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Quasi Three-Dimensional Electrical Conductor Having Alternating Mixed Stacks: Tetrakis(methyltelluro)tetrathiafulvalene ($TTeC_1$-TTF)·TCNQ Complex

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Tetrakis(methyltelluro)tetrathiafulvalene ($TTeC_1$-TTF) and TCNQ give a 1:1 CT complex with alternating mixed stacks whose electrical conductivity along the stacking direction is 1.0×10^{-2} S cm^{-1}. Quasi three-dimensional electrical conductivity was observed owing to its unique crystal structure where exist the two equivalent neighboring stacks linking each other with short Te···N contacts. These properties are compared with those of TTC_1- and newly prepared $TSeC_1$-TTF·TCNQ complexes.

$TTeC_1$-TTF (Fig. 1) [1,2] provides many attractive features in the field of single component organic systems. Especially noted are its high mobility (20-30 cm^2/V s) and low resistivity (8.1×10^4 Ω cm) which are scarcely observed in this field.[2] The appearance of these properties are ascribed to the strong Te···Te atomic contacts in the crystal. Added to the above features of $TTeC_1$-TTF, the on-site Coulomb repulsive energy of the molecule is considered to be small. These features of $TTeC_1$-TTF provide a stimulative opportunity for testing the possibility of having high dimensionality with high conductivity in its CT complexes.

Greenish black rhomboidal crystals ($1 \times 1 \times 0.2$ mm^3) of $TTeC_1$-TTF·TCNQ were obtained by mixing the hot dichloroethane solution of $TTeC_1$-TTF[1] with that of TCNQ and cooled at about -30 °C. The elemental analysis of this complex (Found: C,26.98; H,1.62; N,5.49; S,12.85%) is consistent with the 1:1 ratio of donor to acceptor (Calcd for $C_{22}H_{16}N_4S_4Te_4$: C,27.10; H,1.65; N,5.75; S:13.15%).

An X-ray crystallography was carried out using RIGAKU AFC-5 automated four-circle diffractometer with the Mo Kα radiation monochromatized by graphite. The ω-2θ ($2\theta \leq 60°$) scan technique was used. The crystal is monoclinic with space group C2/c. The lattice constants are a = 15.659(3), b = 8.207(2), c = 22.234(4) Å, β = 91.98(1)°, V = 2855(1) $Å^3$, and Z = 4. The final R value was 0.0567. The molecular structure of $TTeC_1$-TTF and TCNQ are shown in Fig. 2. TCNQ is almost planar but two of four methyl groups of $TTeC_1$-TTF are out of the residual molecular plane whose planality is within

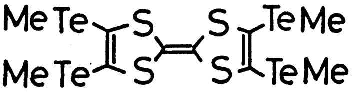

Fig. 1. $TTeC_1$-TTF.

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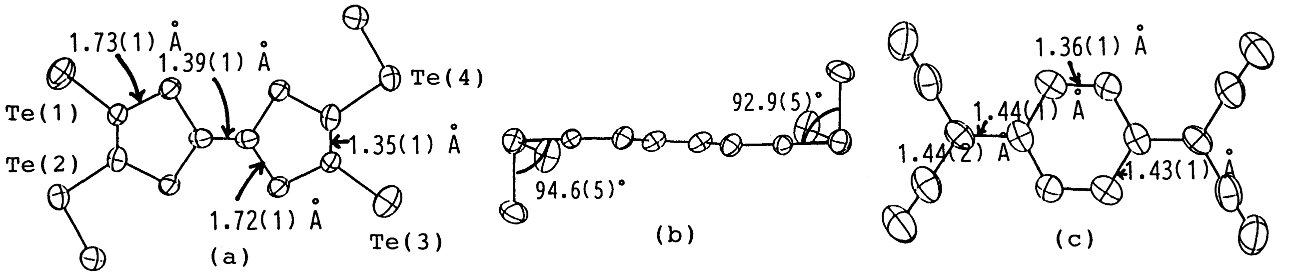

Fig. 2. Molecular structures of $TTeC_1$-TTF (a,b) and TCNQ (c) in the $TTeC_1$-TTF·TCNQ complex.

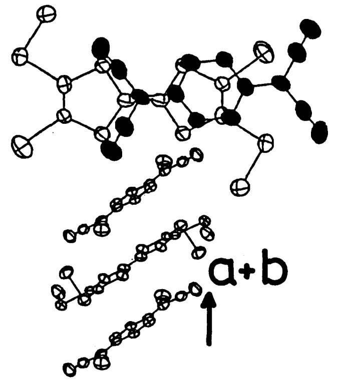

Fig. 3. Molecular overlap along the stacks.

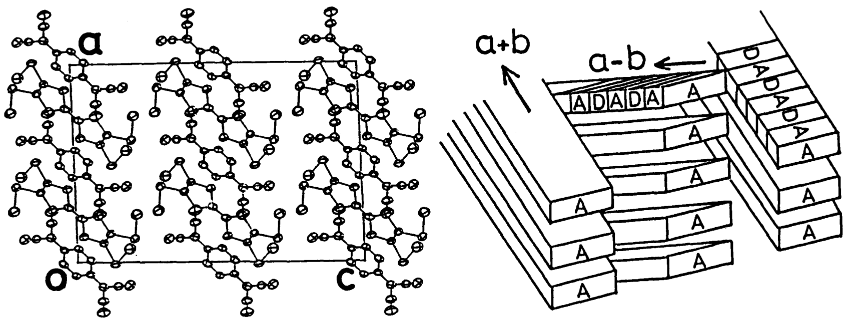

Fig. 4. Molecular arrangement and its schemetic representation of the $TTeC_1$-TTF·TCNQ comlex.

0.1 Å. $TTeC_1$-TTF and TCNQ form the uniform mixed stacks of DA type and the interplanar distance between the best molecular planes is considerably short (3.38 Å). The overlap of the neighboring donor and acceptor along the stacking direction is shown in Fig. 3. This DA type stack has two kinds of stacking directions along which the arrangement of molecules is completely identical (Fig. 4). One direction is [1 1 0] and the other is [1 $\bar{1}$ 0]. These equivalent columns lie along the c axis with the dihedral angle of 55.3° to each other and have short atomic contacts between them. As illustrated by broken lines in Fig. 5, the tellurium atoms linked to the terminal carbon atoms within the molecular plane of the TTF moiety (Fig. 2a; Te(2) and Te(4)) closely contact to the nitrogen atoms of TCNQ, contrary to the case of $TTeC_2$-TTF·TCNQ complex which has no short atomic contacts using tellurium atoms due to the large steric hindrance of ethyl groups.[3)] This Te··N distance is 3.39 Å and significantly shorter than the sum of

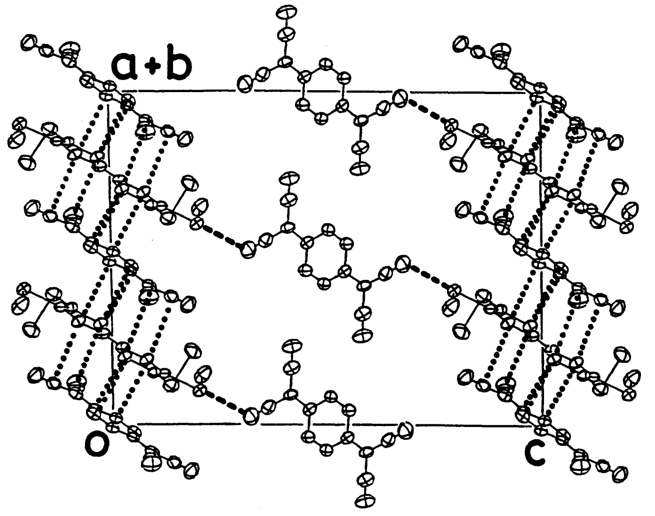

Fig. 5. Atomic contacts in the $TTeC_1$-TTF·TCNQ complex.

the van der Waals (vdW) radius of Te and N (3.56 Å). Within the DA stacks there are also short S··C contacts indicated by the dotted lines in Fig. 5. These distances are 3.38, 3.45, 3.46, 3.48, and 3.52 Å, and shorter than the sum of the vdW radius of sulfur and carbon (3.57 Å). Consequently the crystal structure of TTeC$_1$-TTF·TCNQ complex reveals three dimensional characteristics.

The electrical resistivities of this complex along the two kinds of stacking directions and the c axis were measured by the standard four-probe method using Au paste. The resistivities along the two stacking directions, [1 1 0] and [1 $\bar{1}$ 0], are identical (100 Ω cm) at room temperature (Ea = 0.11 eV). The anisotropy of the resistivity along the two kinds of stacking directions and the c axis is about $\rho_{[110]} : \rho_{[1\bar{1}0]} : \rho_{[001]} = 1 : 1 : 10$. This result clearly indicates that this complex is a quasi three-dimensional conductor. This small anisotropy manifests the three-dimensional electronic structure and suggests that Te··N contacts play the important role for the transport properties.

The redox potentials of TTeC$_1$-TTF and TCNQ were measured by the cyclic voltammetry (vs. SCE, in 0.1 M Bu_4NBF_4/CH_2ClCH_2Cl). The difference between the second ($E^2_{1/2}$) and the first ($E^1_{1/2}$) redox potentials (ΔE) is a measure for the on-site Coulomb repulsive energy. This value of TTeC$_1$-TTF (0.39 V) is comparable to that of TMTSF.1) The difference between the first redox potentials of a donor and an acceptor has been used to estimate the ionicity of the ground state of a CT complex. $E^1_{1/2}$ of TTeC$_1$-TTF (0.51 V) and that of TCNQ (0.32 V) indicate that the difference (0.19 V) meets the requirement of a partial CT state (-0.02 - 0.34 V)4) for the complex. The UV-VIS and IR spectra are quite informative to estimate the ionicity of the complex. UV-VIS (612 and 361 nm in KBr) and IR (2175, 1578, 1503, 1168, 824, 710 cm^{-1} in KBr) spectra of the TTeC$_1$-TTF·TCNQ complex cannot be ascribed to the superposition of those of neutral TCNQ and TTeC$_1$-TTF molecules. The CT band is observed in the near infrared region (1970 nm) in the nujol mulls. These results strongly suggest that this complex is in a partial CT state and are consistent with the degree of CT estimated by the Kistenmacher's equation5) using the bond length of TCNQ (0.56). However the wavenumber of CN stretching cannot be used to estimate the ionicity, since the wavenumber (2175 cm^{-1}) is much smaller than that of a TCNQ radical anion (2183 cm^{-1}),6) probably owing to the strong atomic contacts between nitrogen and tellurium atoms.

The structural and physical properties of TTeC$_1$-TTF·TCNQ are compared with those of the analogous complexes, TTC$_1$-TTF·TCNQ7) and newly prepared TSeC$_1$-TTF·TCNQ. The crystal structure of the TSeC$_1$-TTF·TCNQ complex has space group of P$\bar{1}$ and the lattice constants of a = 9.538(1), b = 17.732(2), c = 8.114(1) Å, α = 93.64(1), β = 91.06, γ = 99.54(1)°, V = 1350.0(3) Å^3 and R = 0.0598. It was revealed that this crystal structure is isomorphous with that of the 1:1 phase of TTC$_1$-TTF·TCNQ complex.7) TSeC$_1$-TTF and TCNQ make the DDAA type mixed stacks only along the [0 1 1] direction as TTC$_1$-TTF·TCNQ does. But the interplanar distances along the stacks are 3.51 Å (D··D), 3.28 Å (D··A), and 3.38 Å (A··A) which mean the DA pair formation in the DAAD sequence. While in the 1:1 TTC$_1$-TTF·TCNQ complex DD and AA pairs are formed. Though the degree of CT calculated by the

Kistenmacher's equation for $TSeC_1$-TTF•TCNQ is 0.48,[5)] the UV-VIS-IR spetrum indicates that the ground state of this complex is in a partial CT state. The ionicity of this complex is estimated to be smaller than that of $TTeC_1$-TTF•TCNQ. The electrical resistivity of $TSeC_1$-TTF•TCNQ was 1.5 x 10^5 Ω cm and as comparable as that of the 1:1 complex of TTC_1-TTF•TCNQ (Table 1). Non-uniform interplanar separations together with the small intermolecular overlaps and relatively weak ionicity of TTC_1- or $TSeC_1$-TTF•TCNQ give good accounts for the fact that the electrical resistivity of TTC_1- or $TSeC_1$-TTF•TCNQ is much higher than that of $TTeC_1$-TTF•TCNQ.

Table 1. Stacking systems and electrical properties of TYC_1-TTF•TCNQ complexes

TYC_1-TTF	D:A	$\rho_{r.t.}/\Omega$ cm	Ea/eV	Ionicity
TTC_1-TTF	1:1 (DDAA)	3.8 x 10^5	0.30	neutral[7)]
	2:1 (DDA)	5.5 x 10^4	0.17	neutral[7)]
$TSeC_1$-TTF	1:1 (DAAD)	1.5 x 10^5	0.35	partial
$TTeC_1$-TTF	1:1 (DA)	1.0 x 10^2	0.11	partial

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