CRYSTAL AND ELECTRONIC STRUCTURES OF CATION RADICAL SALTS BASED ON BEDSe-TSeF, Se-ANALOGUE OF BEDT-TTF

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ABSTRACT
The Se-based organic donors, BEDSe-TSeF and BPDS-TSeF, were synthesized from carbon diselenide. In the neutral state, these molecules are non-planar and paired.

Three types of cation radical salts of BEDSe-TSeF were electrochemically prepared and showed multiphasic characters. (BEDSe-TSeF)PF$_6$ is a semiconductor, but its crystal and electronic structures would predict the existence of the three-dimensional (3D) organic metal. Although the crystal structure of (BEDSe-TSeF)$_2$AuBr$_2$ is very similar to that of the superconducting β-type BEDT-TTF salt, this compound is a semiconductor and has a quasi-1D electronic structure. (BEDSe-TSeF)AuBr$_2$ has a complicated 2D crystal structure, and is highly conductive.

INTRODUCTION
Since the discovery of the superconductivity of the BEDT-TTF salts, the multi-dimensional system has attracted considerable interest. BEDSe-TSeF (ES), and BPDS-TSeF (PS), Se-analogues of the BEDT-TTF family, are the key-donors in the design of the organic metal and superconductor. In this paper, we report multiphasic characters of the BEDSe-TSeF salts.

\[ \text{BEDSe-TSeF (X=-(CH}_2)_2-) } \]  
\[ \text{BPDS-TSeF (X=-(CH}_3)_3-) } \]  

Abbreviations used: BEDT-TTF(ET) = bis(ethyleneedithio)tetrathiafulvalene, 
BEDSe-TSeF(ES) = bis(ethylene diseleno)tetraselenafulvalene, BPDS-TSeF(PS) = bis(propylene diseleno)tetraselenafulvalene.
RESULTS

Neutral BEDSe-TSeF and BPDSe-TSeF molecules

BEDSe-TSeF was synthesized according to the method of Lee et al. [1]. BPDSe-TSeF was obtained by almost same procedure. The crystal of neutral BEDSe-TSeF is isostructural with that of BEDT-TTF [2], which indicates that the packing motif of the BEDSe-TSeF molecule is very similar to that of BEDT-TTF. The crystal contains pairs of BEDSe-TSeF molecules (Fig. 1). The neutral BEDSe-TSeF molecule is non-planar. Compared to BEDT-TTF, the crystal of BEDSe-TSeF increases in the number of the intra- and inter-dimer chalcogen-chalcogen contacts shorter than the van der Waals distance.

The crystal of BPDSe-TSeF also contains paired BPDSe-TSeF molecules. The neutral BPDSe-TSeF molecule is non-planar (Fig. 1).

Fig. 1. Paired BEDSe-TSeF (a) and BPDSe-TSeF (b) molecules.

Crystal and electronic structures of cation radical salts of BEDSe-TSeF

The cation radical salts based on BEDSe-TSeF were obtained by electrochemical oxidation of solutions containing BEDSe-TSeF and supporting electrolyte under N2. Crystal data are given in Table 1.

TABLE 1
Crystal data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>a</th>
<th>b</th>
<th>c (Å)</th>
<th>α</th>
<th>β</th>
<th>γ (°)</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEDSe-TSeF(PS)</td>
<td>M P21/c</td>
<td>10.871</td>
<td>12.681</td>
<td>13.353</td>
<td>94.59</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ES)PF6</td>
<td>M C2/m</td>
<td>14.868</td>
<td>11.003</td>
<td>6.114</td>
<td>104.07</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ES)2AuBr2</td>
<td>T PT</td>
<td>17.210</td>
<td>8.101</td>
<td>6.815</td>
<td>106.39</td>
<td>95.78</td>
<td>103.02</td>
<td>1</td>
</tr>
</tbody>
</table>

M: monoclinic, T: triclinic.
(BEDSe-TSeF)PF$_6$ [3]. (BEDSe-TSeF)PF$_6$ is a semiconductor with rather high 
$\sigma_{R.T.}$ (=7 S cm$^{-1}$). In the crystal of (BEDSe-TSeF)PF$_6$, the (BEDSe-TSeF)$^+$ units 
are stacked uniformly along the c axis. In this uniform stack, intermolecular 
Se$\cdots$Se distances slightly longer than the van der Waals distance (4.0 Å) are 
observed. Additional two types of short interstack Se$\cdots$Se distances (3.56 and 
3.98 Å) along the <114> and <112> directions lead to the 3D Se$\cdots$Se network. 
In this structure, the side-by-side arrangement, the most characteristic 
structural feature of the BEDT-TTF compounds, does not exist.

In order to investigate the effect of the 3D Se$\cdots$Se network on the 
electronic structure, we first calculated intermolecular overlap integrals (S) 
of the HOMO (highest occupied molecular orbital) of BEDSe-TSeF [4]. Anisotropy 
of S values is smaller than that in the Bechgaard salts (TMTSF)$_2$X. A simple 
tight-binding band calculation [5] gives the Fermi surface which consists of 
two distorted planes. In spite of the 3D Se$\cdots$Se network, the Fermi surface 
remains open, which is related to the degree of band filling. In this 
compound, the energy band is half-filled. If the conduction level is 3/4 
filled, we obtain the 3D closed Fermi surface. This means that the 2:1 salt 
with the similar 3D Se$\cdots$Se network would be a 3D metal.

(BEDSe-TSeF)$_2$AuBr$_2$ [6]. We have obtained two types of AuBr$_2$ salts of 
BEDSe-TSeF; (BEDSe-TSeF)$_2$AuBr$_2$ and (BEDSe-TSeF)AuBr$_2$.

The crystal structure of (BEDSe-TSeF)$_2$AuBr$_2$ is very similar to that of the 
organic superconductor $\beta$-(BEDT-TTF)$_2$X (X=I$_3$, IBr$_2$, and AuI$_2$) (Fig. 3). The 
crystal contains dimers of BEDSe-TSeF units, which align along the b axis. 
Along the c axis, there exists the side-by-side arrangement of BEDSe-TSeF 
molecules. Compared to the BEDT-TTF compounds, the replacement of the
Fig. 3. Crystal structure of (BEDSe-TSeF)$_2$AuBr$_2$.

Fig. 4. Energy band and "Fermi surface" of (BEDSe-TSeF)$_2$AuBr$_2$.

Chalcogen atom (S + Se) has added short intermolecular chalcogen-chalcogen distances based on the inner selenium atoms.

This compound is a semiconductor. Figure 4 shows energy band and "Fermi surface" of (BEDSe-TSeF)$_2$AuBr$_2$ obtained by the simple tight-binding method. Unlike the $\beta$-type salt with the 2D-closed Fermi surface, (BEDSe-TSeF)$_2$AuBr$_2$ has a 1D plane-like "Fermi surface". The HOMO energy bands are separated into the upper and lower bands and there exists a mid gap between them. The upper band is half-filled. In this case, the on-site Coulomb repulsion will make the
system semiconducting, because the existence of the mid gap reduces the effective band width. Such a 1D character of the electronic structure is also observed in $\beta'$-(BEDT-TTF)$_2$I$_3$ which is also semiconducting [7]. This is a result of the large anisotropy of the intermolecular overlap integrals of the HOMO and strong dimerization. It must be emphasized that the sign and absolute value of the intermolecular overlap integral of the HOMO are sensitive to the relative orientation, especially the angle between the molecular plane and the interaction direction [8]. In the $\beta$-type salt with a vestige of the 1D column structure, a small modification of the molecular arrangement causes serious change in the electronic structure and sometimes reduces the system to 1D one.

(BEDSe-TSeF)AuBr$_2$. The crystal of (BEDSe-TSeF)AuBr$_2$ contains a complicated 2D structure (Fig. 5). The unit cell contains a tetradic unit of BEDSe-TSeF and two other BEDSe-TSeF molecules arranged among the tetrads with their

Fig. 5. Crystal structure of (BEDSe-TSeF)AuBr$_2$
molecular planes almost perpendicular to those in the tetrad, leading to the 2D donor sheet parallel to the bc plane. It should be noted that AuBr$_2$ anions are distributed into this cation sheet. We propose that this anion arrangement is closely related to the charge distribution rule accompanied by the increased dimensionality [9]. It should be recalled that in the ionic crystals, the lattice is stabilized mainly by the electrostatic interaction. Increase of the dimensionality means enhancement of the close contacts among the same ions which leads to increase of the electrostatic lattice energy. There will be several ways to avoid such an energetically unfavorable situation. In this compound, the repulsion among the (BEDSe-TSeF)$^+$ cations is reduced by the AuBr$_2^-$ anions distributed into the sheet. In the cation sheet, the anion does not interrupt the conduction path. Indeed, this compound is highly conductive ($\sigma_{R,T} = 150$ Scm$^{-1}$).

CONCLUSIONS

The cation radical salts of BEDSe-TSeF have provided new aspects of the molecular (and crystal) design for the multi-dimensional molecular conductor. The dimensionality of the BEDSe-TSeF compounds ranges from 1D to (potentially) 3D. Various new properties and functions will appear in the multi-dimensional system. BEDSe-TSeF is one of the most important donors which can construct the multi-dimensional system.

REFERENCES

4 The molecular orbitals were calculated by the extended Hückel method. The parameters for the calculations were taken from E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, 14 (1974) 177.
5 The calculations were based on the approximation that the transfer integral is proportional to the overlap integral.