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Crystal and Electronic Structures of (BEDSe-TSeF)$AuBr_2$

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The crystal of the semiconducting 1:1 compound of BEDSe-TSeF, (BEDSe-TSeF)$AuBr_2$ ($\rho_{R.T.}$=7 Ω cm, E_a=0.13 eV) contains a two-dimensional array of closely spaced donor molecules. Half the $AuBr_2$ anions are distributed into this cation sheet, and electrostatically stabilize the sheet structure, indicating a new way to obtain stable multi-dimensional crystal structure.

Recent progress in the organic conductor constructed by BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) has opened a way to a multi-dimensional molecular conductor which is not based on the column structure.[1] The multi-dimensionality frequently circumvents the usual problem of the Peierls instability. There are some molecular designs to enhance the ability to increase the dimensionality of the electronic structure. Selenium substitution is one of the simplest ways. We report here a complicated two-dimensional crystal structure of a 1:1 salt of BEDSe-TSeF (bis(ethylenediseleno)tetraselenafulvalene), a Se-analogue of BEDT-TTF, and consider an electronic structure of this compound. We also report an electronic structure of ε-(BEDT-TTF)$_2I_3(I_8)_{0.5}$ whose packing motif of cations and anions is very similar to that of (BEDSe-TSeF)$AuBr_2$.

BEDSe-TSeF was prepared by the method of Lee et al.[2] Black elongated plates of (BEDSe-TSeF)$AuBr_2$ were electrochemically obtained from a CS_2-benzonitrile (1:1) solution of BEDSe-TSeF and (n-Bu)$_4$N$AuBr_2$ (at a constant current of 1 μA, under N_2). Crystal data: $C_{10}H_8Se_8AuBr_2$, Triclinic, P$\bar{1}$, a=17.63(1), b=16.24(1), c=12.46(1) Å, α=116.64(6), β=107.84(7), γ=92.85(6)°, V=2961 Å^3, Z=6. The structure was solved by the direct method and refined by the block-diagonal least-squares method, using independent 4540 reflections ($2\theta \leq 55°$, $|F_o| > 3\sigma(|F_o|)$). The final R value was 0.083.

As shown in Fig. 1, (BEDSe-TSeF)$AuBr_2$ has a complicated two-dimensional crystal structure. A unit cell contains a tetradic BEDSe-TSeF unit (molecules 1, 1', 2, and 2', in Fig. 1b) and two other BEDSe-TSeF molecules (molecules 3 and 3') arranged among the tetrads with their molecular planes almost perpendicular to those in the tetrad. Dihedral angles between molecular planes are 81° (1'•••3)

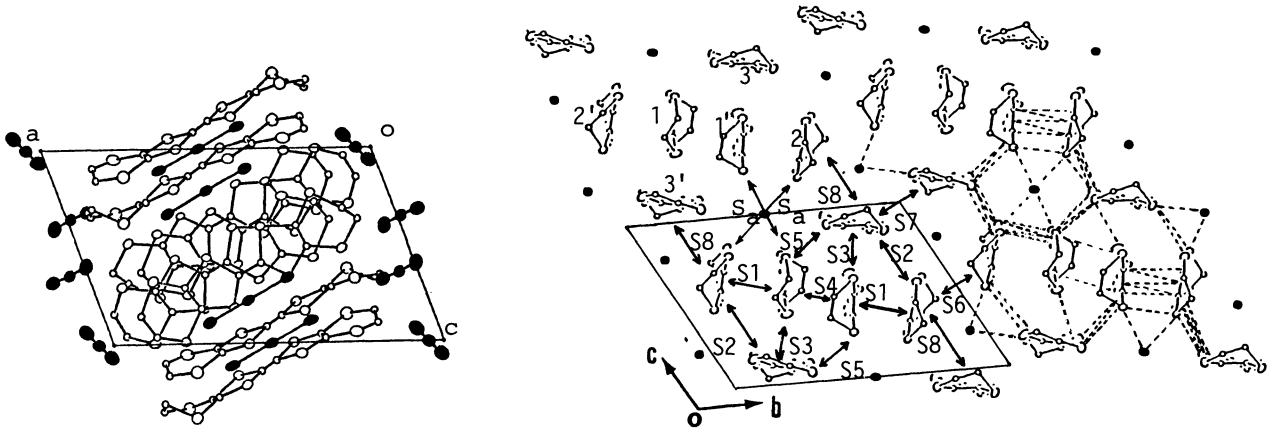

Fig. 1. Crystal structure of (BEDSe-TSeF)$AuBr_2$. Short Se•••Se (<4.0 Å) and Se•••anion (Se•••Br shorter than 3.6 Å; positions of the anion are represented by those of Au) distances are shown by dotted lines. Overlap integrals ($S \times 10^{-3}$) of the HOMO are: S1;-24.34, S2;3.29, S3;-2.76, S4;10.89, S5;-7.85, S6;5.52, S7;14.78, S8;12.51.

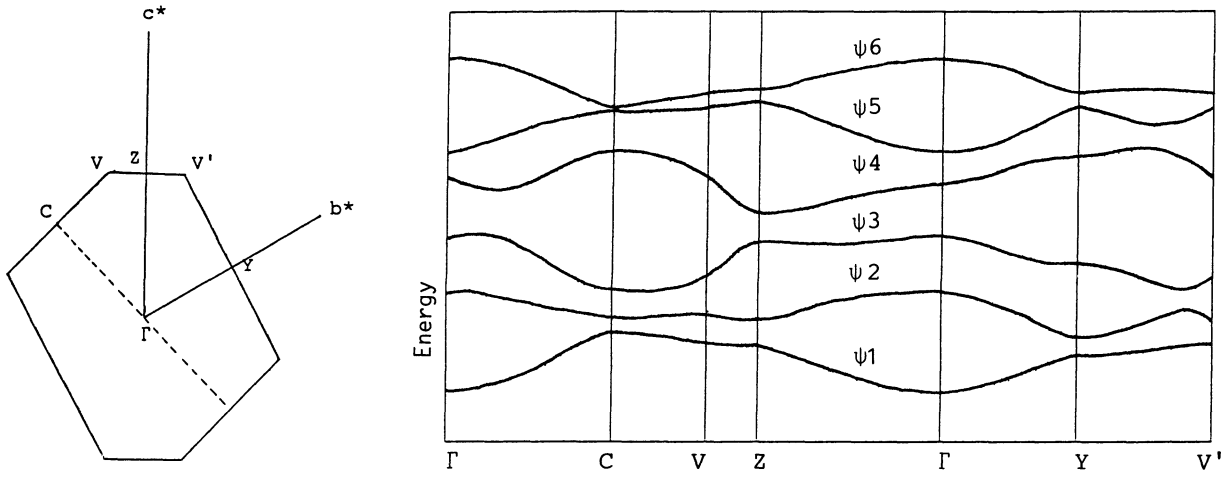

Fig. 2. Band structure of (BEDSe-TSeF)$AuBr_2$.

and 92° (2...3), respectively. In the tetrad, molecular spacings are ca. 3.88 Å (1...1') and ca. 3.67 Å (1'•••2).

It should be noted that half the $AuBr_2$ anions are distributed into the cation sheet. There are several intermolecular Se•••Br distances, shorter than 3.95 Å (sum of the van der Waals radii of Se (2.00 Å) and Br(1.95 Å)), especially in this sheet. Anomalously short intermolecular Se•••anion distance is also observed in the organic metal $(TSeT)_2X$ (TSeT=5,6,11,12-tetraselenotetracene, X=Cl, Br), and possibility of the electron transfer through the halogen atom has been suggested.[3] Although the Se•••Br distances in (BEDSe-TSeF)$AuBr_2$ are slightly longer than those in $(TSeT)_2Br$ (the minimum intermolecular Se•••Br distances are 3.14 Å in $(TSeT)_2Br$ and 3.37 Å in (BEDSe-TSeF)$AuBr_2$), contribution of the anion to the electron transfer would not be neglected.

Although increase of the dimensionality suppresses the Peierls instability, there are other types of instability of metallic state caused by the increased dimensionality. We have observed typical examples in the $(BMDT\text{-}TTF)_3X$ system (BMDT-TTF=bis(methylenedithio)tetrathiafulvalene: X=PF_6, ClO_4, BF_4).[4] The crystal structures of this system show strong two-dimensional character. In these ionic crystals, the lattice is stabilized mainly by the electrostatic lattice energy. Increase of the dimensionality means enhancement of the close contacts among ions with the same charge, which leads to a decrease of the electrostatic lattice energy. In order to avoid such an energetically unfavorable situation, the average formal charge of the donor molecule in $(BMDT\text{-}TTF)_3X$ becomes smaller compared with the $(BEDT\text{-}TTF)_2X$ system (+1/2→+1/3). The examination of the C=C and C-S bond lengths shows that the plus charge is distributed unequally and there exist neutral molecules. The neutral BMDT-TTF molecules reduce the repulsion among the charged BMDT-TTF molecules, but they frequently interrupt the conduction path or reduce the system to one-dimensional one.

On the other hand, in $(BEDSe\text{-}TSeF)AuBr_2$, the $AuBr_2$ anions distributed into the cation sheet would reduce the repulsion among the $(BEDSe\text{-}TSeF)^+$ cations and stabilize the lattice. This is a new way to construct the stable multi-dimensional crystal structure in molecular conductors. If the anion does not interrupt the conduction path or moreover contributes to the electron transfer, the multi-dimensional electronic structure would be obtained.

In order to understand the electronic structure of $(BEDSe\text{-}TSeF)AuBr_2$, we first calculated the overlap integrals (S) of the HOMO (highest occupied molecular orbital) of the donor molecule (Fig. 1b).[5] The strongest interaction is observed within the tetrad (S1) and there exists a fairly strong interaction (S8) between the tetrad and the vertical molecule (molecule 3). There exists only a weak interaction (S6) among the tetrads. Using the approximation that the transfer integral is proportional to the overlap integral, we have carried out tight-binding band calculation for the two-dimensional donor network (Fig. 2). Since $(BEDSe\text{-}TSeF)AuBr_2$ contains six donor molecules per unit cell, there occur six bands $\psi1$-$\psi6$ derived from the HOMO's of the donor molecules. Due to the formal charge of $(BEDSe\text{-}TSeF)^+$, these HOMO bands are half-filled. Existence of an energy gap between $\psi3$ and $\psi4$ indicates that this compound is a semiconductor. Since it is difficult to estimate the inter-cation interaction through the anion, we tentatively introduced an interaction S_a (see Fig. 1b), and performed band calculations using various S_a values ($-10 \leq S_a \times 10^3 \leq 10$). Although the energy gap between $\psi3$ and $\psi4$ became very small (nearly zero) when $S_a=-10\times10^{-3}$, we did not obtain metallic band structure for this compound. Electrical resistivity measurements have shown that $(BEDSe\text{-}TSeF)AuBr_2$ is a semiconductor with $\rho_{R.T.}=7$ (Ω cm) and a small activation energy (in the temperature range of 120-302 K) $E_a=0.13$ (eV).

The packing motif in ε-$(BEDT\text{-}TTF)_2I_3(I_8)_{0.5}$ (ε-salt) is very similar to that in $(BEDSe\text{-}TSeF)AuBr_2$. This ε-salt was reported to be a superconductor at first.[6] Recently, however, Shibaeva et al. have stated that later studies have revealed semiconductive character of the ε-salt.[7] We have investigated the electronic

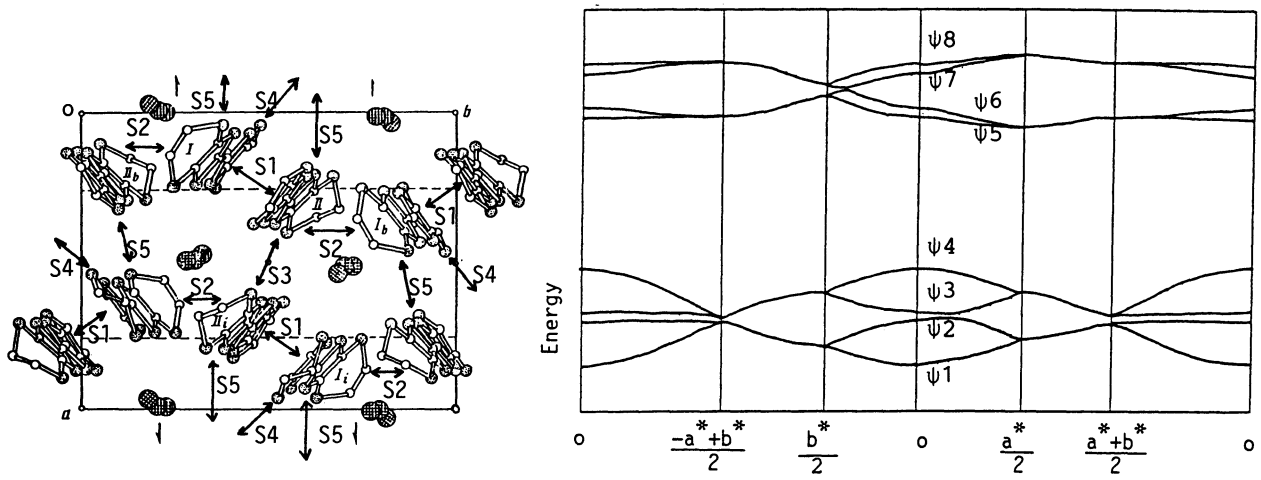

Fig. 3. Crystal and band structures of ε-(BEDT-TTF)$_2$I$_3$(I$_8$)$_{0.5}$. Overlap integrals (S × 10^{-3}) of the HOMO are: S1;-29.3, S2;-5.74, S3;6.00, S4;-0.43, S5;-4.13.

structure of the ε-salt on the basis of the crystal structure reported in Ref. 7. Examination of the overlap integrals (S) of the HOMO of BEDT-TTF (Fig. 3) indicates that the two-dimensional cation sheet in the ε-salt is constructed by dimerized BEDT-TTF units which are weakly interrelated to each other. Due to the formal charge of $(BEDT\text{-}TTF)^+$, the HOMO bands ψ1-ψ8 are half-filled. Figure 3 shows that there exists a large energy gap between ψ4 and ψ5 and this ε-salt is a typical semiconductor.

In conclusion, (BEDSe-TSeF)AuBr$_2$ has provided a new structural motif, two-dimensional cation sheet stabilized by included anions, for multi-dimensional molecular conductors. This structural motif would produce many kinds of variation, some of which would exhibit metallic electronic structure.

References

1) H. Kobayashi, R. Kato, and A. Kobayashi, Synthetic Metals, in press.
2) V. Y. Lee, E. M. Engler, R. R. Schumaker, and S. S. P. Parkin, J. Chem. Soc., Chem. Commun., 1983, 235.
3) I. F. Shchegolev and E. B. Yagubskii, "Extended Linear Chain Compounds," ed by J. S. Miller, Prenum Press (1982), Vol. 2, pp. 385-434; R. P. Shibaeva, ibid., pp. 435-467, and references therein.
4) R. Kato, H. Kobayashi, T. Mori, A. Kobayashi, and Y. Sasaki, Solid State Commun., 55, 387 (1985).
5) The atomic parameters for the extended Hückel calculations were taken from E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, 14, 177 (1974).
6) R. P. Shibaeva, V. F. Kaminskii, and E. B. Yagubskii, Mol. Cryst. Liq. Cryst., 119, 361 (1985).
7) R. P. Shibaeva, R. M. Lobkovskaya, E. B. Yagubskii, and E. E. Kostyuchenko, Kristallografiya, 31, 455 (1986).

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