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ORGANIC METALS: ELECTROCRYSTALLIZATION OF THE COMPLEXES OF NAPHTHACENO[5,6-cd:11,12-c'd']BIS[1,2]DITHIOLE AND THEIR ELECTRICAL CONDUCTIVITIES

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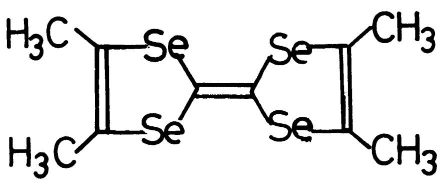
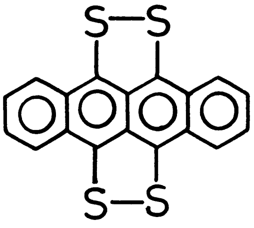
The complexes of naphthaceno[5,6-cd:11,12-c'd']bis[1,2]dithiole with inorganic anions (Cl^-, Br^-, I^-, ClO_4^-, BF_4^-, PF_6^-, and SbF_6^-) were obtained as crystals by an electrochemical technique. The temperature dependences of their electrical conductivities were measured. The PF_6 complexes showed 762 $(\Omega\ cm)^{-1}$ at room temperature, and it was metallic above 220 K.

The discoveries of the organic superconductivities of the complexes of tetramethyltetraselenafulvalene (TMTSF) with inorganic anions such as PF_6 and ClO_4 have stimulated greatly the studies on the highly conductive organic materials.$^{1)}$ These superconductive complexes were obtained by an electrochemical technique. The donor molecule, naphthaceno[5,6-cd:11,12-c'd']bis[1,2]dithiole (abbreviated as TTT) has also been known to produce highly conductive organic complexes.$^{2)}$ However, the complexes of TTT were obtained mainly by a cosublimation of a donor and an acceptor molecules or by mixing their solutions. The complexes of TTT produced by the electrochemical technique are also expected to show high conductivities. Kathirgamanathan and Rosseinsky reported that they could obtain TTT $I_{0.72}$ and $TTT(NO_3)_{0.74}$ by the electrochemical technique, using acetonitrile as a solvent.$^{3)}$ However, we could not reproduce their experimental results because of the



TMTSF



TTT

insolubility of TTT in acetonitrile even at the elevated temperatures. By using 1,1,2-trichloroethane (TCE) as a solvent, we could obtain the complexes, TTT $X_n(TCE)_m$, ($X = Cl$, Br, I, ClO_4, BF_4, PF_6 and SbF_6), as crystals by the electrochemical technique. Temperature dependences of their electrical conductivities were measured.

TTT was synthesized and purified by the reported procedures.[4)] The typical conditions of the electrocrystallization are as follows. A TCE solution (20 ml) of tetrabutylammonium salt (90 mg) and 15 mg of TTT was poured into the anode cell. To the cathode cell was poured the TCE solution (20 ml) of the tetrabutylammonium salt (90 mg). The two cells were separated by a glass filter. After the solution was bubbled by nitrogen gas for 10 min, the cell was immersed into a water bath thermostated at 30°C. The potential was selected to give a current of 1 - 5 μA between the platinum wire electrodes. It took three days to one week for the crystals to grow up as needles at the surface of the anode. Although all TTT were not soluble into the solvent, and some of them were found at the bottom of the anode cell initially, they were gradually dissolved as the electrochemical reaction proceeded. When a homogeneous solution of TTT was used, on the other hand, crystals did not grow up because of the too dilute concentration of TTT, and thereby of the insufficient supply of TTT molecule to the electrode surface.

Table 1 summarizes the complexes obtained, the typical sizes of the crystals, room temperature conductivities, and activation energies (only in the cases of semiconductive materials). Complexes with nonstoichiometric compositions were obtained, and some of them contained the solvent. Temperature dependences of the electrical conductivities of $TTT(PF_6)_{0.61}$, TTT $I_{0.90}(TCE)_{0.20}$, and $TTT(SbF_6)_{0.64}$ are shown in Fig. 1. In the case of $TTT(PF_6)_{0.61}$, two kinds of crystals were obtained, which can be distinguished from the appearances. The thin crystal (crystal 1 in Fig. 1) was more conductive than the thick one (crystal 2 in Fig. 1). $TTT(PF_6)_{0.61}$ (crystal 1) was the most conductive material, and it showed metallic behavior above 220 K. Its maximum conductivity was 1,050 $(\Omega\ cm)^{-1}$ at 220 K. $TTT(PF_6)_{0.61}$ (crystal 2) also showed metallic behavior above 190 K. TTT $I_{0.90}(TCE)_{0.20}$ showed almost no activation energy of the conductivity above 160 K. The conductivities of $TTT(PF_6)_{0.61}$ and TTT $I_{0.90}(TCE)_{0.20}$ decreased gradually at the lower temperature range like many low-dimensional conductors.[5)] The temperature dependences of the conductivities of TTT $X_n(TCE)_m$ ($X = SbF_6$, Cl, ClO_4, and BF_4) showed semiconductive behavior below room temperature.

We also tried to obtain the complexes of naphthaceno[5,6-cd:11,12-c'd']bis[1,2]-

diselenole(selenium analogue of TTT, and abbreviated as TSeT) by the same method as mentioned above. However, we obtained only microcrystalline complexes in the cases of TSeT X_n (X = I, ClO_4, and PF_6). Thus, TCE is an inappropriate solvent for the electrocrystallization of TSeT complexes.

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Table 1. The Complexes, Crystal Sizes, Room Temperature Conductivities, and Activation Energies of the Conductivities.

Complexes[a)]	Crystal Sizes/mm^3	Conductivities/$(\Omega cm)^{-1}$ [b)]	Activation Energy/eV[c)]
TTT $Cl_{0.75}(TCE)_{0.52}$	0.01 x 0.03 x 1	1.47 (S4)	0.05, 0.03
TTT $Br_{0.70}(TCE)_{0.16}$	0.01 x 0.007 x 0.5	45 (S2)	
TTT $I_{0.90}(TCE)_{0.20}$	0.01 x 0.02 x 2.5	158 (S4)	
TTT$(ClO_4)_{0.56}$	0.01 x 0.02 x 0.7	6×10^{-3} (S2)	0.08, 0.05
TTT$(BF_4)_{0.25}(TCE)_{0.20}$	0.01 x 0.05 x 2	2.5×10^{-2} (S2)	0.07, 0.05
TTT$(PF_6)_{0.61}$			
crystal 1	0.03 x 0.01 x 4	762 (S4)	
crystal 2	0.05 x 0.02 x 3	99 (S4)	
TTT$(SbF_6)_{0.64}$	0.01 x 0.02 x 1	40 (S4)	0.02

a) Determined by the elemental analyses of carbon and hydrogen of the complexes. The calculated and observed values coincided within 0.3 % with each other.

b) S4 and S2 mean the conductivities measured by a four probe method, and that measured by a two probe method, respectively.

c) The values show the activation energies of the conductivities at the higher and the lower temperature ranges, respectively. The temperature range: 293 - 185 K and 185 - 109 K for TTT $Cl_{0.75}(TCE)_{0.52}$; 293 - 160 K and 160 - 98 K for TTT$(ClO_4)_{0.56}$; 293 - 148 K and 148 - 126 K for TTT$(BF_4)_{0.25}(TCE)_{0.20}$.

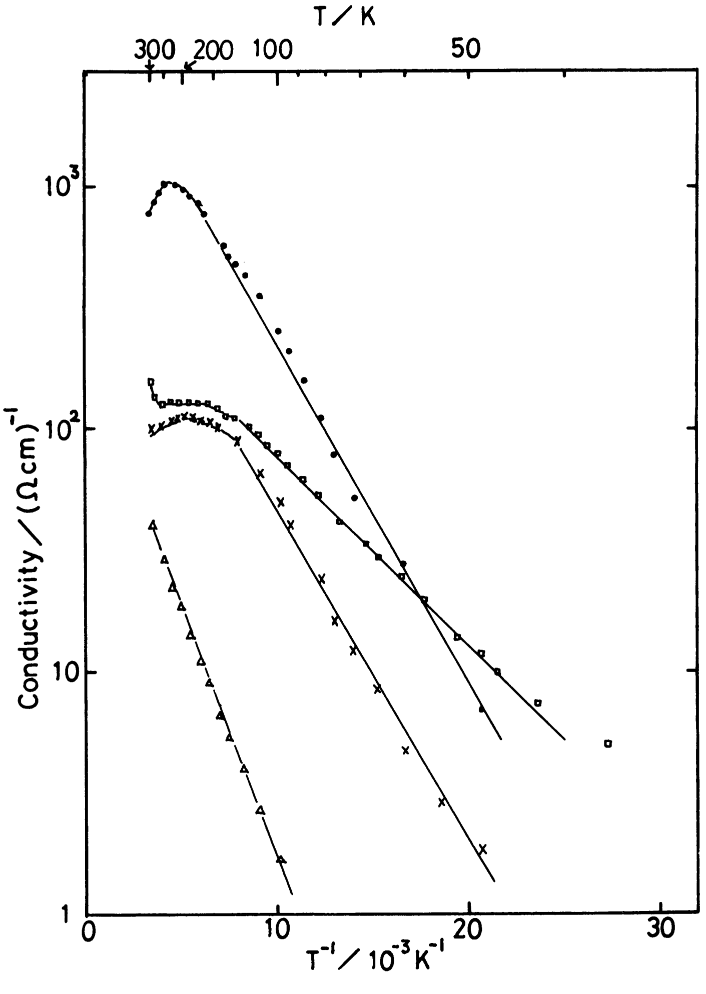

Fig. 1 Temperature dependences of the electrical conductivities of TTT complexes.

—●— $\mathrm{TTT(PF_6)_{0.61}}$ (crystal 1);

—X— $\mathrm{TTT(PF_6)_{0.61}}$ (crystal 2);

—□— $\mathrm{TTT\ I_{0.90}(TCE)_{0.20}}$

—△— $\mathrm{TTT(SbF_6)_{0.64}}$

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5) The activation energies of the conductivities of $\mathrm{TTT(PF_6)_{0.61}}$ (crystal 1), $\mathrm{TTT(PF_6)_{0.61}}$ (crystal 2), and $\mathrm{TTT\ I_{0.90}(TCE)_{0.20}}$ at the lower temperature range were 0.013, 0.012, and 0.0065 eV, respectively.

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