stacking pattern of β and β' phases.

The β' structure clearly shows dimerization along the stack. The electrical property is 1D semiconducting and low temperature ESR as well as magnetic susceptibility measurement indicate antiferromagnetic coupling. The packing motif of the β'' structure is similar to that of $(ET)_2(ClO_4)(TCE)_{0.5}$ and band calculations suggest semimetallic behavior which is consistent with the fact that β''-$(ET)_2AuBr_2$ is metallic to 1.4 K but does not superconduct even under pressures up to 5.6 kbar. There are several techniques for phase identification. Besides single crystal x-ray diffraction, the ESR linewidth technique is very sensitive and efficient. Usually different phases give different room temperature ESR linewidths but due to the large anisotropy in linewidths, an overlap is possible, e.g. $AuBr_2^-$ anion (Table II). Another limitation is that a few phases which are prepared by iodine oxidation, do not give apparent ESR signals.[13] A less conventional technique for non-destructive phase identification is reflective infrared with microscope attachment.[29] While α phases give a featureless continuum from 4000 to 600 cm^{-1}, β phases show a sharp vibrational band near 1280 cm^{-1}. All three β-$(ET)_2X$ salts show superconductivity except that disordered I_2Br^- anion has a detrimental effect.

The superconductivity in β-$(ET)_2X$ complexes has been confirmed in many physical measurements, namely four probe conductivity, rf penetration depth, specific heat,[30] tunnelling gap measurement,[31] etc. β-$(ET)_2I_3$ has interesting structural features. At room temperature it has disordered ethylene ends due to two possible configurations; below 200 K it modulates to alleviate unfavorable ethylene hydrogen and anion interactions;[32] under anisotropic pressure, however, it further transforms to a more efficient packing motif, β*, which is a high T_c state (8 K) yet avoids unfavorably close H•••I contacts.[9] The correlation between T_c and unit cell volume has been rationalized in terms of electron-phonon coupling and lattice softness.[33]

Recently, a report suggested that α-$(ET)_2I_3$ is transformed to β-$(ET)_2I_3$ through heating.[34] In order to identify whether this transformation is general among other anions, we carried out a high temperature ESR study on α-$(ET)_2IBr_2$. We are interested in the IBr_2^- anion because while β-$(ET)_2I_3$ can be grown exclusively (vide supra), β- and α-$(ET)_2IBr_2$ always grow simultaneously and no procedure is known for separating these phases other than characterizing every crystal, which is extremely tedious. We took a single crystal of α-$(ET)_2IBr_2$ and slowly heated it in an ESR cavity. Linewidth broadened slightly from 50 G at 300 K to 70 G at 400 K (Figure 5).

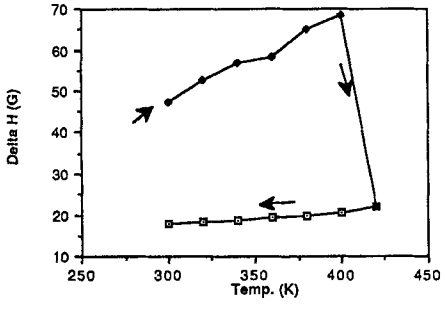

FIGURE 5 Solid state transformation of α- to β-$(ET)_2IBr_2$ followed by the ESR linewidth technique.

A sudden drop to 23 G in linewidth is observed at 410 K. The crystal remains β phase after the transformation whether it is slow-cooled or quenched from 410 K to room temperature. The most interesting part of this experiment is that the phase transition temperature is far below its melting point and the crystal remains crystalline. β phase unit cell is confirmed by Weissenberg x-ray diffraction and this is an authentic solid state to solid state phase transformation.

CONCLUSION

In this article we limited our discussion to ET salts with tetrahedral and linear anions. We demonstrated that anion size plays an important role in determining the stoichiometry of ET based materials. Among the tetrahedral anions, metallic behavior is observed only when medium size anions are present. Linear anions of different length can modify the ET network and the corresponding electrical properties. The semiconducting α phase is converted to the superconducting β phase via solid state transformation. In order to modify the commonly observed 1D system in organics which leads to low temperature instability, many current efforts have been devoted to increasing the dimensionality in the donor network and decreasing the on-site Coulomb repulsion by using Se, Te, or mixed S/Se, S/Te donors.[35-38] Superconductivity has been reported in a half-ET half-TMTSF unsymmetric donor system.[39] Although the highest T_c known to date has jumped to 93 K in cuprate based superconductors,[40] there are remarkable similarities in terms of the 2D nature in both inorganic and ET systems. The organic metals still offer a challenge in terms of rational design and basic understanding of the structure and property correlations.

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