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Structure of Hexamethylenetetratellurafulvalene Diiodide

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Abstract. C₁₂H₁₂I₂Te₄, *M_r* = 920.44, monoclinic, *P*2₁/*n*, *a* = 10.942 (2), *b* = 14.924 (2), *c* = 11.415 (2) Å, β = 104.32 (1)°, *V* = 1806.0 (5) Å³, *Z* = 4, *D_x* = 3.38 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 100.7 cm⁻¹, *F*(000) = 1592, *T* = 294 K, *R* = 0.033 for 1828 observed reflections. One of the Te atoms is bonded to the two I atoms, which are on either side of the molecular plane. The Te—I distances are 2.963 (1) and 2.961 (1) Å, which means oxidation at the Te atom instead of at the C=C bonds.

Introduction. In the exploration of organic conductors much attention has been paid to hexamethylenetetratellurafulvalene (HMTTeF) as an interesting electron donor (Wudl & Aharon-Shalom, 1982). The larger van der Waals radius and lower electronegativity of the tellurium compared to those of sulfur and selenium are expected to enhance the metallic character of the organic radical salts. The electrical conductivity and the structures for several charge-transfer complexes of HMTTeF with TCNQF₄ (Li, Matsuzaki, Onomichi, Sano & Saito, 1986) and PF₆ (Kikuchi, Yakushi, Kuroda, Ikemoto, Kobayashi, Honda, Katayama & Tanaka, 1985; Li, Matsuzaki, Kato, Kobayashi, Kobayashi & Sano, 1986) have been studied. The plate-like crystals of

HMTTeF·*X_n* (*X* = Cl, Br and I; *n* < 1) have been found to show metallic character in the range from 100 to 300 K and to remain fairly conductive at 5 K (Matsuzaki, Li & Sano, 1986). It is well known that electrical conductivity is dependent on the crystal structure for organic radical salts. We report here the structure of a rhombic iodine derivative of HMTTeF and try to understand its conduction behaviour from a structural point of view.

Experimental. Single crystals of (HMTTeF)I₂ were prepared from a mixture of HMTTeF (10 mg) dissolved in CS₂ (20 ml) and (*n*-Bu)₄N₃I₃ (70 mg) in CH₃CN (20 ml) by an electrochemical method. The black rhombic crystals were obtained after passing a current of 0.5–1.0 μA through the mixture, under a nitrogen atmosphere, for one week. The conductivity value measured for a compressed pellet of (HMTTeF)I₂ powder was 4.1 × 10⁻³ S m⁻¹ at room temperature.

Crystal 0.2 × 0.2 × 0.2 mm. Nicolet R3m/E four-circle diffractometer, graphite-monochromated Mo *K*α (λ = 0.71069 Å) radiation; cell parameters by a least-squares fit for 25 centred reflections (10 < 2θ < 26°); reflection data 2θ_{max} = 45°, ω-scan mode, scan speed 4.88° min⁻¹, scan width 1.2°. Intensity

Table 1. *Final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^3$) with e.s.d.'s in parentheses for (HMTTeF)₂*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{eq}(\text{\AA}^2)$ |
|-------|------------|-----------|------------|------------------------|
| Te(1) | 6661 (1) | 859 (1) | 5597 (1) | 40 (1) |
| Te(2) | 9429 (1) | 1293 (1) | 4603 (1) | 45 (1) |
| Te(3) | 4702 (1) | 1413 (1) | 2569 (1) | 45 (1) |
| Te(4) | 7500 (1) | 1620 (1) | 1576 (1) | 48 (1) |
| I(1) | 7108 (1) | -1005 (1) | 4914 (1) | 48 (1) |
| I(2) | 6229 (1) | 2710 (1) | 6339 (1) | 57 (1) |
| C(1) | 7410 (11) | 1261 (8) | 4153 (11) | 40 (5) |
| C(2) | 6702 (10) | 1390 (7) | 3043 (11) | 37 (4) |
| C(11) | 8423 (11) | 835 (8) | 6788 (11) | 42 (4) |
| C(12) | 9481 (12) | 997 (8) | 6406 (11) | 42 (5) |
| C(13) | 10641 (11) | 928 (9) | 7427 (11) | 49 (5) |
| C(14) | 10146 (12) | 562 (12) | 8471 (12) | 63 (6) |
| C(15) | 8692 (12) | 684 (11) | 8116 (11) | 57 (6) |
| C(21) | 4705 (11) | 1267 (8) | 753 (10) | 44 (5) |
| C(22) | 5793 (12) | 1349 (9) | 383 (11) | 48 (5) |
| C(23) | 5549 (12) | 1261 (10) | -950 (11) | 53 (5) |
| C(24) | 4129 (13) | 1073 (10) | -1389 (11) | 57 (6) |
| C(25) | 3564 (11) | 1117 (9) | -258 (11) | 51 (5) |

Table 2. *Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses for (HMTTeF)₂*

| | | | |
|-------------------|-----------|-------------------|-----------|
| Te(1)—I(1) | 2.963 (1) | Te(1)—I(2) | 2.961 (1) |
| Te(1)—C(1) | 2.10 (1) | Te(1)—C(11) | 2.07 (1) |
| Te(2)—C(1) | 2.14 (1) | Te(2)—C(12) | 2.09 (1) |
| Te(3)—C(2) | 2.12 (1) | Te(3)—C(21) | 2.08 (1) |
| Te(4)—C(2) | 2.10 (1) | Te(4)—C(22) | 2.06 (1) |
| C(1)—C(2) | 1.33 (2) | C(11)—C(12) | 1.36 (2) |
| C(11)—C(15) | 1.49 (2) | C(12)—C(13) | 1.50 (2) |
| C(13)—C(14) | 1.53 (2) | C(14)—C(15) | 1.55 (2) |
| C(21)—C(22) | 1.36 (2) | C(21)—C(25) | 1.49 (2) |
| C(22)—C(23) | 1.48 (2) | C(23)—C(24) | 1.54 (2) |
| C(24)—C(25) | 1.56 (2) | | |
| I(1)—Te(1)—I(2) | 178.7 (1) | I(1)—Te(1)—C(1) | 86.5 (3) |
| I(2)—Te(1)—C(1) | 94.5 (3) | I(1)—Te(1)—C(11) | 88.2 (3) |
| I(2)—Te(1)—C(11) | 91.0 (3) | C(1)—Te(1)—C(11) | 92.3 (5) |
| C(1)—Te(2)—C(12) | 90.4 (5) | C(2)—Te(3)—C(21) | 89.9 (5) |
| C(2)—Te(4)—C(22) | 90.4 (5) | Te(1)—C(1)—Te(2) | 113.4 (5) |
| Te(1)—C(1)—C(2) | 122.8 (9) | Te(2)—C(1)—C(2) | 123 (1) |
| Te(3)—C(2)—Te(4) | 113.6 (5) | Te(3)—C(2)—C(1) | 125 (1) |
| Te(4)—C(2)—C(1) | 121.7 (9) | Te(1)—C(11)—C(12) | 121.1 (9) |
| Te(1)—C(11)—C(15) | 126 (1) | C(12)—C(11)—C(15) | 113 (1) |
| Te(2)—C(12)—C(11) | 122.4 (8) | Te(2)—C(12)—C(13) | 126 (1) |
| C(11)—C(12)—C(13) | 111 (1) | C(12)—C(13)—C(14) | 104 (1) |
| C(13)—C(14)—C(15) | 107 (1) | C(11)—C(15)—C(14) | 103 (1) |
| Te(3)—C(21)—C(22) | 121.0 (8) | Te(3)—C(21)—C(25) | 125 (1) |
| C(22)—C(21)—C(25) | 114 (1) | Te(4)—C(22)—C(21) | 122.1 (9) |
| Te(4)—C(22)—C(23) | 127 (1) | C(21)—C(22)—C(23) | 111 (1) |
| C(22)—C(23)—C(24) | 105 (1) | C(23)—C(24)—C(25) | 107 (1) |
| C(21)—C(25)—C(24) | 103 (1) | | |

checks for two standard reflections showed no significant variation; 2365 independent reflections, 1828 observed with $I > 2.5\sigma(I)$, L_p and empirical absorption corrections, max. and min. transmission coefficients 0.889 and 0.716.

The coordinates of the Te and I atoms were obtained by direct methods and the other atoms were located by difference Fourier syntheses. The structure was refined on F by a block-diagonal least-squares method. All non-H atoms were refined

anisotropically and H atoms isotropically in the rigid group with C—H 0.96 \AA . $R = 0.033$, $wR = 0.037$, $S = 1.18$ for 1828 observed reflections and 175 variables, where $w^{-1} = \sigma^2(F_o) + 0.0003(F_o)^2$, $(\Delta/\sigma)_{\max} = 0.03$, min. height in the final difference map -0.65 and max. 0.87 e \AA^{-3} , 0.98 \AA from an I atom. Final atomic coordinates with their e.s.d.'s are listed in Table 1.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed with *SHELXTL* (Sheldrick, 1983) program system on an Eclipse S/140 computer.

Discussion. Bond lengths and angles of the (HMTTeF)₂ molecule are listed in Table 2. The molecular structure is shown in Fig. 1 and the crystal packing in Fig. 2.

In the present compound (HMTTeF)₂ exists as a neutral molecule rather than discrete ionized units as observed in α - and β -(HMTTeF)₄(PF₆)₂ (Kikuchi *et al.*, 1985; Li *et al.*, 1986). The Te(1) atom is bonded to two I atoms which are on either side of the molecular plane in a near linear arrangement. The Te(1)—I bond lengths of 2.963 (1) and 2.961 (1) \AA are longer than the sum of covalent radii for Te and

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and close contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53899 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

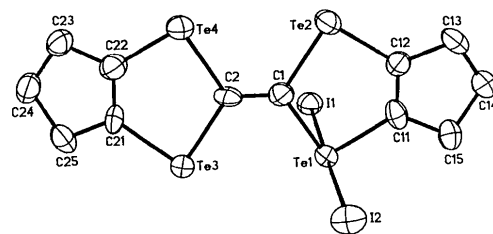


Fig. 1. Molecular structure of (HMTTeF)₂.

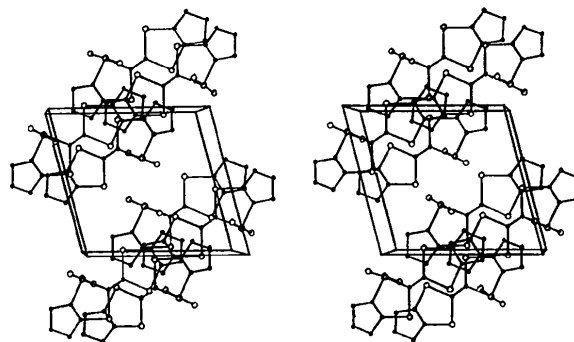


Fig. 2. Crystal-packing arrangement of (HMTTeF)₂ viewed down the b axis with the c axis horizontal and the a axis vertical.

I (2.70 Å), indicative of some ionic bond character. While the Te(1)—C bond lengths are comparable with those for the other Te atoms, the bond angle C(1)—Te(1)—C(11) is significantly greater than the other corresponding values. This difference can be a result of the different bond modes, namely *sp*³*d* hybridization for Te(1) and nearly pure *p* orbitals adopted for the other Te atoms. Moreover, Te—C bond lengths involving central carbons are slightly longer than those involving side ones, which can be ascribed to the steric repulsion between the Te atoms around the linkage of two central C atoms. In the charge-transfer salts of HMTTeF the C=C bond lengths were found to be increased on oxidation (Kikuchi *et al.*, 1985). A comparison of C=C bond lengths between this compound and the neutral HMTTeF molecule (Carroll, Lakshminantham, Cava, Wudl, Aharon-Shalom & Cox, 1982) shows little difference and suggests that oxidation is not occurring at the C=C bonds.

The molecules of (HMTTeF)₂ are partly stacked in the **b** direction, which is different from the complete stacking in (HMTTeF)₄(PF₆)₂ where three HMTTeF molecules with partially oxidized C=C bonds are stacked in a column with particular benefit for π -electron transfer. As seen in Fig. 2, a layer arrangement is formed in the direction perpendicular to the molecular planes. The Te(2) atom is in contact with C(21) and C(22) [3.86 (1) and 3.84 (1) Å] of the upper molecule ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) and with C(12) [3.89 (1) Å] of the lower molecule ($2 - x, -y, 1 - z$). The shortest intermolecular Te—I contact is 3.717 (1) Å.

In summary, the oxidation takes place mainly on the Te(1) atom in the title compound resulting in no π -electron transfer from the C=C bonds. This is why the compound does not exhibit the expected conductivity. Despite all this, the compound provides an interesting example of the iodides of HMTTeF and further supports the proposal that the oxidation of HMTTeF may originate from the tellurium lone pairs (Wudl & Aharon-Shalom, 1982). For the plate-like crystal of the other I salt (Matsuzaki, Li & Sano, 1986), however, it may be that oxidation results from π -electron transfer on the basis of its Raman spectrum and metallic conduction. Because of different crystallization conditions for the two compounds, it is clear that the oxidation of HMTTeF is related to the solvents and electrolytes used in electrocrystallization.

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Structure of the Cryptate (2.1.1) Dihydrochloride Dihydrate at 120 K

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Abstract. 4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]-icosane dihydrochloride dihydrate, C₁₄H₃₀N₂O₄²⁺·2Cl⁻·2H₂O, *M_r* = 397.34, monoclinic, *P*2₁/*n*, *a* = 18.956 (11), *b* = 12.939 (8), *c* = 8.338 (5) Å, β = 102.62 (5)°, *V* = 1995.7 Å³, *Z* = 4, *D_x* =

1.322 Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.36$ mm⁻¹, *F*(000) = 856, *T* = 120 K, final *R*(*F*) = 0.063 for 2632 independent observed reflections. In the crystal the cryptate dication has the *endo-endo* conformation with the protons on both N atoms