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THREE-DIMENSIONAL INTERMOLECULAR Se···Se NETWORK IN (BEDSe-TSeF)PF_6

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In the crystal of (BEDSe-TSeF)PF_6 (space group; C2/m), there exists face-to-face overlap of the BEDSe-TSeF molecules along the c axis. Intermolecular interaction by the short Se···Se contact is also observed in the <1,1,2> and <1,1,4> directions, which results in the three-dimensional Se···Se network.

Two-dimensional structural and electronic nature of the BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) compounds, some of which are the organic superconductors, leads to the idea that multi-dimensional nature of the electronic system is closely related to the stabilization of the metallic state.[1)] At present, three-dimensional electronic system is searched with keen interest, as the ultimate goal of the multi-dimensionality. In this paper, we report three-dimensional intermolecular Se···Se network observed in the crystal structure of (BEDSe-TSeF)PF_6, where BEDSe-TSeF (bis(ethylenediseleno)tetraselenafulvalene) is the selenium analogue of BEDT-TTF, and consider its effect on the electronic structure.

Black needles of (BEDSe-TSeF)PF_6 were obtained by the electrochemical oxidation (at a constant current of ca. 0.1 μA) of a solution containing BEDSe-TSeF[2)] and n-Bu_4NPF_6 in 2:1 mixture of chlorobenzene and carbon disulfide under N_2. The crystal data: $C_{10}H_8Se_8PF_6$, Monoclinic, space group C2/m, a=14.868(4), b=11.003(5), c=6.114(2) Å, β=104.07(3)°, V=970.2 Å^3, Z=2. Intensities were measured on a Rigaku automated diffractometer with Mo Kα radiation. The number of the observed independent reflections ($2\theta \lesssim 60°$, $|Fo|<3\sigma(|Fo|)$) was 848. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The final R value was 0.098. Final positional parameters are given in Table 1.

The molecular structure of (BEDSe-TSeF)$^+$ is shown in Fig. 1. The center of (BEDSe-TSeF)$^+$ is on the inversion center and the two-fold axis, and the long axis lies on the mirror plane. The terminal ethylene groups are positioned out of the plane of the rest of the molecule and show the positional disorder.

As shown in Fig. 2, (BEDSe-TSeF)$^+$ units repeat by a unit translation *c*. The molecular plane is largely inclined with respect to the c axis. Along the c axis, the face-to-face overlap of (BEDSe-TSeF)$^+$ units is observed and the mode of

Table 1. Fractional atomic coordinates (x 10^4) with their estimated standard deviations

Atom	x	y	z
Se(1)	725(3)	1428(3)	2609(6)
Se(2)	2018(3)	1650(3)	7518(6)
C(1)	246(33)	0	1043(62)
C(2)	1415(23)	618(26)	5186(48)
C(3)	3084(27)	650(43)	8568(83)
C(3')	2780(62)	451(86)	9774(153)
P	0	5000	5000
F(1)	116(40)	5277(71)	7550(89)
F(2)	779(21)	4026(28)	5553(55)

C(3) and C(3') are carbon atoms in the terminal ethylene groups which show the positional disorder.

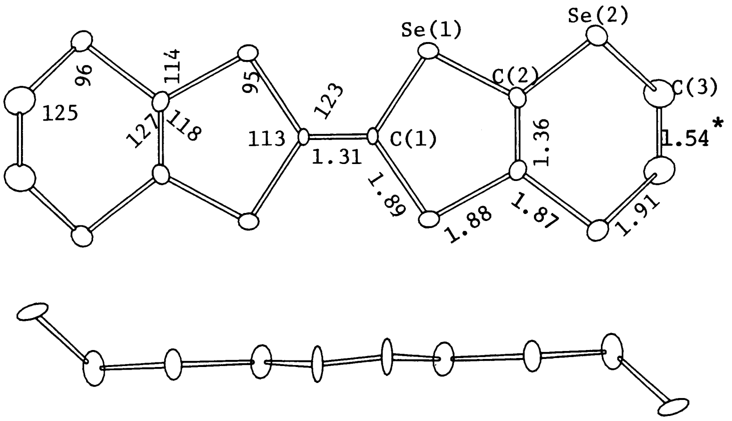

Fig. 1. Molecular structure of BEDSe-TSeF$^+$. The standard deviations of the bond lengths and angles are 0.01-0.09 Å and 1-3°, respectively. * C(3)-C(3') distance.

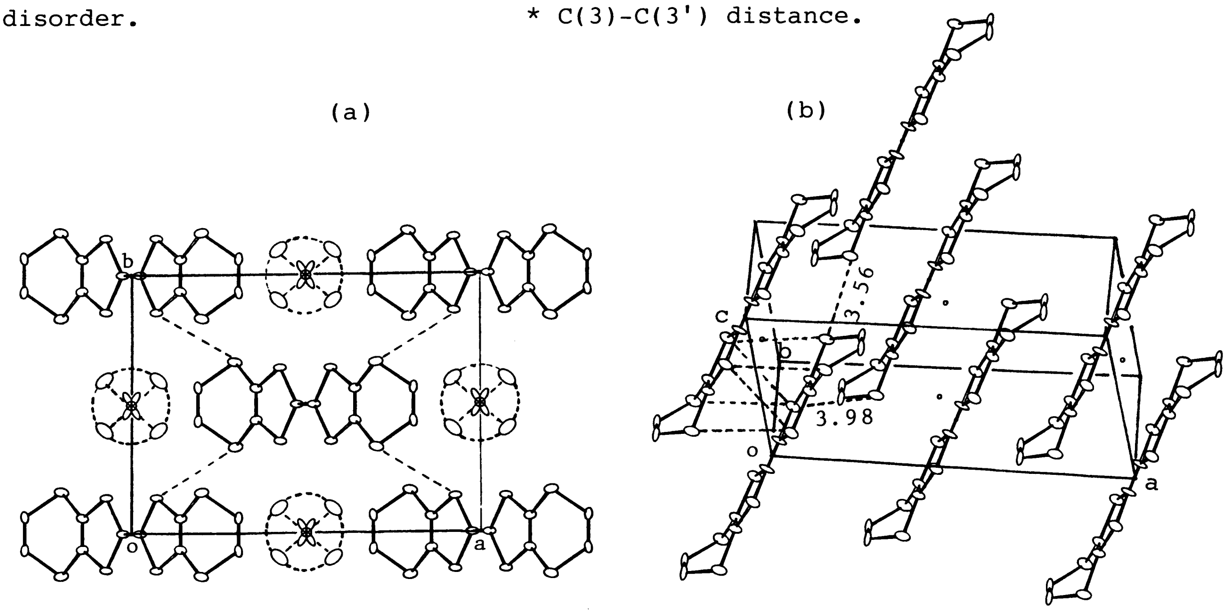

Fig. 2. Crystal structure of (BEDSe-TSeF)PF_6. PF_6^- anion shows orientational disorder. In Fig. 2b, the positions of P are indicated with open circles.

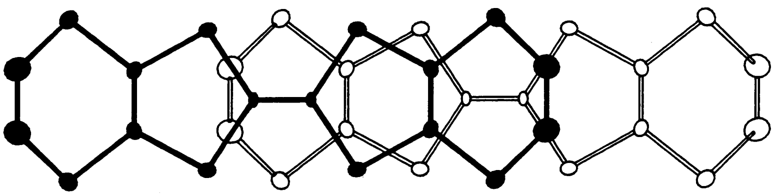

Fig. 3. Mode of intermolecular overlapping.

overlapping is shown in Fig. 3. Short intermolecular Se···Se distances (4.03-4.07 Å) in this uniform stack are slightly longer than the van der Waals distance (4.0 Å).

Two types of short interstack Se···Se distances (3.56(5) and 3.98(6) Å) are observed along the <114> and <112> directions. These interstack short Se···Se distances achieve the three-dimensional Se···Se network.

Table 2. Overlap integrals($\times 10^3$) of the HOMO in (BEDSe-TSeF)PF_6

direction			ratio
S_c	<001>	-14.36	1
S_{p1}	<112>	-2.94	0.20
S_{p2}	<114>	0.21	0.015

In the BEDT-TTF compounds, the side-by-side array of BEDT-TTF plays an important role in the formation of the two-dimensional S···S network.[1] In (BEDSe-TSeF)PF_6, the side-by-side array of BEDSe-TSeF is prevented by PF_6^- anions and an adjacent (BEDSe-TSeF)$^+$ unit is largely displaced in the a axis direction. The selenium atoms in the heterorings incorporated to the TSeF moiety, however, make the Se···Se contacts in the transverse direction possible.

Such a three-dimensional intermolecular Se···Se network will have an effect on the band structure. Table 2 shows intermolecular overlap integrals (S) of the HOMO (highest occupied molecular orbital) of BEDSe-TSeF, which are calculated by the extended Hückel method.[3] The interaction is maximum along the face-to-face overlapping direction (S_c). In spite of the shortest Se···Se distance, S_{p2} is small, because this interaction is $p\pi$-$p\pi$ type, and is based on the outer selenium atoms (Se(2)) whose contribution to the HOMO is smaller than that of the inner selenium atom (Se(1)). The value of the anisotropy parameter $\alpha=S_{p1}/S_c=0.2$ is larger than that in $(TMTSF)_2X$ ($\alpha \approx 0.1$),[4] which indicates the three-dimensional interaction in the electronic structure.

For the calculation of the band structure, we used the primitive unit cell containing one (BEDSe-TSeF)$^+$ unit. The primitive vectors $\mathbf{a}_p$, $\mathbf{b}_p$, and $\mathbf{c}_p$ are given by the vectors $\mathbf{a}/2-\mathbf{b}/2+\mathbf{c}$, $\mathbf{a}/2+\mathbf{b}/2+\mathbf{c}$, and $\mathbf{c}$, respectively. The lattice constants of this primitive unit cell are $a_p=10.041$, $b_p=10.041$, $c_p=6.114$ Å, $\alpha_p=64.60$, $\beta_p=64.60$, $\gamma_p=66.45°$. Using the approximation that the transfer integral (t) is proportional to the overlap integral (t=-ES; E is a constant of the order of the energy of HOMO ($\approx$10 eV)), tight-binding approximation gave the simple energy band,

$$E(\mathbf{k})=2t_c[\cos(\mathbf{kc})+\alpha(\cos(\mathbf{ka})+\cos(\mathbf{kb}))]$$

where we ignore t_{p2}. The shape of the Fermi surface depends only on α. The energy band is half filled. If $\alpha=0$, the Fermi surface consists of two planes ($k_z=\pm\pi/2c$). Figure 4 shows the Fermi surface of (BEDSe-TSeF)PF_6 ($\alpha=0.2$). The Fermi surface consists of two distorted planes. In spite of rather large α value, the Fermi surface remains open. It should be noticed that the dimensionality of the electronic system depends on the degree of band filling. If the conduction level is 3/4 filled, as is often observed in a number of organic metals and superconductors, we obtain the closed Fermi surface. This indicates that the 2:1 complex with the similar three-dimensional Se···Se network would be a three-dimensional metal.

Althogh poor quality of crystals hampered electrical conductivity measurement of (BEDSe-TSeF)PF_6, preliminary measurement showed that (BEDSe-TSeF)PF_6 is a semiconductor ($\sigma_{R.T.} \simeq 1$ S cm^{-1}). For the explanation of the semiconductive behavior we must introduce other factors which we ignored in the above discussion, including the electron-electron interaction. In any case, it should be important that (BEDSe-TSeF)PF_6 retains the one-dimensional character in spite of the three-dimensional Se···Se network. Nevertheless the crystal structure of (BEDSe-TSeF)PF_6 would predict the existence of the three-dimensional organic metal.

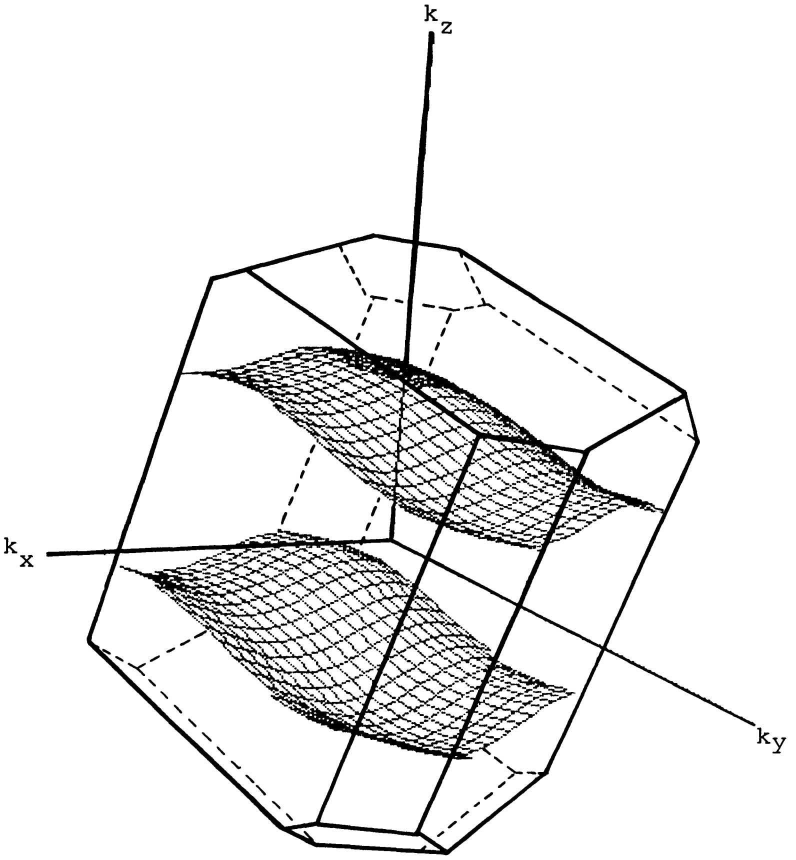

Fig. 4. Fermi surface of (BEDSe-TSeF)PF_6.

References

1) H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, Mol. Cryst. Liq. Cryst., 107, 33 (1984); G. Saito, T. Enoki, H. Inokuchi, and H. Kobayashi, J. Physique Colloq., 44, C3-1215 (1983).

2) V. Y. Lee, E. M. Engler, R. R. Schumaker, and S. S. P. Parkin, J. Chem. Soc., Chem. Commun., 1983, 235.

3) The calculations were made using the program written by Dr. T. Mori. The parameters for the extended Hückel calculations were taken from E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, 14, 177 (1974).

4) T. Mori, A. Kobayashi, Y. Sasaki, and H. Kobayashi, Chem. Lett., 1982, 1923.

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