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Crystal and Electronic Structures of (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K and NH$_4$)

Hatsumi MORI,* Shoji TANAKA, Masashi OSHIMA,**,† Gunzi SAITO,**,†† Takehiko MORI,***
Yusei MARUYAMA,*** and Hiroo INOKUCHI
International Superconductivity Technology Center, Koto-ku, Tokyo 135
**Institute for Solid State Physics, Roppongi, Minato-ku, Tokyo 106
***Institute for Molecular Science, Okazaki 444
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The crystal structures of (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K at 298 and 104 K and M=NH$_4$ at 298 K) were determined by X-ray analyses. A donor layer and an anion sheet stack alternately along the *b*-axis. The packing pattern of the donor is close to α-phase, while an anion sheet constructs a thick two-dimensional polymer plane parallel to (010). The linkage of ··SCN··$\dot{\text{K}}$ (or NH$_4$) ··NCS··$\dot{\text{H}}$g··SCN in an anion sheet is very unique. The band structure calculation indicates both a closed and an open Fermi surfaces, resembling that of κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$].

Bis(ethylenedithiolo)tetrathiafulvalene, BEDT-TTF, is a prominent donor since it affords a variety of complexes from insulators, metals, and superconductors.[1] Actually, the chemical and physical properties of these complexes could be controlled to some extent by the anion that we selected and under what conditions the complexes were prepared and treated. For example, β-(BEDT-TTF)$_2$I$_3$ has three kinds of superconducting states with T_c's of 1.5, 2.0, and 8.0 K, depending on the pressure or heat treatment.[1b] The T_c's of the β-(BEDT-TTF)$_2$X, X=I$_3$ (high T_c phase, 8.0 K), AuI$_2$ (T_c=3.4—5.0 K) and IBr$_2$ (2.7 K) become higher upon increasing the length of the linear anion or increasing the unit-cell volume (V_c) of the salts.[2] The various phases for (BEDT-TTF)$_2$I$_3$ also have a similar T_c dependence on V_c/n, where n is the number of the conduction electron, namely β (T_c=8.0 K, V_c/n=852 Å^3),[1b] θ (3.6, 1693/2)[1d] and κ (3.6, 1688/2).[1e] Therefore, it has been postulated that there is a good correlation between T_c and V_c/n for BEDT-TTF superconductors. However, we have observed a superconducting transition at 10.4 K in κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$][1a] which has almost the same donor packing pattern and unit-cell parameters as those of κ-(BEDT-TTF)$_2$I$_3$.[1e]

On the basis of these experimental results we have proposed a correlation between T_c and the effective donor volume ($V_{eff}=(V_c-V_{anion})/n$, where V_{anion} is the anion volume) (Fig. 1).[3] The effective volume is the area shared by an electron in a unit cell. A larger effective volume in which a loose packing of donors is formed gives a weaker overlap integral of the donors. Consequently, the bandwidth, $4t$, based on a simple model becomes relatively smaller, which affords a larger density of states and a higher T_c. Therefore, if a larger effective volume can be constructed without any destruction of the molecular packing, a higher T_c is expected from Fig. 1. In order to require a larger effective volume, a variety of molecular designs are available. One of them is to use a bigger and bulkier anion than Cu(NCS)$_2$. The Cu(NCS)$_2$ anion forms a zig-zag one-dimensional (1D) flat polymer, and the polymers construct a 2D insulating sheet which frames the 2D conducting layer of BEDT-TTF molecules in κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$].[1a] The dimensionality of the complex does not depend only on the intralayer interactions. The interlayer transfer integral, $t_\perp$, provides the degree of three-dimensionality and modifies the cylindrical 2D Fermi surface to cause a warping. The degree of warping may thus depend on the thickness of the anion layer when anions form a rigid polymer on a bridged anion sheet. It is very interesting to see the effect of the anion thickness (or degree of three dimensionality) on the appearance of superconductivity in 2D BEDT-TTF salts in order to obtain more clear insight into the mechanism of

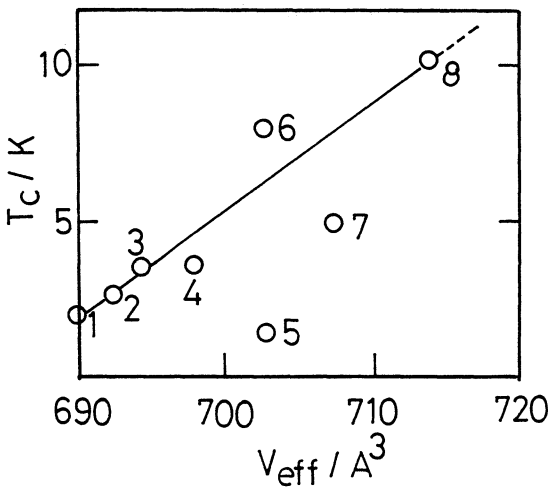

Fig. 1. Correlation between effective volume (=(V_c/$-V_{anion}$)/n) of some BEDT-TTF superconductors and their T_c's. 1: ReO$_4$, 2: β-IBr$_2$, 3: κ-I$_3$, 4: θ-I$_3$, 5: low T_c β-I$_3$, 6: high T_c β-I$_3$, 7: β-AuI$_2$, and 8: κ-Cu(NCS)$_2$ salts of BEDT-TTF.

† Present address: Japan Carlit Co. Ltd., Gunma 377.
†† Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606.

superconductivity and in order to design organic superconductors.

In the course of our investigation of BEDT-TTF salts with a metal-pseudohalide anion that are candidate polymers, we recently came across (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K and NH$_4$).[4] The M=K and NH$_4$ systems are isostructural. The temperature dependences of the electrical resistivities for (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K and NH$_4$) were confirmed to be metallic down to 0.5 and 1.5 K, respectively, although a resistivity peak appeared around 100 K where the resistivity is about twice as large as that at room temperature for both salts. The investigation of the electrical resistivity for the M=NH$_4$ salt below 1.5 K is now under way.[5] Moreover, a large enhancement of the Shubnikov-de Haas (SdH) oscillation above 22.5 T and angle-dependent quantum oscillations were observed for (BEDT-TTF)$_2$[KHg(SCN)$_4$].[6] The SdH oscillation period (0.0015 T^{-1}) corresponded to 16 % of the first Brillouin zone. It is also notable that these complexes contain cations (K$^+$ or NH$_4^+$) that have never been observed in BEDT-TTF complexes, as far as we know. In this paper we report on the crystal structures of (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K at 298 K and 104 K and M=NH$_4$ at 298 K) as well as the calculated band structure for (BEDT-TTF)$_2$[KHg(SCN)$_4$] at 104 K.

Experimental

Single crystals for X-ray structure analysis were prepared by the electrochemical oxidation of BEDT-TTF in the presence of KSCN (or NH$_4$SCN), Hg(SCN)$_2$, and 18-crown-6 ether in a mixture solvent of 1,1,2-trichloroethane and volume 10% of absolute ethanol for about a month. The use of a mixed solvent is very critical for the inclusion of K$^+$ (or NH$_4^+$). The crystal data are shown in Table 1. The intensities were collected by the ω-2θ scan technique on a Rigaku automated four-circle diffractometer (Mo $K\alpha$, $2\theta<60°$) and were corrected for the usual Lorentz and polarization effect, though not for absorption. The structure was solved by the Patterson method and the succeeding Fourier syntheses and refined by the block-diagonal least-squares procedure ($|F_o|>3(|F_o|)$) by using UNICS III program system.[7] The atomic scattering factors were taken from International Table for X-ray Crystallography.[8] ORTEP[9] was used for drawing of the molecular and crystal structures. All H atoms were located by the calculation based upon the sp$_3$ model and were refined with isotropic temperature factors. The anisotropic thermal parameters were adopted for all non-hydrogen atoms.[10]

Results and Discussion

The atomic parameters for (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K at 298 K and 104 K and M=NH$_4$ at 298 K) are listed in Table 2(a), (b), and (c), respectively. Since

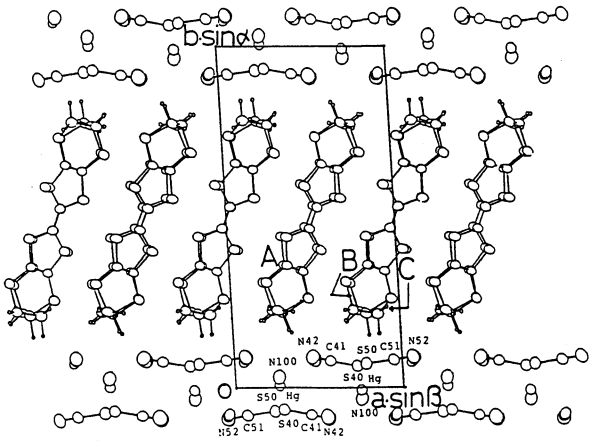

Fig. 2. Crystal structure of (BEDT-TTF)$_2$[NH$_4$Hg(SCN)$_4$] projected along the c-axis at 298 K.

Table 1. Crystallographic Data of (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K and NH$_4$)

	(BEDT-TTF)$_2$[KHg(SCN)$_4$]		(BEDT-TTF)$_2$[NH$_4$Hg(SCN)$_4$]
	298 K	104 K	298 K
Chemical formula	$HgKS_{20}C_{24}N_4H_{16}$		$HgS_{20}C_{24}N_5H_{20}$
FW	1241.3		1220.3
System	triclinic	triclinic	triclinic
Space group	P$\bar{1}$	P$\bar{1}$	P$\bar{1}$
a/Å	10.082 (10)	9.948 (2)	10.091 (1)
b/Å	20.565 (4)	20.505 (11)	20.595 (2)
c/Å	9.933 (2)	9.833 (4)	9.963 (1)
α/°	103.70 (2)	103.34 (4)	103.65 (1)
β/°	90.91 (4)	90.53 (3)	90.53 (1)
γ/°	93.06 (4)	92.80 (3)	93.30 (1)
V/Å^3	1997.0 (21)	1948.8 (14)	2008.1 (3)
Z	2	2	2
D_x	2.07	2.12	2.02
R	0.070	0.042	0.047
No. of reflections	7636	10292	6301
$2\theta_{max}$/°	60	60	60
λ (Mo K_α)/Å	0.709260	0.709260	0.709260

the ionic radii of K^+ (1.33 Å) and NH_4^+ (1.43 Å) are almost the same, both systems are isostructural and show identical unit-cell parameters (Table 1). Therefore, we mainly focused on the M=NH$_4$ crystal.

The crystal structure for (BEDT-TTF)$_2$[NH$_4$Hg(SCN)$_4$] is depicted in Fig. 2. A BEDT-TTF layer and an anion sheet stack alternately along the b-axis, which is a characteristic structure for an organic conductor. The crystal comprises three kinds of BEDT-TTF molecules (one BEDT-TTF molecule (A), two halves of BEDT-TTF molecules (B and C)), one NH$_4$ cation, and one [Hg(SCN)$_4$] anion. The intramolecular distances and angles are shown in Table 3. The C=C bond distances in BEDT-TTF molecules are

Table 2 (a). Atomic Parameters (×10^5: Hg Atom, ×10^4: Non-Hg Atoms) and Equivalent Isotropic Thermal Parameters with e.s.d.'s in Parentheses of (BEDT-TTF)$_2$[KHg(SCN)$_4$] at 298 K

$B_{eq}=8/3\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\boldsymbol{a}_j$.

Atom	x	y	z	B_{eq}
Hg	25123(7)	598(3)	24902(7)	2.1
S(A1)	1881(4)	3082(2)	2721(4)	2.5
S(A2)	4470(4)	2641(2)	401(4)	3.0
S(A3)	3146(4)	4431(2)	3183(4)	2.5
S(A4)	5254(4)	4085(2)	1165(4)	2.7
S(A5)	4508(4)	5964(2)	4087(4)	2.4
S(A6)	6525(4)	5583(2)	1978(4)	2.7
S(A7)	5479(4)	7381(2)	4951(4)	2.6
S(A8)	7892(4)	6912(2)	2423(4)	2.6
S(B1)	9500(4)	2615(2)	4877(4)	2.9
S(B2)	7036(4)	3083(2)	2818(4)	2.9
S(B3)	10346(4)	4056(2)	5562(4)	2.6
S(B4)	8332(4)	4424(2)	3756(4)	2.7
S(C1)	9552(4)	2604(2)	−213(4)	2.8
S(C2)	6887(4)	3109(2)	−1911(5)	3.2
S(C3)	10456(4)	4046(2)	431(4)	2.6
S(C4)	8256(4)	4433(2)	−1112(4)	2.8
C(A1)	2339(16)	2238(7)	1862(15)	2.5
C(A2)	2850(15)	2211(7)	374(14)	2.3
C(A3)	3194(14)	3588(6)	2293(13)	1.8
C(A4)	4171(14)	3430(6)	1369(14)	1.8
C(A5)	4581(14)	4696(7)	2450(14)	2.0
C(A6)	5113(15)	5337(7)	2795(14)	2.3
C(A7)	6611(14)	6424(7)	2920(14)	2.0
C(A8)	5694(13)	6592(6)	3894(13)	1.5
C(A9)	7288(17)	7740(7)	3080(14)	2.5
C(A10)	6965(15)	7863(7)	4652(14)	2.2
C(B1)	7927(16)	2169(8)	4228(17)	3.1
C(B2)	7529(18)	2254(8)	2822(17)	3.2
C(B3)	9206(14)	3413(6)	4650(14)	1.7
C(B4)	8318(13)	3590(6)	3837(14)	1.8
C(B5)	9730(14)	4678(6)	4860(14)	1.8
C(C1)	8706(17)	2138(7)	−1777(16)	2.7
C(C2)	7208(16)	2266(8)	−1734(19)	3.3
C(C3)	9235(14)	3416(6)	−347(14)	1.8
C(C4)	8270(14)	3600(6)	−1029(14)	1.8
C(C5)	9732(14)	4678(6)	−140(14)	1.9
S20	504(4)	770(2)	3147(4)	2.6
S30	4678(4)	788(2)	2581(4)	2.7
S40	2734(4)	−644(2)	4278(4)	2.5
S50	2108(4)	−700(2)	73(4)	2.7
C21	588(16)	830(8)	4841(16)	2.8
C31	4583(15)	831(8)	897(17)	2.8
C41	4326(18)	−784(8)	3998(15)	3.2
C51	439(16)	−817(7)	209(14)	2.4
N22	692(16)	871(8)	6082(14)	4.4
N32	4539(14)	861(8)	−261(14)	3.9
N42	5472(15)	−930(7)	3835(15)	3.8
N52	−686(14)	−906(8)	291(14)	4.2
K	2549(4)	326(2)	7643(4)	3.1

Table 2 (b). Atomic Parameters (×10^5: Hg Atom, ×10^4: Non-Hg Atoms) and Equivalent Isotropic Thermal Parameters with e.s.d.'s in Parentheses of (BEDT-TTF)$_2$[KHg(SCN)$_4$] at 104 K

$B_{eq}=8/3\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\boldsymbol{a}_j$.

Atom	x	y	z	B_{eq}
Hg	24996(3)	652(1)	24797(3)	1.6
S(A1)	1881(2)	3075(1)	2734(2)	2.1
S(A2)	4493(2)	2624(1)	359(2)	2.8
S(A3)	3149(2)	4434(1)	3189(2)	2.2
S(A4)	5267(2)	4082(1)	1115(2)	2.4
S(A5)	4516(2)	5967(1)	4098(2)	2.2
S(A6)	6553(2)	5585(1)	1943(2)	2.4
S(A7)	5487(2)	7393(1)	4986(2)	2.4
S(A8)	7923(2)	6922(1)	2398(2)	2.4
S(B1)	9522(2)	2598(1)	4864(2)	3.2
S(B2)	7003(2)	3082(1)	2817(2)	2.5
S(B3)	10355(2)	4052(1)	5579(2)	2.3
S(B4)	8308(2)	4429(1)	3757(2)	2.6
S(C1)	9549(2)	2595(1)	−213(2)	2.4
S(C2)	6895(2)	3092(1)	−1942(2)	3.0
S(C3)	10452(2)	4046(1)	494(2)	2.3
S(C4)	8263(2)	4428(1)	−1154(2)	2.4
C(A1)	2346(7)	2246(3)	1852(6)	1.9
C(A2)	2860(6)	2203(3)	382(6)	2.3
C(A3)	3183(6)	3594(3)	2292(6)	1.5
C(A4)	4176(6)	3425(3)	1350(6)	1.8
C(A5)	4596(6)	4704(3)	2429(6)	1.4
C(A6)	5144(6)	5331(3)	2790(6)	2.0
C(A7)	6653(6)	6417(3)	2906(6)	1.8
C(A8)	5704(6)	6601(3)	3902(6)	1.5
C(A9)	7306(7)	7741(3)	3101(6)	1.9
C(A10)	6988(6)	7864(3)	4648(6)	1.8
C(B1)	7917(6)	2167(3)	4266(7)	2.9
C(B2)	7478(7)	2240(3)	2828(7)	3.4
C(B3)	9234(6)	3406(3)	4655(6)	2.3
C(B4)	8303(6)	3580(3)	3835(6)	2.4
C(B5)	9722(6)	4686(3)	4866(6)	1.8
C(C1)	8731(6)	2132(3)	−1758(6)	2.3
C(C2)	7231(6)	2248(3)	−1777(7)	3.4
C(C3)	9260(6)	3406(3)	−295(6)	2.1
C(C4)	8239(6)	3585(3)	−1037(6)	2.1
C(C5)	9729(7)	4685(3)	−139(6)	1.8
S20	459(2)	778(1)	3147(2)	1.9
S30	4686(2)	793(1)	2583(2)	1.8
S40	2722(2)	−641(1)	4298(2)	2.0
S50	2121(2)	−712(1)	63(2)	1.8
C21	579(6)	813(3)	4865(7)	2.4
C31	4628(6)	810(3)	886(7)	2.6
C41	4372(6)	−767(3)	4073(6)	1.8
C51	444(7)	−792(3)	162(6)	1.2
N22	671(6)	858(3)	6073(6)	2.8
N32	4584(6)	837(3)	−287(6)	2.3
N42	5493(6)	−883(3)	3805(6)	2.8
N52	−728(6)	−872(3)	223(6)	2.3
K	2546(1)	298(1)	7637(1)	1.9

Table 2 (c). Atomic Parameters ($\times10^5$: Hg Atom, $\times10^4$: Non-Hg Atoms) and Equivalent Isotropic Thermal Parameters with e.s.d.'s in Parentheses of $(BEDT\text{-}TTF)_2[NH_4Hg(SCN)_4]$ at 298 K

$$B_{eq}=8/3\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j.$$

Atom	x	y	z	B_{eq}
Hg	25178(4)	655(2)	24907(4)	2.9
S(A1)	1890(2)	3083(1)	2716(2)	3.2
S(A2)	4460(2)	2639(1)	398(3)	3.6
S(A3)	3150(2)	4435(1)	3185(2)	3.2
S(A4)	5250(2)	4085(1)	1170(2)	3.3
S(A5)	4508(2)	5963(1)	4085(2)	3.2
S(A6)	6519(2)	5579(1)	1975(2)	3.4
S(A7)	5477(2)	7381(1)	4948(2)	3.3
S(A8)	7875(2)	6908(1)	2419(2)	3.3
S(B1)	9499(2)	2618(1)	4885(3)	3.5
S(B2)	7052(2)	3083(1)	2827(3)	3.6
S(B3)	10349(2)	4059(1)	5569(2)	3.2
S(B4)	8341(2)	4425(1)	3748(2)	3.3
S(C1)	9552(2)	2605(1)	−215(3)	3.4
S(C2)	6895(2)	3111(1)	−1896(3)	3.9
S(C3)	10459(2)	4046(1)	429(2)	3.3
S(C4)	8258(2)	4438(1)	−1108(2)	3.4
C(A1)	2346(9)	2256(4)	1853(9)	3.0
C(A2)	2854(8)	2213(4)	403(8)	2.9
C(A3)	3175(8)	3595(3)	2308(8)	2.6
C(A4)	4148(8)	3434(4)	1382(8)	2.7
C(A5)	4592(9)	4703(4)	2441(9)	2.9
C(A6)	5127(8)	5336(4)	2806(9)	2.8
C(A7)	6598(8)	6411(3)	2916(8)	2.5
C(A8)	5682(8)	6589(3)	3894(8)	2.4
C(A9)	7311(9)	7726(4)	3118(8)	3.0
C(A10)	6967(8)	7849(4)	4632(8)	2.7
C(B1)	7946(9)	2175(4)	4233(11)	3.8
C(B2)	7508(11)	2255(4)	2841(10)	3.9
C(B3)	9221(8)	3414(4)	4664(8)	2.6
C(B4)	8316(8)	3584(4)	3831(9)	2.7
C(B5)	9732(8)	4681(4)	4861(9)	2.8
C(C1)	8686(9)	2153(4)	−1750(9)	3.4
C(C2)	7223(9)	2280(4)	−1738(11)	3.8
C(C3)	9254(8)	3415(4)	−338(9)	2.7
C(C4)	8239(8)	3599(4)	−1029(9)	2.7
C(C5)	9727(9)	4680(4)	−140(8)	2.9
S20	515(2)	778(1)	3125(2)	3.4
S30	4668(2)	801(1)	2605(2)	3.4
S40	2717(2)	−647(1)	4257(2)	3.2
S50	2134(2)	−701(1)	93(2)	3.5
C21	613(9)	839(4)	4826(9)	3.3
C31	4630(9)	824(4)	930(9)	3.4
C41	4313(9)	−795(4)	4025(8)	3.0
C51	492(9)	−811(4)	170(8)	3.1
N22	648(9)	900(4)	6012(9)	4.7
N32	4635(10)	851(5)	−215(9)	5.1
N42	5409(9)	−908(5)	3891(9)	4.9
N52	−640(9)	−910(4)	206(8)	4.5
N100	2561(8)	317(4)	7651(8)	4.4

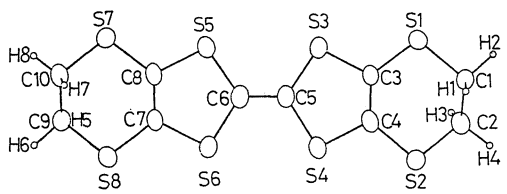

Fig. 3. Molecular structure of BEDT-TTF.

reasonable for $\eta=0.5$, the degree of charge transfer.[11] A not so large thermal motion of the ethylene groups in BEDT-TTF molecules for the $M=NH_4$ salt was observed, even at room temperature, compared with those of κ-$(BEDT\text{-}TTF)_2[Cu(NCS)_2]$[1a] and β-$(BEDT\text{-}TTF)_2I_3$[1b] (Table 2(c)). Neither the $M=NH_4$ salt nor the M=K salt affords a large thermal motion of the ethylene groups at 298 and 104 K.

Figure 4 shows the arrangement of the donor molecules along the long molecular axis. There are two kinds of stacking modes along the c-axis (I and II); in the mode I, the stacking molecules, A_1 and A_2, are related to each other by an inversion center, whereas in the mode II, donors B and C are on the inversion center and stack alternately. Short S··S contacts (<3.6 Å) are found not within a column but between columns (I and II), as shown in Fig. 5. Very similar S··S contacts were obtained for the M=K system at room temperature. At 104 K the number of S··S contacts increased for the M=K system (Fig. 5). θ-$(BEDT\text{-}TTF)_2I_3$[1d] and α-$(BEDT\text{-}TTF)_2I_3$[12] also have a similar zig-zag donor arrangement and transverse S··S contacts. A BEDT-TTF molecule comprises three planes of tetrathio-substituted ethylene moieties. The dihedral angles between the least-square plane of the central tetrathio-substituted ethylene moiety in A and that in B or that in A and that in C are listed in Table 4. These angles (76 and 82°) are relatively closer to that of θ-$(BEDT\text{-}TTF)_2I_3$ (79.6°) rather than those of α-$(BEDT\text{-}TTF)_2I_3$ (59.4 and 70.4°). However, when we include the periodicity of BEDT-TTF

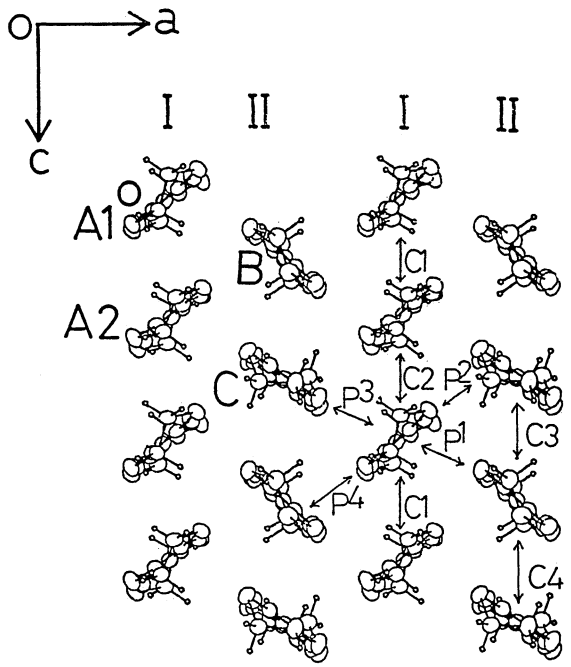

Fig. 4. Molecular arrangement of $(BEDT\text{-}TTF)_2[NH_4Hg(SCN)_4]$ projected along the molecular long axis. The calculated overlap integrals are c1= −1.9, c2=6.8, c3=−1.1, c4=−1.4, p1=−10.0, p2= −9.7, p3=13.3, and p4=13.2×10^{-3}.

Table 3. Intramolecular Distances and Angles of (BEDT-TTF)$_2$[NH$_4$Hg(SCN)$_4$] at 298 K

Intramolecular distances/Å			
S(A1)-C(A1)	1.806(8)	S(B1)-C(B1)	1.802(9)
S(A1)-C(A3)	1.735(8)	S(B1)-C(B3)	1.744(8)
S(A2)-C(A2)	1.799(8)	S(B2)-C(B2)	1.793(9)
S(A2)-C(A4)	1.747(7)	S(B2)-C(B4)	1.740(8)
S(A3)-C(A3)	1.747(7)	S(B3)-C(B3)	1.764(7)
S(A3)-C(A5)	1.758(9)	S(B3)-C(B5)	1.742(9)
S(A4)-C(A4)	1.745(8)	S(B4)-C(B4)	1.753(8)
S(A4)-C(A5)	1.736(8)	S(B4)-C(B5)	1.758(8)
S(A5)-C(A6)	1.736(8)	C(B1)-C(B2)	1.500(15)
S(A5)-C(A8)	1.745(8)	C(B3)-C(B4)	1.343(12)
S(A6)-C(A6)	1.745(9)	C(B5)-C(B5)[a]	1.356(10)
S(A6)-C(A7)	1.746(7)	S(C1)-C(C1)	1.783(9)
S(A7)-C(A8)	1.745(7)	S(C1)-C(C3)	1.744(8)
S(A7)-C(A10)	1.809(8)	S(C2)-C(C2)	1.806(10)
S(A8)-C(A7)	1.747(8)	S(C2)-C(C4)	1.734(8)
S(A8)-C(A9)	1.792(8)	S(C3)-C(C3)	1.755(8)
C(A1)-C(A2)	1.522(12)	S(C3)-C(C5)	1.744(9)
C(A3)-C(A4)	1.354(11)	S(C4)-C(C4)	1.748(8)
C(A5)-C(A6)	1.348(10)	S(C4)-C(C5)	1.743(9)
C(A7)-C(A8)	1.351(11)	C(C1)-C(C2)	1.513(13)
C(A9)-(A10)	1.517(12)	C(C3)-C(C4)	1.349(12)
		C(C5)-C(C5)[b]	1.362(11)
Angles/°			
C(A1)-S(A1)-C(A3)	102.7(4)	C(B1)-S(B1)-C(B3)	100.7(4)
C(A2)-S(A2)-C(A4)	100.5(4)	C(B2)-S(B2)-C(B4)	102.3(4)
C(A3)-S(A3)-C(A5)	95.6(4)	C(B3)-S(B3)-C(B5)	95.3(4)
C(A4)-S(A4)-C(A5)	96.0(4)	C(B4)-S(B4)-C(B5)	95.1(4)
C(A6)-S(A5)-C(A8)	95.6(4)	S(B1)-C(B1)-C(B2)	114.9(7)
C(A6)-S(A6)-C(A7)	95.0(4)	S(B2)-C(B2)-C(B1)	114.2(6)
C(A8)-S(A7)-C(A10)	102.2(4)	S(B1)-C(B3)-C(B4)	127.9(6)
C(A7)-S(A8)-C(A9)	100.6(4)	S(B1)-C(B3)-S(B3)	115.0(5)
S(A1)-C(A1)-C(A2)	113.4(6)	S(B3)-C(B3)-C(B4)	117.0(6)
S(A2)-C(A2)-C(A1)	112.8(5)	S(B2)-C(B4)-C(B3)	128.9(6)
S(A1)-C(A3)-C(A4)	129.0(5)	S(B2)-C(B4)-S(B4)	113.6(5)
S(A1)-C(A3)-S(A3)	114.3(4)	S(B4)-C(B4)-C(B3)	117.5(6)
S(A3)-C(A3)-C(A4)	116.7(6)	S(B3)-C(B5)-S(B4)	115.1(4)
S(A2)-C(A4)-C(A3)	127.2(6)	S(B3)-C(B5)-C(B5)[a]	123.4(6)
S(A2)-C(A4)-S(A4)	115.6(5)	S(B4)-C(B5)-C(B5)[a]	121.5(6)
S(A4)-C(A4)-C(A3)	117.1(5)	C(C1)-S(C1)-C(C3)	98.7(4)
S(A3)-C(A5)-S(A4)	114.3(4)	C(C2)-S(C2)-C(C4)	103.1(4)
S(A3)-C(A5)-C(A6)	122.9(6)	C(C3)-S(C3)-C(C5)	95.2(4)
S(A4)-C(A5)-C(A6)	122.8(7)	C(C4)-S(C4)-C(C5)	95.4(4)
S(A5)-C(A6)-S(A6)	115.2(4)	S(C1)-C(C1)-C(C2)	112.6(6)
S(A5)-C(A6)-C(A5)	124.1(7)	S(C2)-C(C2)-C(C1)	113.4(6)
S(A6)-C(A6)-C(A5)	120.7(6)	S(C1)-C(C3)-C(C4)	126.7(6)
S(A6)-C(A7)-C(A8)	117.5(6)	S(C1)-C(C3)-S(C3)	116.2(5)
S(A6)-C(A7)-S(A8)	113.7(4)	S(C3)-C(C3)-C(C4)	116.9(6)
S(A8)-C(A7)-C(A8)	128.9(5)	S(C2)-C(C4)-C(C3)	129.0(6)
S(A5)-C(A8)-C(A7)	116.7(5)	S(C2)-C(C4)-S(C4)	113.8(5)
S(A5)-C(A8)-S(A7)	115.4(4)	S(C4)-C(C4)-C(C3)	117.2(6)
S(A7)-C(A8)-C(A7)	127.9(6)	S(C3)-C(C5)-S(C4)	115.3(4)
S(A8)-C(A9)-C(A10)	113.5(6)	S(C3)-C(C5)-C(C5)[b]	122.3(7)
S(A7)-C(A10)-C(A9)	113.7(5)	S(C4)-C(C5)-S(C5)[b]	122.4(7)

a)=(2−x, 1−y, 1−z) b)=(2−x, 1−y, −z).

Table 4. Dihedral Angles of (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K at 298 K and 104 K and M=NH$_4$ at 298 K)

	(BEDT-TTF)$_2$[KHg(SCN)$_4$]		(BEDT-TTF)$_2$[NH$_4$Hg(SCN)$_4$]
	298 K	104 K	298 K
A1-B	81.9°	82.4°	82.3°
A2-B	75.7	78.2	75.6
B-C	6.2	4.3	6.6

arrangement along the long molecular axis, the total packing pattern for (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M= K and NH_4) resembles that of α-(BEDT-TTF)$_2$I$_3$, rather than that of θ-(BEDT-TTF)$_2$I$_3$. Namely, every two BEDT-TTF donor of θ-(BEDT-TTF)$_2$I$_3$ repeats along the long molecular axis, whereas one donor arranges equivalently for α-(BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=NH_4 and K). Therefore, if we classify the BEDT-TTF salts by a three-dimensional packing pattern of the donors, the Hg systems studied here should be called α-phase.

The Hg systems have a curious anion arrangement. The anion layer comprises a triple-sheet (y=0, $\pm$0.08) parallel to the *ac*-plane. The y=0 sheet containing Hg^{2+} and NH_4^+ (or K^+) cations is sandwiched by y=$\pm$0.08 sheets where linear SCN groups are located. As shown in Fig. 6, the Hg atom is tetrahedrally coordinated by two S atoms of the SCN groups on the upper y=+0.08 sheet and another two S atoms on the lower y=−0.08 sheet. The two coordinated SCN groups on the upper (or lower) sheet are parallel to each other. Also, the two upper-coordinated SCN groups are arranged almost perpendicularly to the other two lower-coordinated SCN groups (Fig. 7). The distance between Hg^{2+} and S, (2.55—2.56 Å) is less than the sum of the ionic radius of Hg^{2+} and the van der Waals radius of S, 2.90 Å (Table 5). On the other hand, NH_4^+ (or K^+) is electrostatically linked by four N atoms of NCS groups to form a pyramid. The N (in NH_4)··N (in NCS) distances (2.95—3.00 Å) are close to the van der Waals radii (2.98 Å) for M=NH_4 salt and K^+··N (in NCS) contacts (2.85—2.89 Å) are almost equal to the sum of the ionic radius of K^+ and the van der Waals radius of N (2.88 Å for M=K salt), respectively. Due to the thermal motion of NH_4^+, the hydrogen atoms could not be determined at room temperature for M=NH_4 salt. Since the ionic radius of NH_4^+ (1.43 Å) is a little larger than that of K^+ (1.33 Å) the contacts of N (in NH_4^+)··N (2.94—3.00 Å) are relatively larger than those of K^+··N (2.85—2.89 Å) by 0.1 Å, corresponding to the difference in the ionic radii between NH_4^+ and K^+. Figure 7 depicts the two-dimensional zig-zag network of ·· $\overset{\vdots}{\underset{\vdots}{NH_4}}$ ·· NCS ·· $\overset{\vdots}{\underset{\vdots}{Hg}}$ ·· SCN ··, spread over the (010) plane. NH_4^+ is replaced by K^+ for the M=K salt. The two-dimensional polymer of $(HgX_4)^{2-}$ (X=SCN and SeCN) was also reported in other inorganic complexes, M(II)Hg(SCN)$_4$ (M(II)= Co, Zn, and Cd) and CoHg(SeCN)$_4$.[13]

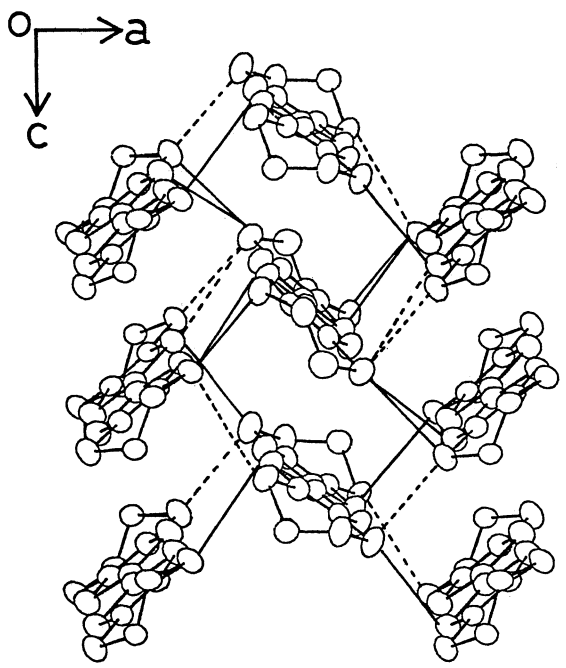

Fig. 5. Short S··S contacts of (BEDT-TTF)$_2$-[NH_4Hg(SCN)$_4$] at 298 K are shown in solid lines (3.47<r(——)<3.55 Å). The dotted lines indicate the increased number of S··S contacts (3.40< r(----)<3.60 Å) for (BEDT-TTF)$_2$ [KHg(SCN)$_4$] at 104 K.

In order to understand the electronic structure, the tight-binding energy band of (BEDT-TTF)$_2$[KHg-(SCN)$_4$] at 104 K was calculated on the basis of the extended Hückel method.[14] The calculated HOMO energy levels of crystallographically independent three donor molecules show no meaningful difference, indicating the absence of any charge separation among the donor molecules. The calculated overlap integrals of donor HOMO are c1=−1.9, c2=6.8, c3=−1.1, c4=−1.4, p1=−10.0, p2=−9.7, p3=13.3, and p4=13.2×10^{-3} (Fig. 4). The transverse interactions (p1-p4) are larger than those along the stack (c1-c4). Therefore, the two-dimensional network of these pre-

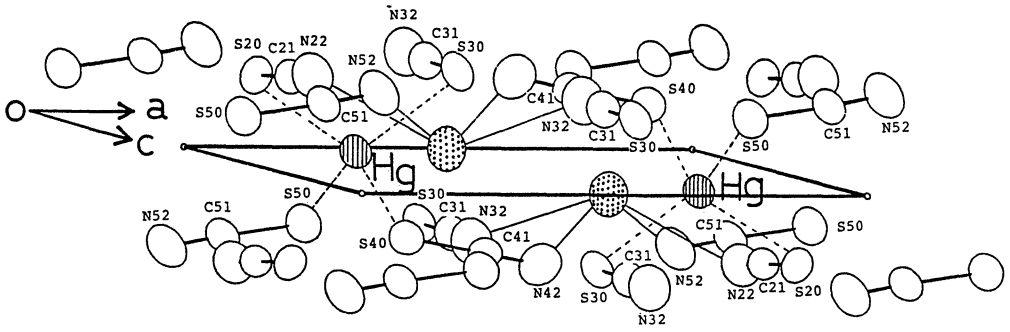

Fig. 6. Molecular arrangement of an anion for (BEDT-TTF)$_2$[NH_4Hg(SCN)$_4$].

Table 5. Bond Lengths (Å) and Angles (°) in an Anion for (BEDT-TTF)$_2$[MHg(SCN)$_4$] (M=K and NH$_4$)

	(BEDT-TTF)$_2$[KHg(SCN)$_4$]	(BEDT-TTF)$_2$[NH$_4$Hg(SCN)$_4$]	
	298 K	104 K	298 K
Hg-S20	2.562(4)	2.561(2)	2.562(2)
Hg-S30	2.569(4)	2.564(2)	2.559(2)
Hg-S40	2.558(4)	2.560(2)	2.557(3)
Hg-S50	2.549(4)	2.551(1)	2.545(2)
K(N100)-N22	2.85(2)	2.852(7)	2.995(13)
K(N100)-N32[a)]	2.85(1)	2.858(6)	2.943(12)
K(N100)-N42[b)]	2.89(2)	2.866(6)	2.948(13)
K(N100)-N52[c)]	2.89(1)	2.868(6)	2.989(12)
S20-Hg-S30	112.0(1)	111.9(1)	111.2(1)
S40-Hg-S50	110.2(1)	109.3(5)	109.2(1)
N22-K(N100)-N32[a)]	135.6(5)	134.9(2)	135.8(4)
N42[b)]-K(N100)-N52[c)]	131.8(4)	132.4(2)	133.0(4)
S20-C21	1.66(2)	1.677(7)	1.672(10)
C21-N22	1.22(2)	1.173(9)	1.159(13)
S30-C31	1.70(2)	1.677(7)	1.681(10)
C31-N32	1.17(2)	1.168(9)	1.155(13)
S40-C41	1.66(2)	1.683(7)	1.664(9)
C41-N42	1.21(2)	1.157(9)	1.146(13)
S50-C51	1.70(2)	1.674(7)	1.664(9)
C51-N52	1.15(2)	1.173(9)	1.151(12)
S20-C21-N22	178.0(15)	178.0(6)	177.4(9)
S30-C31-N32	178.9(16)	178.5(6)	178.1(9)
S40-C41-N42	174.9(16)	177.1(6)	178.1(9)
S50-C51-N52	178.9(15)	177.6(6)	177.7(8)

a)=(x, y, 1+z) b)=(1−x, −y, 1−z) c)=(−x, −y, 1−z.)

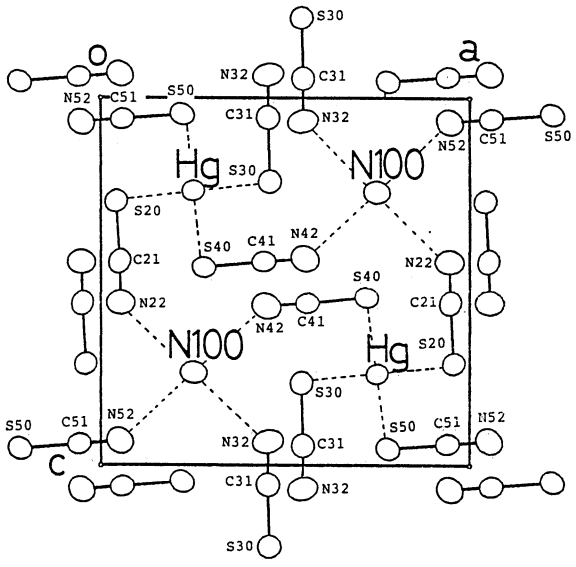

Fig. 7. Anion arrangement projected along the b*-axis.

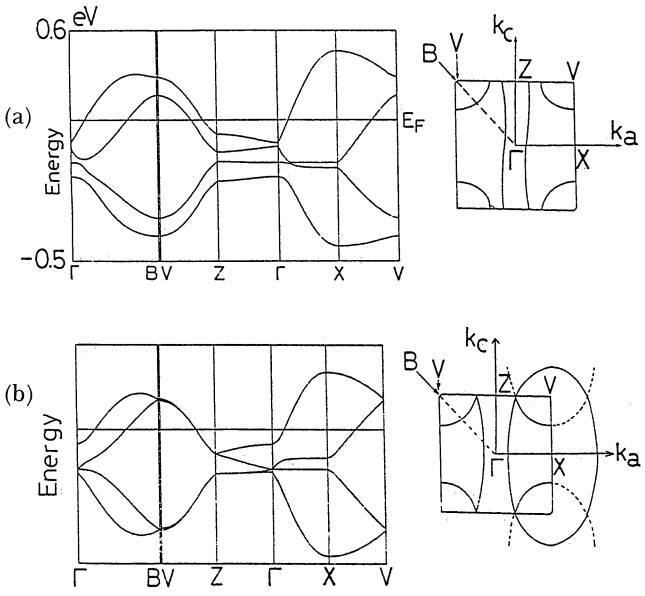

Fig. 8. (a) Energy band structure calculated from overlap integrals of c1=−1.9, c2=6.8, c3=−1.1, c4=−1.4, p1=−10.0, p2=−9.7, p3=13.3, and p4=13.2×10^{-3} and (b) energy band structure based on the simple model whose overlap integrals are c1=c2=c3=c4=−1.4, p1=p2=−9.8, and p3=p4=13.3×10^{-3} for (BEDT-TTF)$_2$ [KHg(SCN)$_4$].

dominant transverse interactions (p1-p4) affords a two-dimensional energy band.

The tight-binding energy band structure calculated from these overlap integrals is provided in Fig. 8(a). The two-dimensional Brillouin zone has a pair of electron-like open Fermi surfaces that run along the c-direction, and a closed hole-like Fermi surface around the V point. Because these Fermi surfaces seem to be very complicated, we consider a simplified model: when we assume c1=c2=c3=c4=−1.4, p1=p2=−9.8, and p3=p4=13.3×10^{-3}, the band structure becomes as shown in Fig. 8(b). This simplification introduces an artificial degeneracy on the ZV zone boundary to

make a large connected elliptical Fermi surface, the cross-section of which is equal to the first Brillouin zone. This is a typical two-dimensional Fermi surface, though it is somewhat elongated along the c-direction. The splitting of the degeneracy on the ZV zone boundary due to the subtle structural distortion separates the open and closed pieces of the Fermi surface, as shown in Fig. 8(a). Similar logic also applies to κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$].[15] The calculated density of states at E_F is 3.94 states/eV, which is close to 3.59 states/eV for κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$].[14]

The Fermiology of (BEDT-TTF)$_2$[KHg(SCN)$_4$] has been intensively investigated by means of magnetotransport measurements.[6] The Shubnikov-de Haas oscillation indicates the presence of a cylindrical Fermi surface, corresponding to the closed Fermi surface in Fig. 8(a). Its experimentally obtained cross-section is 16% of the first Brillouin zone, in qualitative agreement with the present calculation (19%). The anisotropy of this closed area, $k_F(a)/k_F(c)=2$, evaluated from the angle-dependent oscillations also seems to be basically consistent with the present calculation (Fig. 8(a)). The warping of the elliptical Fermi surface was confirmed by investigations of the angle-dependent oscillations; $t_\perp$ was estimated as being about 5 meV. The magnetotransport properties of (BEDT-TTF)$_2$[NH$_4$Hg(SCN)$_4$] will be reported soon.

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