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Electrical Conductivity of HMTTeF Radical Salts

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Single crystals of HMTTeF•X_n (X=Cl, Br, I, PF_6, AsF_6, and ClO_4) were prepared by the electrochemical method. The in-plane conductivities of the plate-like chloride, bromide, and iodide crystals were found to show metallic temperature dependence in the range from 300 to ca. 100 K, and to maintain fairly high values even at 5 K. In these metallic salts, HMTTeF was found to be in the state of mixed-valency by Raman spectroscopy.

Occurrence of superconductivity in organic radical salts composed of tetramethyltetraselenafulvalene (TMTSF) and bis(4,5-ethylenedithiolo)-tetrathiafulvalene (BEDT-TTF) is known to be closely related to their two-dimensional nature of the electronic system derived from the interchalcogen interaction.[1-4] Hexamethylenetetratellurafulvalene (HMTTeF),[5] which was first synthesized by Wudl and Aharon-Shalom,[6] is expected to provide radical salts of enhanced two-dimensionality due to the large van der Waals radius of tellurium atom.[7] Saito et al.[8] and Cowan et al.[9] studied the electrical conductivity of several charge transfer complexes of HMTTeF with TCNQ and related electron acceptors, and found that the complexes with TCNQ and 2,5-dimethyl-TCNQ showed metallic conduction. These complexes are regarded as two-chain systems, both components being contributable to the metallic conduction. In order to understand the role of large tellurium atom in the metallic conduction, one-chain systems, i. e., radical salts of HMTTeF, have been investigated. Kikuchi et al. have reported the crystal-structure of triclinic $(HMTTeF)_4(PF_6)_2$,[10] and we have reported another modification, monoclinic $(HMTTeF)_4(PF_6)_2$.[11] These crystalline salts, monoclinic[11] and triclinic,[12] however, were semiconductors. Here we report the metallic conduction found for some HMTTeF radical salts and correlate it to their Raman spectra.

HMTTeF was purchased from Aldrich Co. and purified by chromatography of its CS_2 solution through a silicagel column. Single crystals of HMTTeF•X_n (X=Cl, Br, I, PF_6, AsF_6, and ClO_4) were grown from the solution of HMTTeF and tetra-n-butylammonium salt of X by the electrochemical method. Crystals large enough for conductivity measurement (ca. 0.5 × 0.5 × 0.03 mm^3 for plates and 1 × 0.05 × 0.05 mm^3 for needles) were obtained after one-week current passage of

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0.5-1.0 μA. Several kinds of solvents were examined for the electrocrystallization, and binary mixed solvents prepared from tetrahydrofuran (THF), chlorobenzene (CB), acetonitrile (AN), and 1,1,2-trichloroethane (TCE) were generally found to give single crystals of good quality, as shown in Table 1. Plate-like crystals were obtained for the Br and Cl salts and mixtures of plates and needles were obtained for the other salts. The composition (n) of the salts determined from the elemental analysis on C and H is presented in Table 1. Other elements could not be analyzed because of interference from tellurium. Electrodes of gold wires, 25 μm in diameter, were attached to crystals by using carbon paste and the conductivity (σ) was measured by the d.c. four-probe method in the region between room and liquid-helium temperatures.

The in-plane conductivity of the Br salt increased with a decrease in temperature down to 100 K and then decreased slowly (Fig. 1). The conductivity below 100 K could not be expressed as a simple exponential function of reciprocal temperature, and maintained fairly high values down to 5 K (Table 1). The Cl salt also showed metallic temperature dependence down to 170 K. The conductivity of a plate-like crystal of the I salt increased with a decrease in temperature, but suddenly dropped at ca. 120 K. The sudden drop in conductivity seems to be caused by microcracks in the sample, because the original conductivity was not restored upon warming above 120 K and the temperature for sudden drop varied from sample to sample. All of the other radical salts obtained were semiconductors with small activation energies (ΔE).

Raman spectra of powdered samples were measured to obtain information about formal charge on an HMTTeF component in the salts, as described in the previous paper.[13] Specific Raman frequencies of donors and/or acceptors in organic conductors are known to depend linearly on formal charge of the component

Table 1. Electrical conductivity and Raman frequency of HMTTeF•X_n

X	σ_{293}/S cm^{-1}	$\Delta E/10^{-2}$eV	ν/cm^{-1}	Solvent (volume ratio)	n
Cl (plate)	360 (1.6)[a]	metallic	1396	THF+CB (3:1)	
Br (plate)	350 (18)[a]	metallic	1395	THF+CB (1:1)	0.5
I (plate)	390 (3.9)[a]	metallic	1391	TCE+AN (3:1)	
(needle I)	87	5.5	1430	THF+TCE(1:1)	0.6
(needle II)	2.6	7.9	1474,1397	TCE+AN (1:1)	0.4
PF_6 (plate)[b]	23	2.3	1461,1406	THF+CB (1:1)	0.5
AsF_6 (plate)	15	2.7	1462,1404	THF+CB (1:1)	0.5
(needle)	8.3	5.6	1459,1395,1363	THF+CB (1:1)	
ClO_4 (needle)	470	8.3	1387	THF+TCE(1:3)	0.5
(rod)	10^{-3}		1455,1355	TCE+AN (1:3)	

a) Conductivitity at 5 K.

b) Twisted strips and needles were also obtained together with plates, but they were too small for the measurement of conductivity.

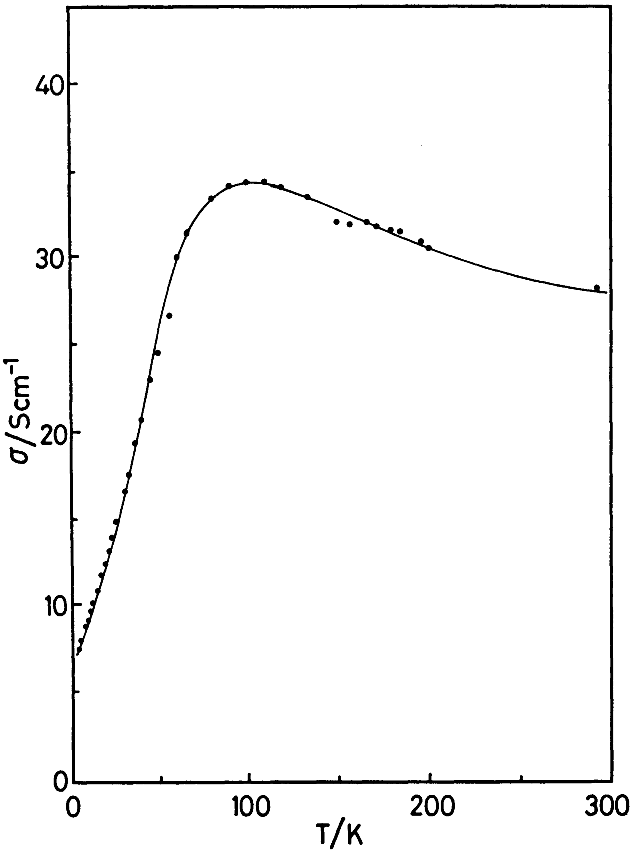

Fig. 1. Temperature dependence of electrical conductivity for HMTTeF•$Br_{0.5}$.

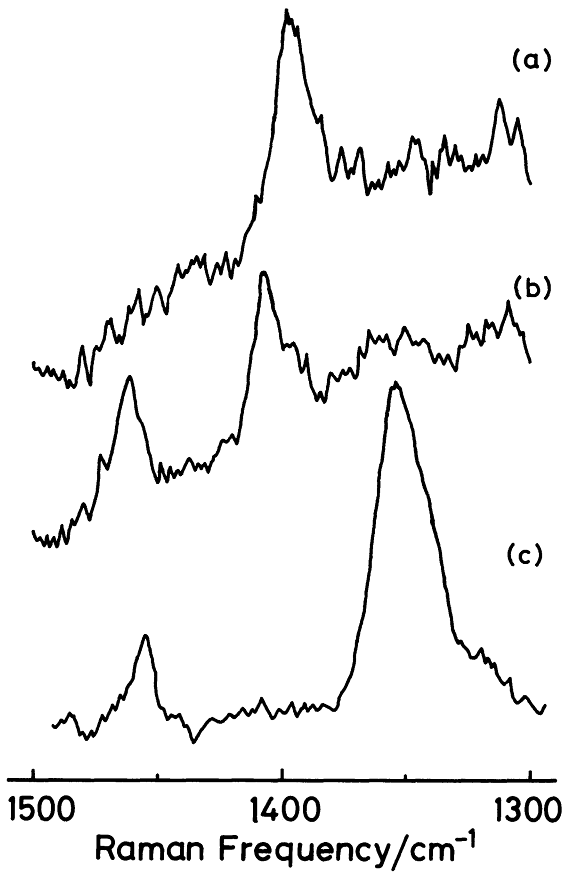

Fig. 2. Raman spectra of HMTTeF salts. (a) Br salt, (b) PF_6 salt (plate), and (c) ClO_4 salt (rod).

species.[14-17] In the case of HMTTeF-$TCNQF_4$,[13] the stretching vibrational frequency of the central C=C bond in HMTTeF was successfully used for the estimation of the formal charge on HMTTeF. Raman spectra of the Br, PF_6, and rod-like ClO_4 salts are shown in Fig. 2. The metallic Br salt as well as the I and Cl salts exhibited only a single Raman band in the frequency region of the stretching vibration of the central C=C bond, as shown in Fig. 2(a) and Table 1. The appearance of such a single band has been ascribed to the merging of a band of neutral HMTTeF species with that of ionized HMTTeF species through the band-motion of conduction electrons.[17,18] Therefore, the observed Raman spectra for the metallic salts provide evidence of HMTTeF in the state of mixed-valency. On the other hand, most of the semiconductive salts showed two-band spectra. For example, the PF_6 salt showed Raman bands at 1461 and 1406 cm^{-1} as shown in Fig. 2(b). The former has been assigned to neutral HMTTeF species and the latter to mixed-valence HMTTeF species on the basis of its crystal-structure analysis.[11] The difference in frequency between 1461 cm^{-1} for the salt and 1472 cm^{-1} for a neutral HMTTeF crystal is ascribed to a crystal field effect. The rod-like crystal of the ClO_4 salt exhibited Raman bands at 1455 and 1355 cm^{-1} as shown in Fig. 2(c). The former is assigned to neutral HMTTeF species and the latter to ionized species, HMTTeF$^+$, of which band is expected to appear around 1360 cm^{-1}.[13] In Table 1, the underlined frequencies are attributable to the neutral species present in the salts. Thus the conductive behavior of each HMTTeF salt is closely related to the feature of its Raman spectrum, and the absence of neutral species in the salt seems to be favorable for occurrence of metallic conduction.

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