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TETRATELLURADICYCLOPENTA[b,g]NAPHTHALENE (TTeDCN)

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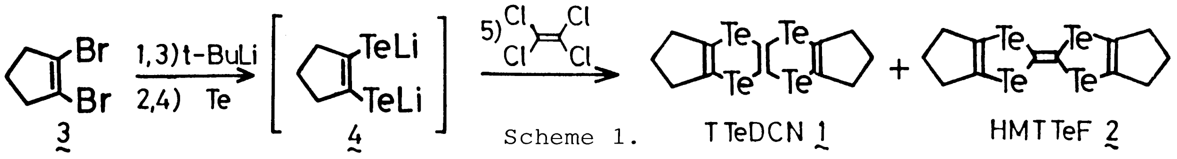
The first synthesis of tetratelluradicyclopenta[b,g]naphthalene (TTeDCN), which is a six-membered ring isomer of hexamethylenetetratellurafulvalene (HMTTeF), is reported. TTeDCN is obtained as yellow microcrystals and gives green single crystals in which TTeDCN forms a complex with HMTTeF in 1:1 molecular ratio.

In order to study the stepwise changes of the electronic properties of organic metals and superconductors by replacing the chalcogen from sulfur to selenium and tellurium atoms, synthesis of a new Te compound is quite desired.1,2) To date, some characteristic features have been already observed in Te compounds. For example, the difference between the first and the second oxidation potentials of Te-containing donor is generally less than that of sulfur or selenium analogue.1,2) The strong interaction between Te atoms seems to be a significant contributor to arrange molecules in crystal, since characteristic stacking modes have been accomplished in the solid Te compounds.1,3,4) Some of their charge transfer (CT) complexes show metallic behavior down to low temperatures and more than one-dimensional characters in the electrical properties are suggested.3,5)

In 1982, Wudl et al. synthesized hexamethylenetetratellurafulvalene (HMTTeF) 2 as the first example of the TTeF family.1) They have identified the product as HMTTeF on the basis of the elemental analysis, mass, IR, and UV-VIS spectra, and X-ray crystallography. In their synthetic method, there is a possibility of producing tetratelluradicyclopenta[b,g]naphthalene (TTeDCN) 1, which is a six-membered ring isomer of HMTTeF (Scheme 1). Hence, the preparation of TTeDCN has been required since that time. Whether TTeDCN can be obtained or not depends on the reaction conditions of the last step where the dilithioditelluride 4 attacks tetrachloroethylene. So we have examined the appropriate reaction conditions very carefully.

In the last step, the reaction was carried out by a dilution method; a THF (10 ml) solution of tetrachloroethylene (15 mmol) was added dropwise to a 0.05 mol dm^{-3} THF-pentane (THF:pentane = 9:1, 300 ml) solution of 4 (30 mmol) within ten minutes at -78 °C. The color of the solution changed from yellow to deep red immediately. The reaction mixture was stirred for forty minutes at -78 °C and stirred for another



Scheme 1.

twenty minutes at -15 °C. Then the reaction temperature was gradually raised to 0 °C over a period of thirty minutes. The solution showed the same deep red color and grayish green precipitates were formed. The precipitates were filtered and washed with ether. The crude product was purified by column chromatography (silica gel, CS_2) and recrystallized from chlorobenzene. Total yield was 63% from **3** based on $C_{12}H_{12}Te_4$. Three kinds of crystal were obtained and they were separated under a microscope; Crystal A (dark brown, main product),$^{6)}$ Crystal B (light green),$^{6)}$ and Crystal C (lemon yellow, microcrystals).$^{6)}$

Crystal A was identified as HMTTeF on the basis of the elemental analysis (C:21.59, H:1.97, N: 0%),$^{7)}$ density (D_m=2.94, D_c=2.965), mass (Fig. 1), IR (Fig. 2), and UV-VIS (Table 1) spectra, and the redox property (Table 2 and Fig. 3) by comparing with the literature data.$^{1)}$

Crystal B exhibits the elemental analysis (C:21.62, H:1.96, N: 0%),$^{7)}$ and the isotope pattern of the parent peak and the fragmentation pattern of mass spectrum (Fig. 1) agreeable with those of Crystal A. In order to identify Crystal B, we have carried out an X-ray crystallography and found that Crystal B is composed of HMTTeF and its six-membered ring isomer (TTeDCN) in 1:1 molecular ratio. The size of the crystal used was 0.2×0.2×0.05 mm^3. The 2726 intensity data were collected by using RIGAKU AFC-5 automated four-circle diffractometer with the Mo Kα radiation monochromatized by graphite. The ω-2θ ($2\theta \leqq 60^\circ$) scan technique was used. The crystal is triclinic with space group $P\bar{1}$. The lattice constants are a=8.566(1), b=11.750(1), c=7.926(1) Å, α=108.68(1), β=92.52(1), γ=89.06(1)°, V=750.6(2) $Å^3$, Z=1, and D_c= 2.95. The absorption correction was applied and the final R value was 0.033. The arrangement of the molecules is illustrated in Fig. 4. Both component molecules have non-planar configuration and the dihedral angle is 57.1° for TTeDCN and 14.3° for HMTTeF (Fig. 5). This dihedral angle of HMTTeF is about twice as large as those obsereved in HMTTeF crystal (7.7 and 8.2° for a HMTTeF molecule).$^{8)}$ The bond lengths of the central C=C bond are 1.295 and 1.321 Å for TTeDCN (C(1)-C(1)') and HMTTeF (C(1)-C(1)'), respectively in Crystal B (Table 3). Both are shorter than the normal C=C bond length (1.34 Å) and even shorter than the C(1)-C(1)' distance of HMTTeF in Crystal A (1.356 Å).$^{1)}$ In Crystal B, TTeDCN and HMTTeF molecules form a mixed stack along the b-axis, and there are short Te••Te contacts indicated by dotted lines (Fig. 4), the distance of which (3.864 Å) is much shorter than the sum of the van der Waals radius of Te (4.12 Å).

Finally we have identified Crystal C. In the mass spectrum of Crystal C, both of the parent peaks and the fragmentation pattern are

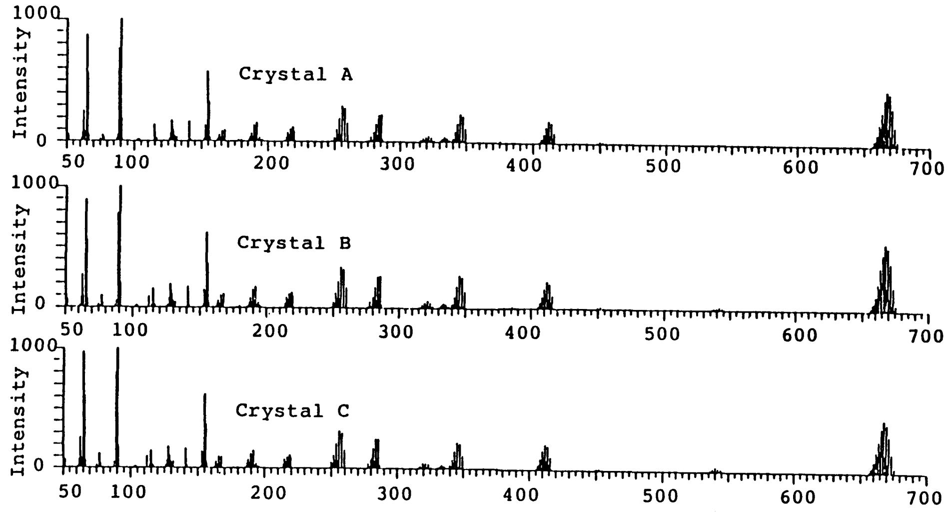


Fig. 1. Mass spectra.

Table 1. UV-VIS spectra (λ/nm)

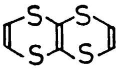
Crystal A[a)]	627	415	335	323	
Crystal B[a)]	623	415	332	317	275
Crystal C[a)]	273				
HMTTeF[1)]	610[b)]	410	335	320	

a) CH_2ClCH_2Cl. b) CS_2.

Table 2. Oxidation potential (E/V)

	$E^1_{1/2}$	$E^2_{1/2}$	E^1_{pa} b)	E^2_{pa} b)	$\Delta E_{1/2}$	ΔE_{pa}
Crystal A	0.39	0.64			0.25	
Crystal B	0.40	0.62	0.74	1.04	0.22	0.30
Crystal C			0.74	1.08		0.34
TTN 5[a,9)]	0.56	0.97[b)]			0.41	

0.1 M Bu_4NAsF_6 /PhCN, vs. Ag/Ag^+. $2E_{1/2}=E_{pa}+E_{pc}$. a) 0.05 M Et_4NClO_4 /CH_3CN, vs. Ag/Ag^+. b) Irreversible.



TTN 5

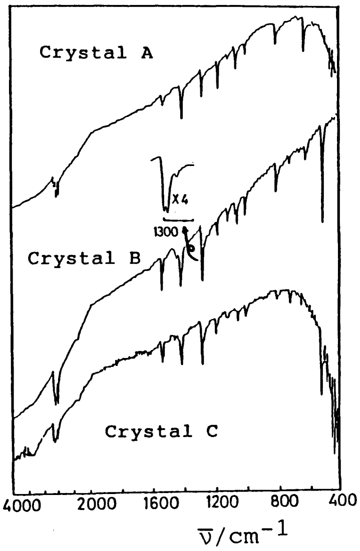


Fig. 2. IR spectra. (in KBr)

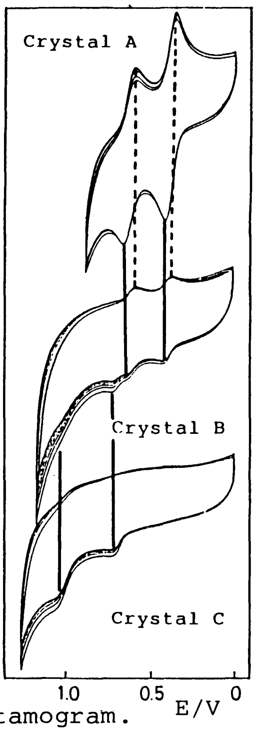


Fig. 3. Cyclic voltamogram.

almost the same as those of Crystal A and B (Fig. 1), and the elemental analysis of Crystal C (C:21.84, H:1.88, N: 0%)[7)] satisfies the molecular formula $C_{12}H_{12}Te_4$. But UV-VIS and IR spectra differ from those of HMTTeF. The absorption peaks in UV-VIS spectrum of Crystal B are attributable to those of Crystal C and A (Table 1). Furthermore, a superposition of the IR absorption bands of Crystal C and A corresponds with the IR spectrum of Crystal B (Fig. 2). Therefore, these data suggest that Crystal C is TTeDCN. This conclusion was made more reliable by the following evidence. A subtraction of the redox peaks of cyclic voltamogram of Crystal A from those of Crystal B corresponds in its peaks to those of Crystal C (Table 2 and Fig. 3). From all of these facts, it is concluded that Crystal C is composed of only TTeDCN.

Redox data show that the difference between the first and the second oxidation potentials ($\Delta E = E^1_{1/2}-E^2_{1/2}$) of TTeDCN (0.28 V)[10)] is smaller than that of tetrathianaphthalene (TTN) 5 (0.41 V).[9)] This decrement of ΔE by replacing sulfur atoms with tellurium atoms is due to the decrement of on-site Coulomb repulsion in the dication state of TTeDCN, as expected. $E^1_{1/2}$ of TTeDCN (0.74 V vs. Ag/Ag^+)[10)] indicates that TTeDCN is an electron donor comparable to DBTTeF and BDMT-TTeF ($E^1_{1/2}$=0.71 and E^1_{pa}= 0.78 V vs. SCE, respectively)[2)]in the donor strength, and might form partial CT state

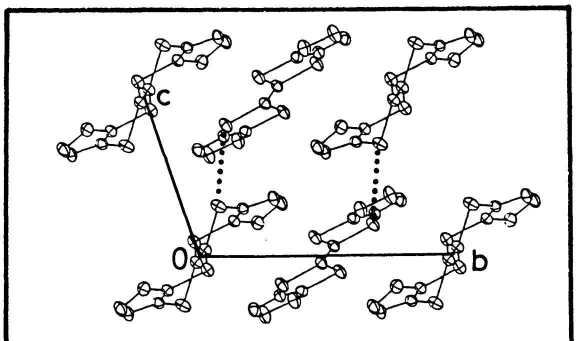


Fig. 4. Molecular arrangement in Crystal B.

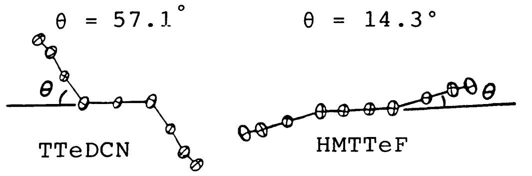


Fig. 5. Dihedral angles.

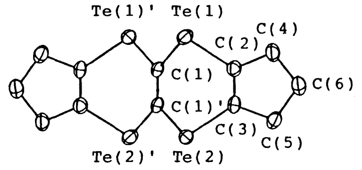
with a strong acceptor whose E_{red} value is between 0.43 and 0.78 V (vs. Ag/Ag$^+$), such as F_4TCNQ and HCBD ($E^1_{1/2}$=0.63 and 0.74 V vs. Ag/Ag$^+$, respectively).[10]

Yamamoto et al. have reported that the isomerization of the dication of TTN **5** to that of TTF in solution was detected by the cyclic voltammetry (scan range is 0–1.5 V vs. Ag/Ag$^+$).[11] But, when we measured the oxidation potentials of TTeDCN in benzonitrile by the cyclic voltammetry, such an isomerization was not observed until 1.5 V (vs. Ag/Ag$^+$).

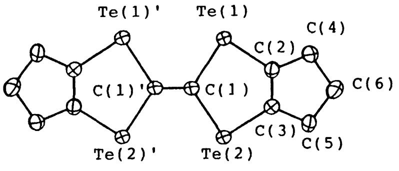
Table 3. Bond lengths and bond angles in Crystal B (distance/Å or angle/°)

Compound	C1-C1'	C1-Te1	Te1-C2	C2-C3	Te1-C1-C1'	C1-Te1-C2	Te1-C2-C3
TTeDCN	1.295(9)	2.130(7)	2.103(7)	1.314(10)	122.8(6)	95.0(3)	124.3(6)
HMTTeF	1.321(9)	2.122(7)	2.080(7)	1.331(10)	122.8(5)	90.2(3)	121.9(5)
HMTTeF[1]	1.356(7)	2.098(5)	2.090(5)			90.2(2)	122.1(4)

TTeDCN



HMTTeF



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6) Mp for Crystal A: decomposed at 270 °C, for Crystal B: decomposed at 258-259 °C, and for Crystal C: gradually decomposed above about 150 °C.
7) Calcd for $C_{12}H_{12}Te_4$: C, 21.60; H, 1.80; N, 0%.
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