CHEMISTRY LETTERS, pp. 1105-1108, 1986.

A Monoclinic Modification of an Ion Radical Salt, $(HMTTeF)_4(PF_6)_2$, and Its Solid State Properties

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A unit cell contains four formula units. In each formula unit, three hexamethylenetetratellurafulvalene (HMTTeF) molecules are stacked to form a triad over which two electrons are delocalized and the remaining one of neutral nature is positioned between the triads. The crystal has an electrical conductivity of 23 S cm^{-1} at 293 K with an activation energy of 0.023 eV.

Since the discovery of organic superconductors composed of tetramethyltetraselenafulvalene or bis(4,5-ethylenedithiolo)tetrathiafulvalene (BEDT-TTF), much attention has been paid on the two-dimensional nature of the electronic system through the interchalcogen interaction.1,2) Hexamethylenetetratellurafulvalene (HMTTeF),3) which was first synthesized by Wudl and Aharon-Shalom,4) is an interesting electron donor, because strong interchalcogen interaction is expected to occur from the viewpoint of a larger van der Waals radius of Te than S and Se and to provide organic salts with enhanced metallic character.5) Saito et al. studied the electrical conductivity of several charge transfer salts of HMTTeF with TCNQ and related electron acceptors.1) Kikuchi et al. prepared a single crystal of $(HMTTeF)_4(PF_6)_2$ and determined its crystal system to be triclinic (which is called α-form hereafter).6) Here we report a new modification of $(HMTTeF)_4(PF_6)_2$ (which is called β-form hereafter) and its solid state properties, such as electrical conductivity and the degree of charge transfer estimated by Raman spectroscopy.

HMTTeF was obtained from Aldrich Co. and purified by chromatography of its CS_2 solution through a silicagel column. Single crystals of β-$(HMTTeF)_4(PF_6)_2$ were grown from a solution of HMTTeF and tetra-n-butylammonium hexafluorophosphate by the electrochemical method through current passage of ca. 0.5 μA.

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Several solvents were examined for the electrochemical crystal-growth, and a 1:1 mixed solvent of tetrahydrofuran (THF) and chlorobenzene was found to give plate-like single crystals of the best quality. A mixed solvent of THF and 1,1,2-trichloroethane (TCE) gave a mixture of platelets, twisted strips and small needles which were not good enough for x-ray crystal-structure analysis. The α-form has been prepared from a 1:1 mixed solvent of TCE and CS_2.$^{6)}$

X-ray crystal-structure analysis of a plate-like single crystal was carried out with the aid of a Rigaku automated 4-circle diffractometer with the Mo Kα radiation. The 4577 independent reflections ($|F_0|>3\sigma(|F_0|)$) were collected ($2\theta \leq 55°$). The structure was solved by the direct method and refined by the block-diagonal least-squares method. The final R-value was 0.085. Crystal data: $(HMTTeF)_4(PF_6)_2$, monoclinic with space group C2/c, a=17.355(3), b=13.777(4), c=28.105(6) Å, β=99.18(2)°, V=6633.8 Å^3, and Z=4.

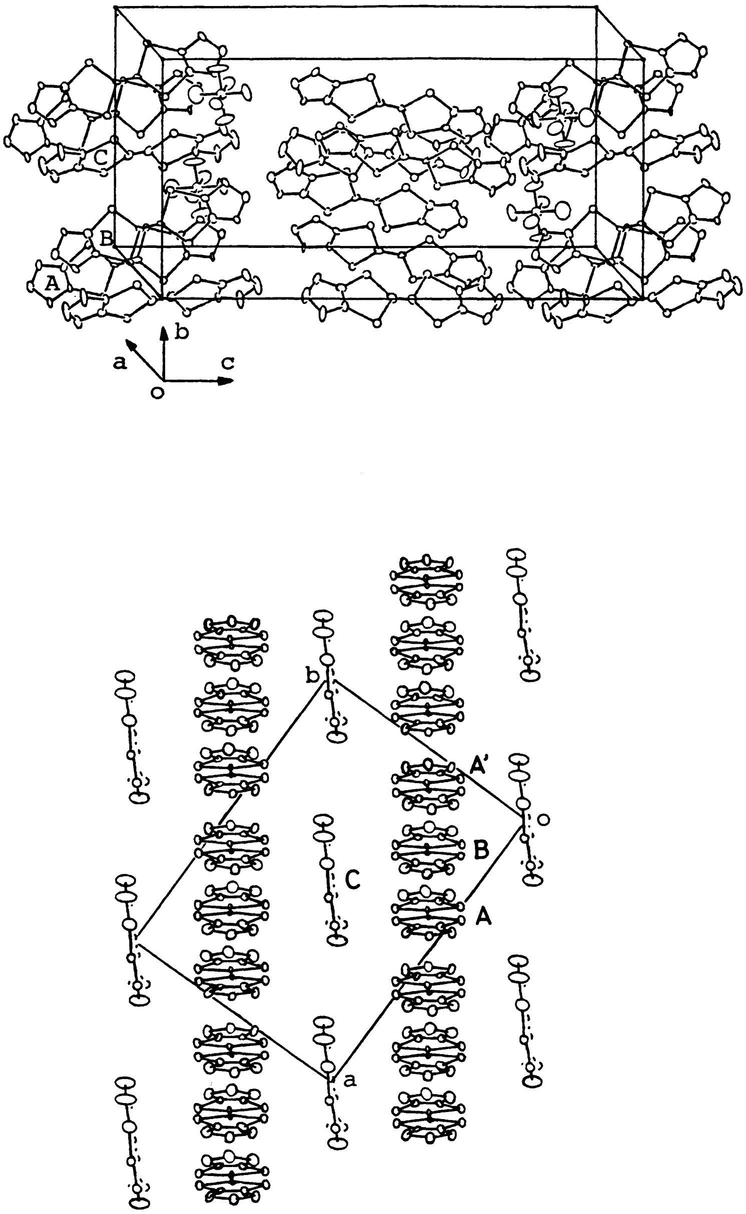

Fig. 1. Crystal structure of β-$(HMTTeF)_4(PF_6)_2$.

The arrangement of the molecules is illustrated in Fig. 1. A unit cell contains four formula units. In each formula unit consisting of four HMTTeF molecules, three (molecules A, B, and A' in Fig. 1) are stacked along [011] to form a trimeric molecular column, and the remaining one (molecule C in Fig. 1) is located in the space between the columns. The molecular plane of C is almost parallel to the stacking direction of A, B, and A' in the column. Molecules B and C are positioned on inversion centers. The dihedral angles between molecular planes are 86.7° for A and C, 86.3° for B and C, and 2° for A and B, respectively.

Some of the bond lengths (Å) and the bond angles (°) in the HMTTeF molecules are shown in Fig. 2. The standard deviations of the bond lengths are: σ(Te-C)=0.03-0.05 Å and σ(C-C)=0.04-0.08 Å. Those of the bond angles are: σ(C-Te-C)≃1.0° and σ(C-C-C)≃σ(C-C-Te)≃2.5°. The mean bond length of P-F is 1.56 Å. The angles of F_i-P-F_j (i,j=1-6) are 88.5-92.2°. The C=C bond lengths of tetrathiafulvalene are known to be increased on ionization,7) and a similar increment is expected to occur for HMTTeF which has a fulvalene skeleton. The C=C bond lengths of molecules A and B are found to be longer than those of molecule C, which indicates that molecules A and B have more ionic character than molecule C. Similar results have been reported for the α-form.6)

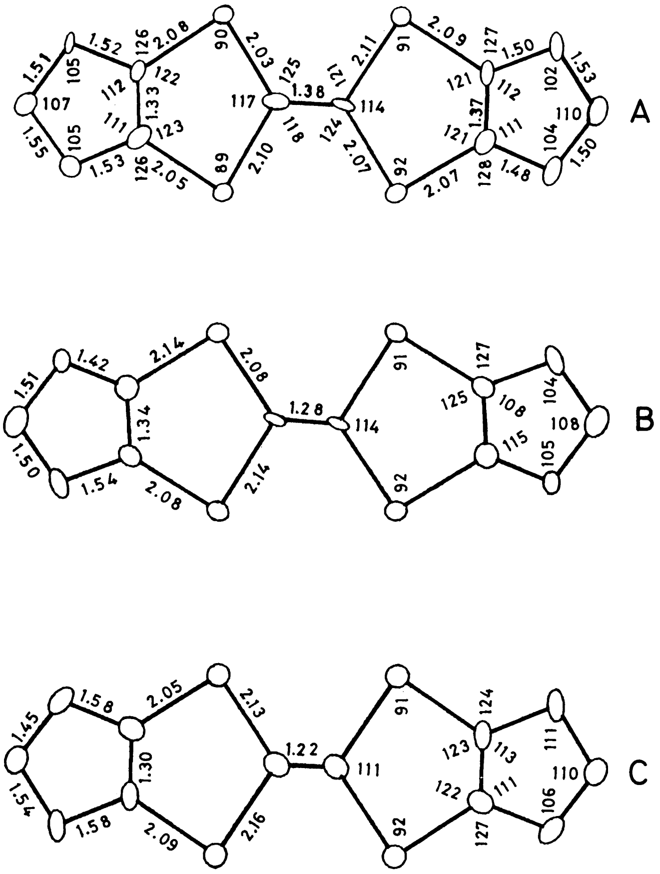

Fig. 2. Molecular geometry of HMTTeF in β-$(HMTTeF)_4(PF_6)_2$.

Coexistence of molecules in different valence-states is also demonstrated by Raman spectroscopy. Spectra of a powdered sample of β-$(HMTTeF)_4(PF_6)_2$ were measured using a JASCO R-800 spectrometer in the back scattering geometry. Excitation wavelengths were 632.8 nm (an NEC GLG-5800 He-Ne laser) and 514.5 nm (an NEC GLG-3200 Ar^+ laser). The sample rotating technique was adopted to prevent samples from decomposition caused by laser irradiation. Raman bands assigned to the stretching vibration (ν_3) of the central C=C bond of HMTTeF were observed at 1461 and 1406 cm^{-1}. The former can be ascribed to a neutral molecule, because the corresponding band for a neutral HMTTeF crystal is observed at 1472 cm^{-1}, the difference of 11 cm^{-1} being probably due to crystal field effect. The band at 1406 cm^{-1} can be ascribed to a molecule in a mixed-valence state. Recently, we have shown a linear relation between the ν_3 frequency and the formal charge on HMTTeF,8) and the frequency observed for β-$(HMTTeF)_4(PF_6)_2$ at 1406 cm^{-1} corresponds to a formal charge of 0.63 on HMTTeF, almost equal to 2/3. This result means that two electrons are delocalized over three HMTTeF molecules in the column within the time scale of vibrational spectroscopy. The ν_3 Raman band for completely ionized HMTTeF is expected to appear around 1360 cm^{-1} from the linear relation.[8)]

The Te-Te distance between A and A′ within an HMTTeF column is 3.85 Å and that between A and B is 3.94 Å, which are smaller than the corresponding values for the α-form (4.02 and 4.10 Å, respectively). Much shorter Te-Te distances are found between the columns: 3.65 Å between molecules B and C, and 3.88 Å between A and C. These short distances exhibit strong interaction between HMTTeF columns and two-dimensionality in the (001) plane through the Te-Te contacts. The van der Waals distance of Te-Te is 4.12 Å.[9)]

The electrical conductivity of a plate-like single crystal was measured in the (001) plane by the d.c. four-probe method in the range of 77-300 K. Good electrical contacts between a crystal and gold-wire electrodes (25 μmϕ) were maintained for several weeks when carbon paste (Fujikura Kasei S-3S) was used in place of silver paste as adhesive. The crystal showed a semiconductive behavior with an activation energy of 0.023 eV and a conductivity of 23 S cm^{-1} at 293 K. The twisted strips and needles were too small for the measurement of the conductivity. The conductivity of the α-form measured by the two-probe method has been reported to be 3 S cm^{-1} at room temperature.[6)]

This work was partially supported by a Grant-in-Aid for the Special Project Research on "The Properties of Molecular Assemblies" (No.58118002) from the Ministry of Education, Science and Culture.

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(Received April 18, 1986)