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| Annua)<br>Design and Synthesis of Potential Organic Superconductors                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                 | 5. FUNDING NUMBERS<br><br>61103D 3484 RS                                                  |                            |
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| 13. ABSTRACT (Maximum 200 words)<br><br>A number of mixed-valence (2:1), conducting salts of bis(ethylenedithio)tetraselenafulvalene (BETS) have been prepared. Four (GaCl <sub>4</sub> , SbF <sub>6</sub> , CF <sub>3</sub> SO <sub>3</sub> and Cu[N(CN) <sub>2</sub> ]Br) have been characterized in detail (X-ray crystallography, DC resistivity from 300-10K, rf penetration depth measurements (0.5K), pressure studies from 0.5-5 kbar at 4K, and tight-binding band calculations). The salts are highly metallic to low temperatures but do not exhibit superconductivity under the experimental conditions explored.<br><br>The synthesis of a new synthetic metal precursor, bis(ethylenedithio)tetrathionaphthalene (BEDT-TTN), is about three-quarters completed.<br><br>Spin density wave (SDW) and charge density wave (CDW) phenomena of three organic superconductors (κ-(BEDT-TTF)Cu[N(CN) <sub>2</sub> ]Cl, (TMTSF) <sub>2</sub> PF <sub>6</sub> , and (TMTSF) <sub>2</sub> ReO <sub>4</sub> , where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and TMTSF is tetramethyltetraselenafulvalene) have been studied in collaboration with Professor J.W. Brill (Department of Physics, University of Kentucky). The three organic metals avert the SDW and CDW transitions under pressure and become superconductors.<br><br>DTIC QUALITY INSPECTED 8 |                                                                 |                                                                                           |                            |
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Design and Synthesis of Organic Superconductors

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ABSTRACT

A number of mixed-valence (2:1), conducting salts of bis(ethylenedithio)tetraselenafulvalene (BETS) have been prepared. Four ( $\text{GaCl}_4$ ,  $\text{SbF}_6$ ,  $\text{CF}_3\text{SO}_3$  and  $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ ) have been characterized in detail (X-ray crystallography, DC resistivity from 300-10K, rf penetration depth measurements (0.5K), pressure studies from 0.5-5 kbar at 4K, and tight-binding band calculations). The salts are highly metallic to low temperatures but do not exhibit superconductivity under the experimental conditions explored.

The synthesis of a new synthetic metal precursor, bis(ethylenedithio)tetrathionaphthalene (BEDT-TTN), is about three-quarters completed.

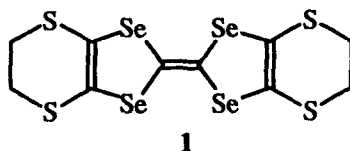
Spin density wave (SDW) and charge density wave (CDW) phenomena of three organic superconductors ( $\kappa$ -(BEDT-TTF) $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ ,  $(\text{TMTSF})_2\text{PF}_6$ , and  $(\text{TMTSF})_2\text{ReO}_4$ , where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and TMTSF is tetramethyltetraselenafulvalene) have been studied in collaboration with Professor J.W. Brill (Department of Physics, University of Kentucky). The three organic metals avert the SDW and CDW transitions under pressure and become superconductors.

RESEARCH SUMMARY

A brief summary is provided of completed research on radical-cation conductors (Donor Systems), radical-anion conductors (Acceptor Systems), and collaborative research projects.

A. Donor Systems

1. Bis(ethylenedithio)tetraselenafulvalene (BETS, 1)



The synthesis and characterization of new conducting salts of BETS has been actively pursued.

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a. Growth of conducting salts. The preparations of a number of radical cation salts of the BETS donor ( $\text{SbF}_6$ ,  $\text{AuCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{TlI}_4$ ,  $\text{GaBr}_4$ ,  $\text{GaCl}_4$ ,  $\text{I}_3$ ,  $\text{IBr}_2$ ,  $\text{CF}_3\text{SO}_3$ ,  $\text{CH}_3\text{SO}_3$ ,  $\text{Cu}(\text{NCS})_2$ , and  $\text{Cu}[\text{N}(\text{CN})_2]\text{X}$  where  $\text{X}=\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) were explored employing standard electrochemical procedures.<sup>1</sup> 1,1,2-Trichloroethane (TCE), TCE-ethanol mixtures, chlorobenzene, and benzonitrile were screened as electrocrystallization solvents. For most of the counterions, TCE ethanol mixtures (5-10% ethanol by volume) provided the best quality crystals. Because of the limited solubility of BETS in most organic solvents, the electrocrystallizations were carried out at 40-50°C. Constant currents of 0.5-1.0  $\mu\text{A}/\text{cm}^2$  were utilized, and the reactions were conducted under dry nitrogen. Four counterion systems have been examined in detail ( $\text{SbF}_6$ ,  $\text{GaCl}_4$ ,  $\text{CF}_3\text{SO}_3$ ,  $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ ).

b. Molecular structures. Single crystal X-ray structures of the four BETS salts were determined at room temperature and ~100K. Key crystallographic parameters are summarized in **Table 1**.

**Table 1.** X-ray crystallographic data for the  $(\text{BETS})_2\text{X}$  salts

| X                                           | T(°K) | Space group        | Cell dimensions (Å)                        | Interaxial angles (°)                          | Unit cell volume (Å <sup>3</sup> ) | Z |
|---------------------------------------------|-------|--------------------|--------------------------------------------|------------------------------------------------|------------------------------------|---|
| $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ | 293   | Pnma               | a=12.961(2)<br>b=31.005(5)<br>c= 8.576(1)  | $\alpha=90$<br>$\beta=90$<br>$\gamma=90$       | 3447                               | 4 |
| $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ | 95    | Pnma               | a=12.755(1)<br>b=30.743(5)<br>c= 8.576(1)  | $\alpha=90$<br>$\beta=90$<br>$\gamma=90$       | 3363                               | 4 |
| $\text{GaCl}_4$                             | 293   | Pnma               | a=11.675(4)<br>b=35.940(14)<br>c= 8.471(3) | $\alpha=90$<br>$\beta=90$<br>$\gamma=90$       | 3555                               | 4 |
| $\text{GaCl}_4$                             | 105   | Pnma               | a=11.537(4)<br>b=35.739(14)<br>c= 8.373(3) | $\alpha=90$<br>$\beta=90$<br>$\gamma=90$       | 3452                               | 4 |
| $\text{CF}_3\text{SO}_3$                    | 293   | P2 <sub>1</sub> /a | a=11.732(2)<br>b= 8.332(1)<br>c=34.972(7)  | $\alpha=90$<br>$\beta=99.68(1)$<br>$\gamma=90$ | 3370                               | 4 |
| $\text{CF}_3\text{SO}_3$                    | 99    | P2 <sub>1</sub> /a | a=11.560(6)<br>b= 8.214(1)<br>c=34.567(1)  | $\alpha=90$<br>$\beta=98.92(0)$<br>$\gamma=90$ | 3243                               | 4 |
| $\text{SbF}_6$                              | 293.5 | C2/c               | a=35.311(9)<br>b= 8.413(1)<br>c=11.590(2)  | $\alpha=90$<br>$\beta=90.41(1)$<br>$\gamma=90$ | 3397                               | 4 |
| $\text{SbF}_6$                              | 102   | Cc                 | a=35.017(7)<br>b= 8.348(1)<br>c=22.417(1)  | $\alpha=90$<br>$\beta=99.96(0)$<br>$\gamma=90$ | 3287                               | 4 |

All of the salts possessed 2:1 donor:anion stoichiometries, layered structures, and kappa packing motifs. In  $\kappa$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> (Pnma) the gallium tetrachloride ions lie on mirror planes at  $y=1/4$  and  $3/4$ ; radical-cation dimer layers alternate with the gallium tetrachloride layers.  $\kappa$ -(BETS)<sub>2</sub>CF<sub>3</sub>SO<sub>3</sub> (P2<sub>1</sub>/a) has two different types of cation layers that alternate with layers of triflate anions. The structure of  $\kappa$ -(BETS)<sub>2</sub>SbF<sub>6</sub> presented formidable crystallographic problems because of disorder in the terminal ethylenedithio groups of the BETS cations. Examination of diffraction data at room temperature and 102K indicated that the crystal belonged to one of the monoclinic space groups Cc or C2/c. Extensive modelling and testing suggested that the appropriate space group is C2/c with both ethylenedithio groups disordered at room temperature and Cc with one end disordered at 102K. The most interesting crystal structure is that of  $\kappa$ -(BETS)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br; it is isostructural with  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br. Of course, the slightly larger selenium atoms cause some modest changes in geometry. The most significant difference appears to be that one of the ethylenedithio groups of  $\kappa$ -(BETS)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br is disordered at 95K with the "staggered" conformation<sup>2</sup> preferred. At this temperature  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br exists exclusively in the "eclipsed" conformation.<sup>2</sup> Detailed analysis of the crystal packings are in progress. Initial results show that the dimeric units of all four salts have the bond-over-ring orientation<sup>3</sup> that is observed in all  $\kappa$ -phase ET superconductors.

c. Resistivity measurements. Room temperature, four-probe resistivities of the four salts were in the range 50-0.06 Scm<sup>-1</sup>.  $\kappa$ -(BETS)<sub>2</sub>SbF<sub>6</sub> is metallic to at least 15K. The resistive profile of  $\kappa$ -(BETS)GaCl<sub>4</sub> is somewhat reminiscent of those of  $\kappa$ -(ET)<sub>2</sub>Cu(NCS)<sub>2</sub><sup>4</sup> and  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br<sup>5</sup> down to about 65K, where extensive cracking of the crystals was observed.  $\kappa$ -(BETS)<sub>2</sub>CF<sub>3</sub>SO<sub>3</sub> is metallic to 80K, where it undergoes a T<sub>MI</sub> transition. All of the  $\kappa$ -(BETS)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br crystals were diamond shaped plates, and the leads were mounted along the a-axis<sup>5</sup>. Nevertheless, the results were variable. Work continues on this system.

d. Rf penetration depth measurements and pressure studies. No Meissner effect was detected at 0.5K in the SbF<sub>6</sub>, GaCl<sub>4</sub>, and Cu[N(CN)<sub>2</sub>]Br salts employing the rf penetration depth technique (~500 KHz).<sup>6</sup> Also, rf impedance measurements<sup>7</sup> at 0.5-5 kbar at temperatures as low as 4K failed to detect superconductivity in  $\kappa$ -(BETS)<sub>2</sub>X crystals, where X=SbF<sub>6</sub>, GaCl<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>, and Cu[N(CN)<sub>2</sub>]Br.

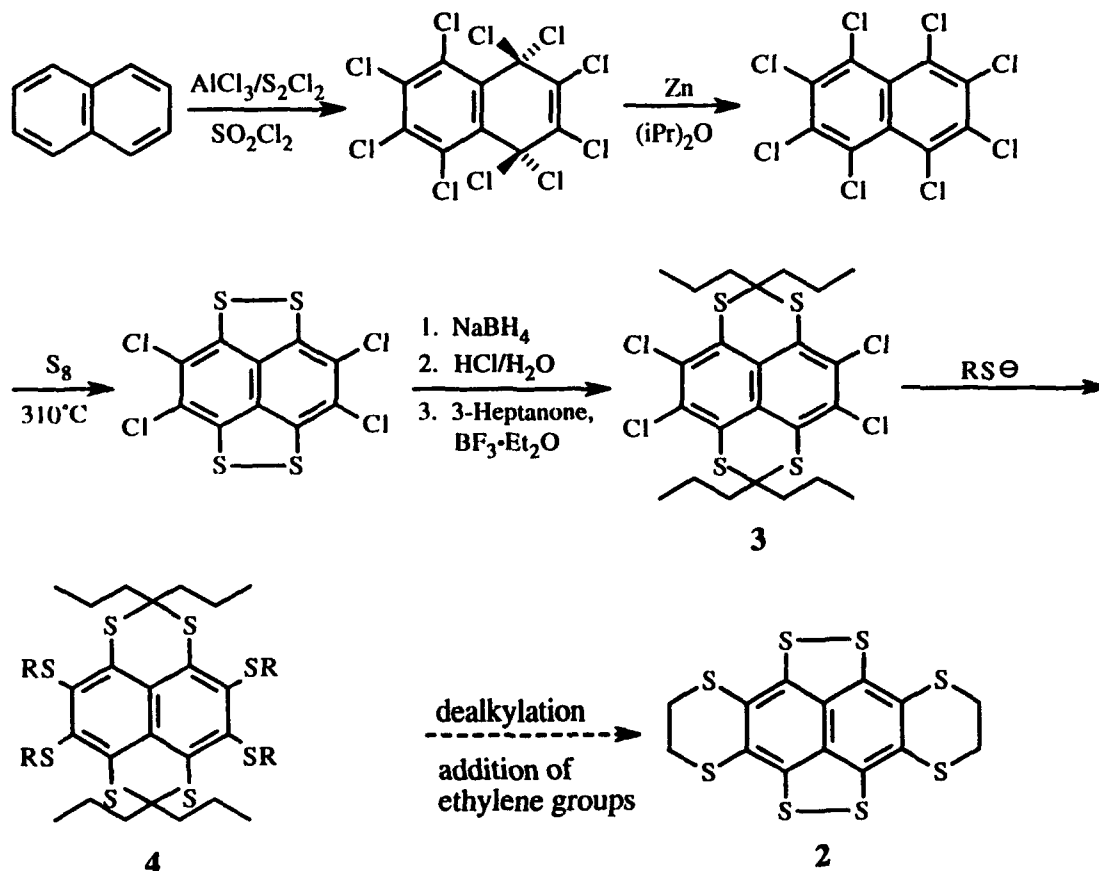
e. Band electronic structures. Preliminary tight-binding band calculations<sup>3</sup> have been completed on the donor layers of the four BETS salts (low temperature crystallographic data). The calculations employed the extended Hückel method and utilized single- $\zeta$ , Slater-type orbitals for the s and p orbitals of the C, S, and Se atoms.

The Fermi surfaces of all of the systems consist of closed, overlapping ovals centered at  $\Gamma$  and its equivalent points in reciprocal space, indicating 2-D metallic character.

The BETS salts examined so far are highly metallic and all possess the kappa packing motif. This system looks very promising and merits thorough investigation.

## 2. Bis(ethylenedithio)tetrathionaphthalene (BEDT-TTN 2).

The proposed synthetic route to BEDT-TTN is shown in Scheme 1.



**Scheme 1.** Proposed synthetic route for the preparation of BEDT-TTN.

A highly efficient synthesis of intermediate **3** has been worked out. Nucleophilic displacement of all four chlorines of **3** employing a variety of nucleophiles has proven to be very difficult. Once the first nucleophile enters, subsequent reactions tend to be on the entering nucleophile and not the remaining chlorines. Systematic screening of various sulfur nucleophiles, solvents and temperature is in progress.

## B. Acceptor Systems

Radical anion based conductors are far more air-sensitive in general than are their radical cation counterparts. This is most likely due to facile oxidation of the radical anions by dioxygen.

A Vacuum Atmospheres glove box has been purchased for use in the growth and characterization of radical anion conductors. The glove box has been vibrationally isolated and equipped for electrocrystallization studies. The methodology for handling air-sensitive materials is being developed.

### C. Collaborations

Several studies with the Brill group at the University of Kentucky have been completed. Personnel from Indiana and Kentucky have exchanged visits to each others facilities.

#### 1. AC Calorimetry at Charge Density Wave (CDW) and Spin Density Wave (SDW) Transitions.

The specific heats at the SDW transition in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl and the CDW transition in (TMTSF)<sub>2</sub>ReO<sub>4</sub> have been measured. No anomaly is observed in the SDW transition. For (TMTSF)<sub>2</sub>ReO<sub>4</sub> there is a sample-dependent latent heat associated with anion ordering.

#### 2. Electric Field Dependence of Young's Modulus of (TMTSF)<sub>2</sub>PF<sub>6</sub>.

The Young's modulus (Y) and internal friction (1/Q) in (TMTSF)<sub>2</sub>PF<sub>6</sub> have measured at 5.5K as functions of electric field. No changes ( $\Delta Y/Y$ ,  $\Delta 1/Q < 2 \times 10^{-4}$ ) are observed at fields up to 100 E<sub>T</sub>, the threshold for SDW depinning, in contrast to what is observed for many sliding CDW materials. A possible explanation is that bulk depinning of the SDW is not observed.

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