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Crystal Structures and Electrical Properties of BEDT-TTF Salts of Mercury(II) Thiocyanate with and without K Ion

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The electrochemical oxidation of BEDT-TTF with $Hg(SCN)_2$, KSCN, and 18-crown-6 ether yielded two different BEDT-TTF salts of mercury(II) thiocyanate depending on the solvent used. The K^+ containing salt, $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$, was metallic down to 1.5 K with various temperature dependences. The crystal structures showed an alternating stacking of two-dimensional networks of BEDT-TTF molecules and of $KHg(SCN)_4$ anions. The other modification $(BEDT\text{-}TTF)_3[Hg(SCN)_3]$ exhibited metal-insulator (MI) transition at around 180 K.

As an extension of our recent observations of superconductivity in κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 10.4 K[1] and 13 K,[2] a variety of pseudohalide metal anions is currently investigated since some of them are able to construct a cluster or polymer anion. In this paper we report the electrical and structural properties of BEDT-TTF salts of Hg(II) thiocyanate.

An electrochemical oxidation of BEDT-TTF (57 mg) in the presence of $Hg(SCN)_2$ (319 mg), KSCN (98 mg), and 18-crown-6 ether (328 mg) in CH_2Cl_2 (100 ml) under 1.0 μA gave long black crystals (≈2x0.25x0.03 mm^3) after 18 days. The elemental analysis of the crystals indicated the composition of $(BEDT\text{-}TTF)_3[Hg(SCN)_3]$ (Found C, 25.54; H, 1.54; N, 3.07; S, 56.04%, Calcd C, 25.92; H, 1.58; N, 2.74; S, 56.63%). This salt shows a broad electronic absorption extending to the IR region indicating a partial charge transfer (CT) state of BEDT-TTF molecules (Fig. 1a). The electrical conductivity at room temperature was 23 S cm^{-1} and metallic down to about 180 K where a sharp MI transition occurred (Fig. 2). The crystal structure of this salt is not available since the crystals obtained were not suited for the work. The valency of the anion $Hg(SCN)_3$ is expected to be -1 just like as $KHg(SCN)_3$.[3]

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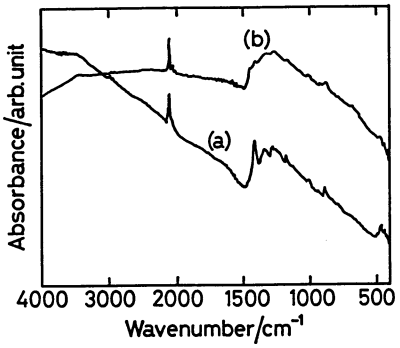

Fig. 1. IR spectra of $(BEDT\text{-}TTF)_3[Hg(SCN)_3]$ (a) and $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$ (b) in KBr.

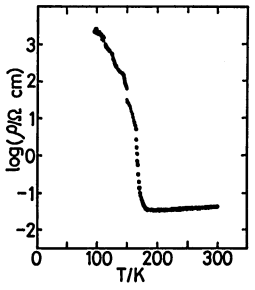

Fig. 2. Temperature dependence of electrical resistivity of $(BEDT\text{-}TTF)_3[Hg(SCN)_3]$.

A use of 1,1,2-trichloroethane (TCE) as a solvent did not give any crystals on the electrocrystallization. But by using a mixed solvent of TCE and 10% volume absolute ethanol, black thick plates (≈1.5x0.3x0.2 mm^3) were harvested under 1.0 μA after 35 days. EPMA measurement indicated the presence of K as well as Hg with almost the same content (atomic %). Elemental analysis suggested the composition of $(BEDT\text{-}TTF)_2KHg(SCN)_4$, though the agreement of sulfur is not excellent (Found C, 23.28; H, 1.30; N, 4.47; S, 49.20%, Calcd C, 23.22; H, 1.30; N, 4.51; S, 51.66%). The IR spectrum definitely indicates the partial CT state and the electronic transition extends lower energy side than that of the K^+ deficient salt (Fig. 1b).

The room temperature conductivities (20-100 S cm^{-1}) and the temperature dependences vary from sample to sample. Three typical behaviors of temperature dependence of normalized resistivities ($R(T)/R_{RT}$) are depicted in Fig. 3. A big enhancement or a weak shoulder of resistivity was observed at around 130 K in Type A or B, respectively, which is reminiscent of the resistivity behavior of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$.[1] Type C sample exhibited no anomaly at all. Despite the different temperature dependences at higher temperatures, all the samples were metallic at lower temperatures. The conductivity at 1.5 K of Type C sample was about 60 times higher than that at room temperature.

The crystal data of the salt at 298 K and 104 K are listed in Table 1. The

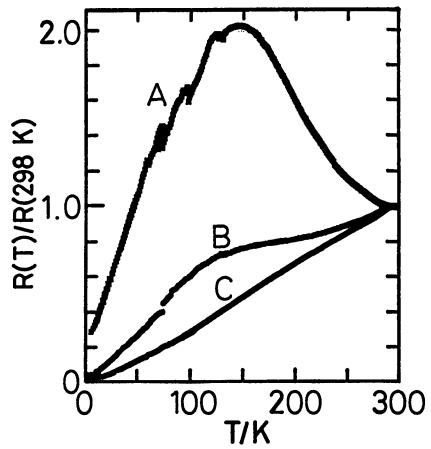

Fig. 3. Temperature dependence of electrical resistivity of $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$.

Table 1. Crystallographic data of $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$ at 298 K/104 K

	298 K	104 K
Crystal System	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a(Å)	10.082(10)	9.948(2)
b(Å)	20.565(4)	20.505(11)
c(Å)	9.933(2)	9.833(4)
α(°)	103.70(2)	103.34(4)
β(°)	90.91(4)	90.53(3)
γ(°)	93.06(4)	92.80(3)
V(Å^3)	1997(2)	1949(1)
Z	2	2
D_x (g/cm^3)	2.065	2.115
D_m (g/cm^3)	2.069	---
Reflections, used	7639	10100
R	0.0696	0.0418

structures were solved by the heavy atom method and refined by using independent reflections ($2\theta<60°$, Mo K_α, $|F_o|>3\sigma(F_o)$) to the R values in Table 1. The thermal parameters were anisotropic for all non-hydrogen atoms and isotropic for hydrogens.

BEDT-TTF molecules form a conducting sheet in the ac-plane which is sandwitched by the insulating layers of anion $KHg(SCN)_4$ along the b-axis (Fig. 4a). There are three crystallographycally independent BEDT-TTF molecules; one (A) is located on the general position and the other two (B and C) are on the inversion center (Fig. 4b). The bond lengths and angles of BEDT-TTF molecules suggest that they have the same formal charge of about +0.5.[4] The two kinds of stacks (AAA·· and BCBC·· along the c-axis) lie alternately along the a-axis with their dihedral angles as shown in Fig. 4b and Table 2. In addition to the face-to-face interactions of BEDT-TTF molecules along the stacking axis, several short S..S atomic contacts (3.435-3.60 Å) were observed along the side-by-side direction (a-axis). These features result in a two-dimensional Fermi surface calculated by the extended Hückel MO[5] and an observation of Shubnikov-de Haas signals[6] in this compound.

The total packing mode of BEDT-TTF molecules is much more similar to α-(BEDT-TTF)$_2I_3$ than that of θ-(BEDT-TTF)$_2I_3$[7] based on the periodicity along the b axis, since every two donors are the repeating unit in the θ-phase while each donor arranges equivalently both in the α-phase and this salt. But the dihedral angles between the molecules in the neighboring columns are considerably different from those of α-(BEDT-TTF)$_2I_3$, dihedral angles of which are 59.4° and 70.4°.[8]

The anion arrangement of this salt is very unique. An anion layer is consisted of triple-sheet (b=0, b=±0.08) parallel to (010) (Fig. 4a). The bottom and top sheets (b=±0.08) are made of zig-zag arrangement of linear SCN groups. The middle sheet (b=0) contains both K and Hg ions, where one of the K ions in a unit cell is electrostatically linked to four SCN groups in the bottom sheet with nitrogen atoms to form a pyramid (K..N 2.85-2.89 Å). The other K ion forms a pyramid in the same way with the SCN ions in the top sheet. The calculated radii of N (1.33-1.37 Å) by using the length of K..N and the ionic radius of K (1.52 Å) is just between the van der Waals (1.5 Å) and covalent radius (0.70 Å) of N indicating the ionic character of the K..N bond. The softer Hg ions are coordinated to four SCN ions, two in the bottom and two in the top sheet, with sulfur atoms to form tetrahedrons. The Hg..S bond lengths (2.55-2.57 Å) are a little longer than the sum of covalent radii (2.52 Å) but considerably shorter than the ionic one (2.95 Å). So, every SCN is linked to K^+ and Hg^{2+} in this manner to construct a thick (6.8 Å) network of infinite

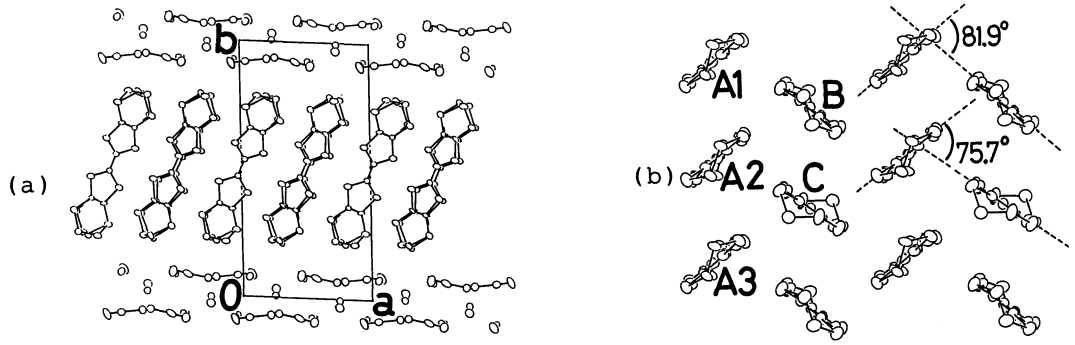

Fig. 4. Crystal structures of (BEDT-TTF)$_2$[$KHg(SCN)_4$] at 298 K along the c-axis (a) and the molecular long axis of BEDT-TTF (b).

Table 2. Dihedral angles and averaged interplanar distances of $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$

	298 K	104 K
A1-B	81.9°	82.4°
A2-C	75.7°	78.2°
B -C	6.2°	4.3°
A1-A2	3.81 Å	3.75 Å
A2-A3	3.76 Å	3.68 Å

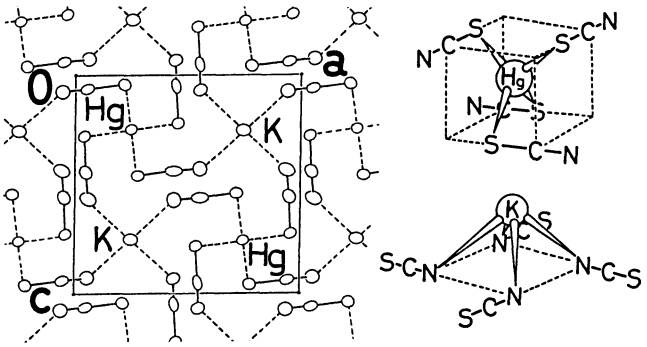

Fig. 5. Triple-sheet structures of anion $KHg(SCN)_4$ and schematic structures of its component clusters.

chains of ..SCN..K..NCS..Hg..SCN.. spreaded in the ac-plane (Fig. 5). Similar structures are reported on inorganic complexes, $M(II)Hg(SCN)_4$ (M(II)= Co, Zn, Cd)[9] which also contain Hg^{2+} tetrahedrally coordinated to sulfur atoms. The structure analysis at 104 K clarified the existence of several short anion..ethylene contacts such as S(anion)..H (2.79-2.96 Å), C(anion)..H (2.68-2.90 Å) and N(anion)..H (2.44-2.68 Å) contacts. The unit cell volume and lattice constants except β, which is almost constant, decreased monotonically with temperatures down to 104 K.

A replacement of K ions of $(BEDT\text{-}TTF)_2[KHg(SCN)_4]$ with NH_4 ions was successfully proceeded by using NH_4SCN instead of KSCN and the crystals were metallic down to 1.5 K. The crystal structures and other properties of this salt are under examination.

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References

1) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett., 1988, 55; G. Saito, H. Urayama, H. Yamochi, and K. Oshima, "Advances in Superconductivity," ed by Kitazawa and Ishiguro, Springer-Verlag (1989), p.107.
2) K. Oshima, R. C. Yu, P. M. Chaikin, H. Urayama, H. Yamochi, and G. Saito, to be submitted.
3) G. S. Zhdanov and V. V. Sanadze, Zhur. Fiz. Khim., 26, 469(1952).
4) H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, Mol. Cryst. Liq. Cryst., 107, 33(1984).
5) T. Mori, private communication.
6) S. Kagoshima and T. Osada, private communication.
7) H. Kobayashi, R. Kato, A. Kobayashi, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett. 1986, 833.
8) K. Bender, I. Hennig, D. Schweitzer, K. Dietz, H. Endres, and H. J. Keller, Mol. Cryst. Liq. Cryst., 108, 359(1984)
9) J. W. Jeffery, Nature, 159, 610(1947), R. W. G. Wyckoff, "Crystal Structures," 2nd ed, Interscience, New York (1963-65), Vols. I-V.

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