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THE CRYSTAL STRUCTURE OF A NEW CHARGE-TRANSFER SALT OF HEXAMETHYLENETETRATELLURAFULVALENE, $(HMTTeF)_4(PF_6)_2$

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The single crystal of $(HMTTeF)_4(PF_6)_2$ was first prepared by the electrochemical method. The X-ray crystal structure analysis revealed that among four HMTTeF molecules in the unit cell, three are stacked to form trimeric molecular column along the a-axis and the remaining one is located between the HMTTeF columns, having very short intermolecular Te-Te distances with the HMTTeF column.

Behaviors as organic conductors and/or superconductors, of tetramethyltetraselenafulvalene (TMTSF) and the related materials are known to be strongly dependent of the intermolecular Se-Se interaction.$^{1)}$ In this connection, it is of great interest to investigate the charge-transfer salts of the tellurium analogues of tetrathiafulvalene and its derivatives since a strong Te-Te interaction can be expected. Recently, hexamethylenetetratellurafulvalene (HMTTeF) was synthesized by Wudl and Ahron-Shalom.$^{2)}$ Saito et al. prepared several charge-transfer salts of HMTTeF with TCNQ and related electron acceptors, and studied their electrical resistivities in the form of compressed powder pellet.$^{3)}$ They reported that some of these salts showed a considerably low resistivity. However, any study on the single crystals of HMTTeF salts has not been reported yet to our knowledge. We report here the preliminary results of the crystal structure of $(HMTTeF)_4(PF_6)_2$. We believe that this is the first structural report concerned with the charge-transfer salts of HMTTeF.

HMTTeF was prepared by the method described by Wudl and Ahron-Shalom,[2] and purified on a silica-gel column by using CS_2 as the solvent. The single crystals of the PF_6 salt were grown from the solution of HMTTeF and Bu_4NPF_6 by the electrochemical method with constant current of 0,5-2.0 μA. Several different solvents were examined for the electrochemical crystal growth. Although most cases gave only twin crystals, we succeeded to obtain single crystals from the 1:1 mixed solution of CS_2 and 1,1,2-trichloroethane (TCE) and from that of CS_2 and tetrahydrofurane, but with different crystal habits: The crystals grown from the former solution were of plate-like shape and those from the latter solution were of needle shape. X-Ray diffraction exhibited that these two are different crystal modidifications. The electrical resistivity of these single crystals was measured along the elongated axis by the two-probe method at room temperature. The conductivity values obtained were 3 $\Omega^{-1}cm^{-1}$ for a plate-like crystal and 60 $\Omega^{-1}cm^{-1}$ for a needle crystal.

We carried out an X-ray crystal structure analysis on the low-conductive modification. The 4954 intensity data were collected for non-zero independent reflections by using a Rigaku automated 4-circle diffractometer with the Cu kα radiation monochromatized by graphite. The crystal size used was 0.6×0.08×0.01 mm^3. The crystal is triclinic with space group $P\bar{1}$, the lattice constants being a=11.336(8), b=14.318(10), c=11.027(13) Å, α=84.65(8), β=101.87(8), γ=98.90°(8), and Z=1. The structure was solved by the Monte-Carlo direct method[4] by use of MULTAN-78 program system[5] and refined by the full-matrix least-squares method with the analytical absorption correction.[6] The final R-value was 0.109, which being still relatively large. The size of the crystal used for the X-ray measurement was quite small as we have mentioned above, because it was not possible to obtain a larger single crystal. This smallness of the crystal caused relatively low S/B ratio in the intensity measurement, which may be the reason for the relatively large R-value in the final stage of the present crystal structure analysis.

The arrangement of the molecules is illustrated in Figs. 1 and 2. The unit cell contains four HMTTeF molecules. Among them, three (the molecules A, B, and

A' in Fig. 1) are stacked along the a-axis to make a trimeric molecular column of HMTTeF, and the remaining one (the molecule C in Fig. 1) is located in the space between HMTTeF columns making its molecular plane almost parallel to the direction of the column. Some of the bond distances within HMTTeF molecule are given in Table 1, together with the values reported for the crystal of HMTTeF.$^{7)}$ Although the standard deviations are considerably large, the bond distances suggest that the HMTTeF molecules in the column are partially ionized while the intercalated molecules are neutral.

The intermolecular spacings in the HMTTeF column are almost equal: 3.72 Å between A and B, and 3.74 Å between A and A'. The mode of the molecular stacking in the column very well resembles that in $(HMTSF)_3(PF_6)_2(C_6H_5Cl)_3$$^{8)}$ as illustrated in Fig. 3. But it should be noted that in the latter case, the solvent molecules are occupying the space between HMTSF columns, whereas HMTTeF molecules are located in the corresponding space in the crystal of $(HMTTeF)_4(PF_6)_2$. The Te-Te distances within the HMTTeF column are 4.02 and 4.10 Å, but much shorter Te-Te distances are found between the columns and the intercalated molecules, the shortest Te-Te distance being 3.67 Å between the molecules B and C, and 3.77 Å

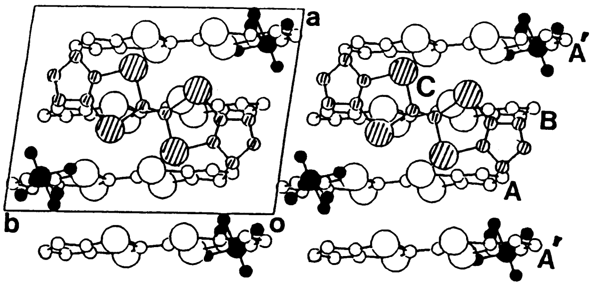


Fig. 1. A side view of the stack. The stacked HMTTeF molecules are A, A' and B, and the intercalated one is C (drawn by hatched circles). PF_6^- anions are drawn by closed circles.

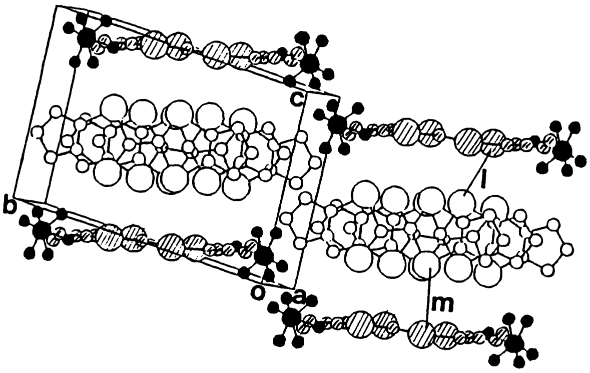
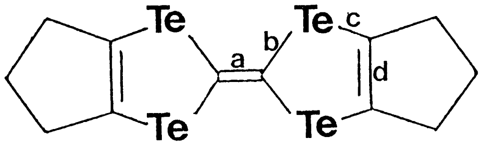


Fig. 2. A view along the direction perpendicular to the molecular plane of stacked HMTTeF. The short Te-Te contacts between the intercalated HMTTeF and the stacked ones are shown as l (=3.67 Å) and m (=3.77 Å).

Table 1. Comparison of the molecular geometry of HMTTeF. A, B, and C correpond to the molecules shown in Fig. 1. N corresponds to the neutral molecule in the HMTTeF crystal.$^{7)}$



	a/Å	b/Å	c/Å	d/Å
A	1.59 (5)	2.05 (4)	2.07 (3)	1.40 (6)
B	1.44 (6)	2.09 (4)	2.07 (3)	1.46 (6)
C	1.23 (6)	2.15 (3)	2.10 (4)	1.28 (6)
N	1.356(7)	2.098(5)	2.090(5)	---

between the molecules A and C. The latter Te-Te distances are quite small in comparison with the van der Waals distance (4.12 Å).[9)] Seemingly there are considerably strong interaction between HMTTeF columns through these short Te-Te contacts.

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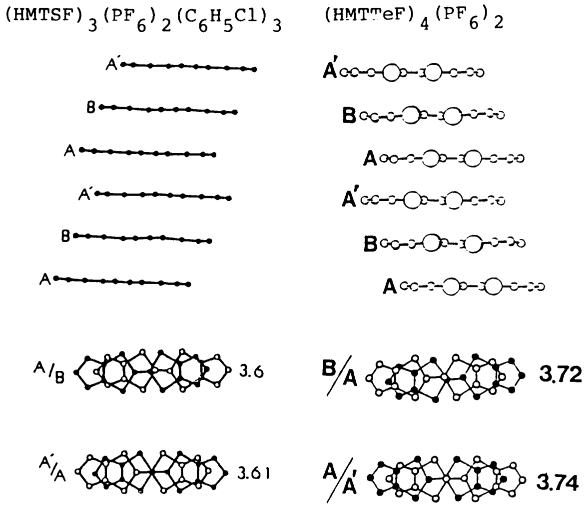

Fig. 3. Comparison of the stacking patterns and molecular overlaps in $(HMTSF)_3(PF_6)_2$-$(C_6H_5Cl)_3$ *and* $(HMTTeF)_4(PF_6)_2$.

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