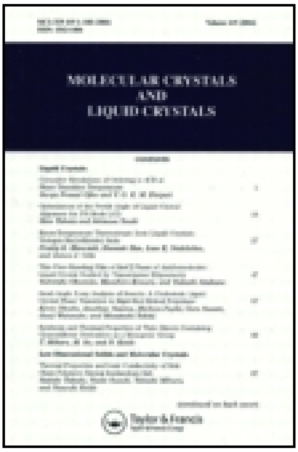

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SYNTHESIS AND CHARACTERIZATION OF RADICAL CATION SALTS DERIVED FROM TETRASELENAFULVALENE AND BIS(ETHYLENE-DITHIO)TETRASELENAFULVALENE

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Abstract New synthetic routes to bis(ethylenedithio)tetraselenafulvalene (BETS) were explored, starting from tetraselenafulvalene (TSF). Several radical cation salts of TSF and BETS were prepared by electrocrystallization. A new kappa phase salt of BETS, κ-$(BETS)_2GaCl_4$, displayed an interesting resistance-temperature profile from 300-35K.

Keywords: organic superconductors, bis(ethylenedithio)tetraselenafulvalene, tetraselenafulvalene

INTRODUCTION

More than forty organic superconductors have been discovered since superconductivity was first observed in di(tetramethyltetraselenafulvalene) hexafluorophosphate [$(TMTSF)_2PF_6$, superconducting transition temperature (T_c) = 0.9K at ~6.5 kbar] in 1980.[1-3] It is noteworthy, however, that about one half of the compounds in this group have been prepared from a single heterocyclic compound, bis(ethylenedithio)-tetrathiafulvalene (**1**, commonly abbreviated BEDT-TTF or, simply, ET).[2] Moreover, ET has been the source of many of the organic superconductors with the highest T_c's. In view of the fact that over 140 radical cation salts have been synthesized from ET in the quest for improved superconducting systems,[4] it is clear that new synthetic metal precursors must be sought in order to maintain the impressive progress[2] that has been achieved in organic superconductor research in the past decade.

The normal and superconducting properties of the best ET-based superconductors bear a much closer resemblance to the high-T_c cuprates than to the conventional BCS superconductors.[5] Both classes of compounds possess layered structures with 2D or quasi-2D conducting networks. Many parallels are also seen in the detailed physics of the organics and the cuprates. There are, of course, significant differences. For example, the band widths of the cuprates are nearly an order of magnitude greater than

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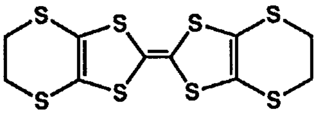
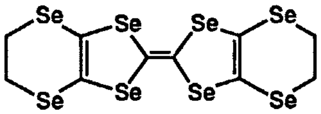
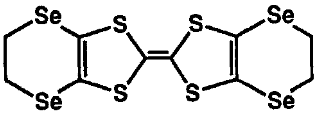
the organics. One readily conceivable way of increasing the band widths of the organic materials would be to replace the sulfurs with chalcogens of higher atomic number.[6] Some possibilities are shown in structures **2**-**4**. All of these compounds have been prepared previously,[7] but their suitability as conducting solid starting materials has not been systematically investigated. This situation is due to a number of factors: limited solubilities of **2**-**4** in common electrocrystallization solvents, discouraging preliminary studies, and the lack of facile synthetic routes to **2**-**4**. In 1989, a convenient one-pot synthesis of bis(ethylenediseleno)tetrathiofulvalene (BEDS-TTF, BEST, **3**) was published;[8] a number of new BEST salts have been prepared, but none exhibit superconductivity.[4]



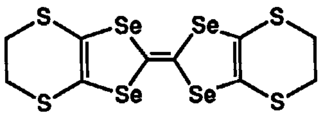
1
BEDT-TTF (ET)



2
BEDS-TSF



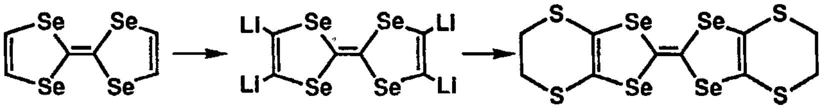
3
BEDS-TTF (BEST)



4
BEDT-TSF (BETS)

In 1983 the first synthesis of bis(ethylenedithio)tetraselenafulvalene (BEDT-TSF, BETS, **4**) was reported.[7e] BETS is a particularly attractive building block for conducting solids. It is roughly the same shape as ET and possesses the terminal ethylenedithio groups that are known to play key roles in several superconducting ET salts.[4] Moreover, the larger inner selenium atoms should facilitate transverse intermolecular interactions.

The main objectives of the present study were to devise an efficient synthesis of BETS and to systematically investigate the preparation and properties of its radical cation salts. The broad synthetic strategy that was adopted for the synthesis of BETS involved the functionalization of tetraselenafulvalene (**5** ⟶ **6** ⟶ **4**). While the present work was in progress, a preliminary report was published of a new synthesis of BETS and the preparation of a number of conducting BETS salts.[9]



5 **6** **4**

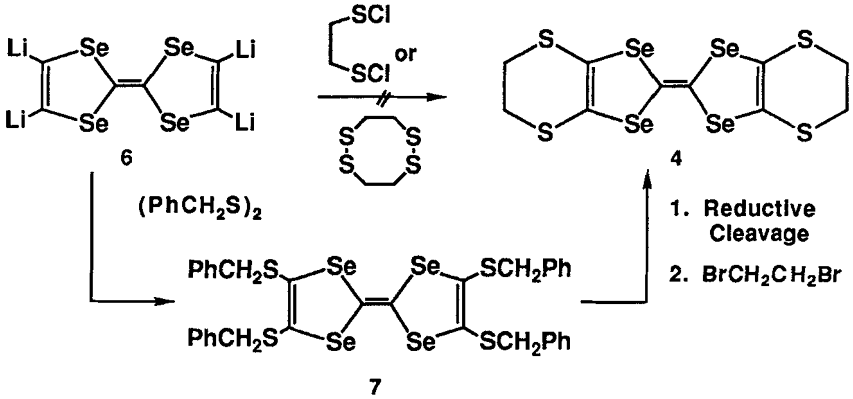
EXPERIMENTAL

The electrochemical syntheses were carried out in glass H-cells utilizing platinum electrodes and following standard electrocrystallization procedures.[10] Electrical resistivity measurements were made using the standard four-probe technique.[11] The X-ray diffractometer that was utilized for the single crystal study of κ-$(BETS)_2GaCl_4$ was designed and constructed locally and has been described previously, as have the data analysis procedures.[12]

RESULTS AND DISCUSSION

BETS Synthesis

Scheme 1 outlines several potential routes to BETS. Numerous attempts to obtain BETS directly from the tetralithio intermediate **6**,[13] employing either 1,2,5,6-tetrathiocyclooctane or the 1,2-disulfenyl chloride of ethane, failed to yield any detectable product (TLC). The most promising pathway at present appears to be one proceeding *via* the tetrabenzylthio intermediate **7**, which can be reproducibly prepared from TSF in over 50% yield. An efficient method for carrying out the final step is still being sought.



SCHEME 1 Potential synthetic routes to BETS.

TSF Salts

About a dozen radical cation salts have been prepared from tetraselenafulvalene.[14] The feasibility of combining this donor with the polymeric copper (I) thiocyanate and copper (I) dicyanamide halide anion systems that have produced some of the best organic superconductors to date[15,16] was explored briefly. A variety of experimental conditions failed to yield acceptable quality crystals with the copper (I) thiocyanate counter ion. The growth of copper (I) dicyanamide halide (X = Cl, Br using $Ph_4PN(CN)_2$ and CuX) crystals from TSF was evaluated in chlorobenzene, tetrahydrofuran, 1,1,2-trichloroethane (TCE), and TCE: ethanol mixtures. TCE: 5% ethanol turned out to be the solvent of choice. X-ray crystallographic examination of a large number of shiny black chloride and bromide plates indicated that both systems were twinned. One useful piece of structural information that was obtained was that the two halides appeared to be isomorphous. Four-probe conductivity measurements indicated that both compounds were semiconductors: $\rho_{300}(Cl)\sim 8 \times 10^3\ \Omega$ cm, $E_a\sim$ 300(15)meV; $\rho_{300}(Br)\sim 5 \times 10^3\ \Omega$ cm, $E_a\sim$ 225(25) meV.

BETS Salts

The attempted growth of BETS salts with the same polymeric anions and the same solvents yielded few crystals of any interest. The only donor-anion combination with some promise was BETS-copper (I) dicyanamide bromide.

In contrast to the polymeric anion experiments, electrocrystallization studies of BETS with *n*-Bu_4NGaCl_4 in TCE: 5% EtOH produced diamond-shaped black plates with ease (T = 40°C, current density = 0.1-1 $\mu A/cm^2$). A small black plate was examined at 105K by X-ray crystallography. It was a mixed-valent compound, $(BETS)_2GaCl_4$, belonging to the Pnma space group (Z = 4). Unit cell dimensions: a = 11.537(4) Å, b = 35.739(14) Å, and c = 8.373(3), Å, yielding a unit cell volume of 3452.5Å.[3]

The conformation of the partially oxidized BETS units in $(BETS)_2GaCl_4$ is similar to the "eclipsed" conformation that is observed in ET charge transfer salts.[4] It is interesting to note the contrasting conformational preference of the ethylene groups in isomeric BEST (**3**) salts; they protrude significantly from the plane, because of the longer (0.1Å) C-Se bonds in the six-membered rings.[4] The disruption of efficient molecular packing by these protrusions may be one of the reasons for the poor conducting properties of BEST salts. The crystal packing of $(BETS)_2GaCl_4$ consists of layers of anions lying on mirror planes at y = 1/4 and 3/4, alternating with layers of partially oxidized BETS molecules. The 36 Å b axis lies in the layered direction, and the a and c axes run parallel to the cation and anion layers. In Figure 1 a radical cation layer is viewed looking down the b axis toward the ethylenedithio end groups. The BETS components are packed in the kappa structural motif.[4]

The room temperature resistance of κ-$(BETS)_2GaCl_4$ crystals (leads mounted on the faces of the plates) is about 0.04-0.05 Ω cm. The temperature dependence of the

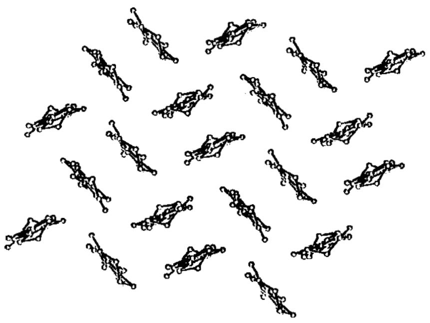


FIGURE 1 The κ-phase packing of κ-$(BETS)_2GaCl_4$.

relative resistivity is shown in Figure 2. The plot is essentially flat (slightly metallic in some crystals) from 300K to about 270K, where it becomes semiconductive (E_a = 20(4) meV). Near 80-100K the resistance decreases. Problems associated with the crystals cracking in the vicinity of 100K prevented an unambiguous mapping of the resistance below this point. Low-temperature studies are continuing. The low temperature resistive behavior of κ-$(BETS)_2GaCl_4$ deserves careful scrutiny, since the general profile of the plot in Figure 2 is reminiscent of the profiles observed in the important superconducting systems, κ-$(ET)_2Cu(NCS)_2$[15] and κ-$(ET)_2Cu[N(CN)_2]Br$.[16]

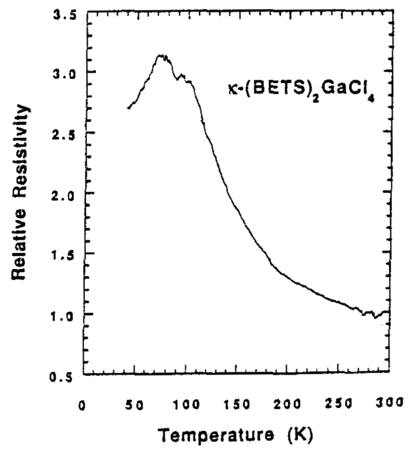


FIGURE 2 Plot of relative resistivity vs. temp for κ-$(BETS)_2GaCl_4$.

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