Crystal Structures of TMEO-TTP and (TMEO-TTP)[$AuBr_2$]·THF

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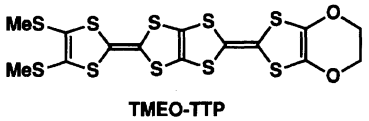
The molecular and crystal structures of the title compounds, where TMEO-TTP is 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5-[4,5-ethylenedioxy-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene, have been investigated by X-ray crystal structure analysis. The BDT-TTP skeleton of neutral TMEO-TTP adopts a slightly flat chair conformation. The crystal has a columnar structure, in which the molecules dimerize in a head-to-tail manner. Several S···S contacts shorter than the sum of the van der Waals radii (3.70 Å) are observed along the transverse direction. (TMEO-TTP)[$AuBr_2$]·THF also has a columnar structure in which the donor molecules dimerize. However, "side-by-side" interaction between the donors is prohibited because the $AuBr_2$ anions and the THF molecules are located at the sides of the donor molecules.

The discovery of superconducting bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts whose critical temperature (T_c) exceeds 10 K[1—4] has aroused considerable interest in preparing new organic superconductors.[5,6] In this connection modification of BEDT-TTF is of interest in order to develop new donors for organic metals.[7—12] A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP), is one of the most promising donors because it has a ladder-like arrangement of sulfur atoms as is observed in BEDT-TTF. Recently we have prepared the parent BDT-TTP and its derivatives, which have yielded many cation radical salts showing metallic conducting behavior.[13—20] Among them, an unsymmetrical donor, 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5-[4,5-ethylenedioxy-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene (TMEO-TTP, depicted as below) gave many cation radical salts with linear and octahedral anions showing metallic conducting behavior down to 0.6 K



TMEO-TTP

Chart 1.

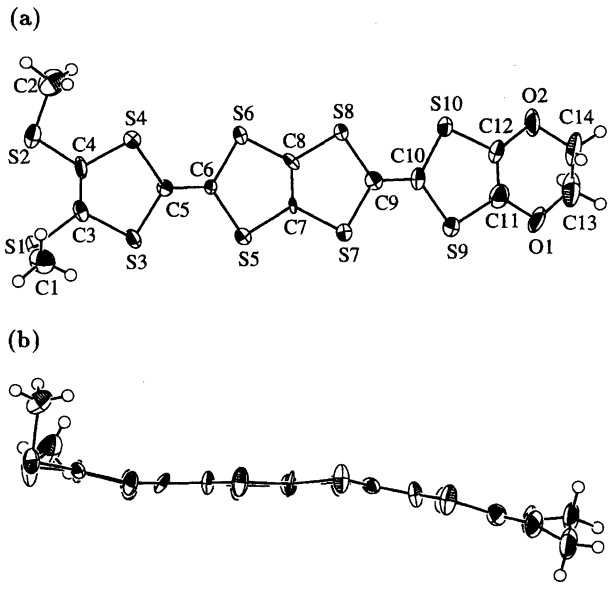


Fig. 1. (a) Molecular structure of TMEO-TTP with atomic numbering scheme, and (b) the side view.

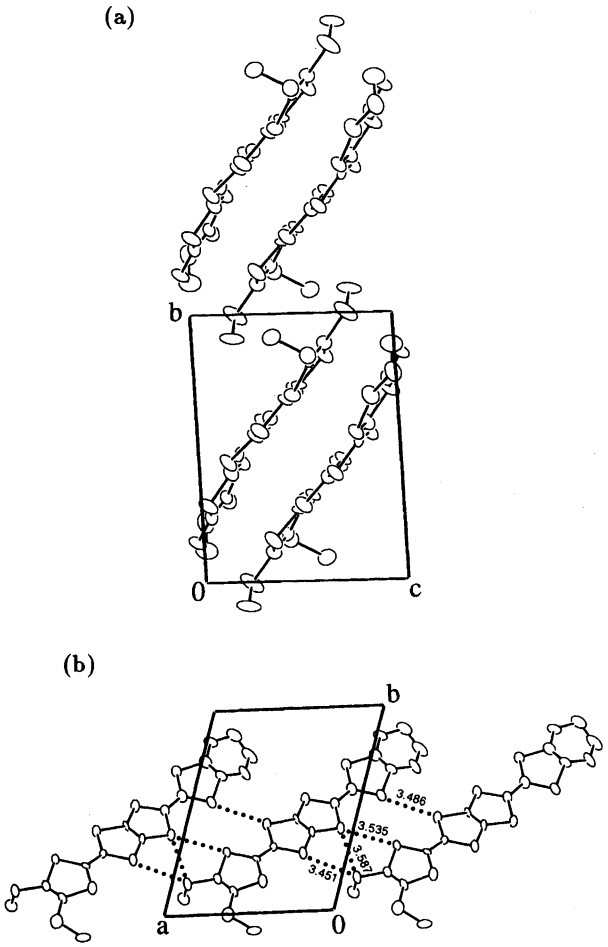


Fig. 2. Crystal structure of TMEO-TTP. (a) Projection onto the *bc* plane and (b) projection onto the *ab* plane.

Table 1. Crystallographic Data of TMEO-TTP and (TMEO-TTP)[$AuBr_2$]·THF

Compound	TMEO-TTP	(TMEO-TTP)[$AuBr_2$]·THF
Molecular formula	$C_{14}H_{10}O_2S_{10}$	$C_{18}H_{18}O_3S_{10}AuBr_2$
Formula weight	530.83	959.71
Crystal size/mm^3	$0.44\times0.13\times0.06$	$0.9\times0.04\times0.04$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.816(4)	11.501(3)
b/Å	12.017(3)	14.330(3)
c/Å	8.880(2)	9.166(3)
α/°	91.15(2)	94.54(2)
β/°	94.63(3)	96.46(2)
γ/°	105.98(3)	103.36(2)
V/Å^3	1002.7(5)	1451.7(7)
Z	2	2
d_{calcd}/g cm^{-1}	1.758	2.196
λ/Å	0.71069	0.71069
Temperature/K	298	298
Absorption coefficient/cm^{-1}	20.15	84.99
R	0.052	0.060
R_w	0.061	0.089
Reflections measured	5153	6978
Reflections used	1291 ($I>3\sigma(I)$)	2248 ($\|F_o\|>3\sigma(F_o)$)

Table 2. Atomic Parameters of TMEO-TTP

Atom	x	y	z	B_{eq}/Å^2
S(1)	0.9083(4)	0.1570(4)	0.4251(5)	3.3(1)
S(2)	0.6219(5)	−0.0040(5)	0.2238(7)	5.8(2)
S(3)	0.7225(4)	0.3054(3)	0.5162(5)	2.73(10)
S(4)	0.4653(5)	0.1562(4)	0.3452(5)	3.7(1)
S(5)	0.5263(4)	0.4362(4)	0.6907(5)	3.4(1)
S(6)	0.2675(4)	0.2866(4)	0.5077(5)	3.2(1)
S(7)	0.3358(4)	0.5528(4)	0.8567(5)	3.3(1)
S(8)	0.0791(4)	0.4026(4)	0.6753(5)	3.0(1)
S(9)	0.1407(5)	0.7139(4)	0.9696(6)	3.8(1)
S(10)	−0.1111(4)	0.5548(4)	0.7920(5)	3.1(1)
O(1)	−0.018(1)	0.8511(9)	1.036(1)	4.0(3)
O(2)	−0.267(1)	0.6911(10)	0.876(1)	4.4(3)
C(1)	0.911(2)	0.086(1)	0.600(2)	4.3(4)
C(2)	0.444(2)	−0.089(1)	0.202(2)	5.7(6)
C(3)	0.738(2)	0.177(1)	0.417(2)	2.2(4)
C(4)	0.623(2)	0.111(1)	0.341(2)	2.8(4)
C(5)	0.536(1)	0.268(1)	0.483(2)	2.2(3)
C(6)	0.454(1)	0.323(1)	0.555(2)	2.2(3)
C(7)	0.358(1)	0.456(1)	0.716(2)	2.4(3)
C(8)	0.246(1)	0.389(1)	0.637(2)	2.4(3)
C(9)	0.151(1)	0.524(1)	0.802(1)	2.2(3)
C(10)	0.072(2)	0.591(1)	0.849(2)	3.3(4)
C(11)	−0.018(2)	0.754(1)	0.960(2)	3.4(4)
C(12)	−0.131(2)	0.682(1)	0.881(2)	2.8(4)
C(13)	−0.148(2)	0.881(2)	0.993(2)	5.8(6)
C(14)	−0.269(2)	0.776(2)	0.993(2)	5.3(6)

(Chart 1).[14,18] In a continuation of these studies, we report herein X-ray crystal structures of neutral TMEO-TTP and (TMEO-TTP)[$AuBr_2$]·THF.

Experimental

TMEO-TTP. Synthesis of TMEO-TTP was carried out as reported before.[14] Single crystals of TMEO-TTP were obtained as dark red plates by recrystallization from carbon disulfide–hexane. Its crystallographic data are listed in Table 1. Intensities' data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo $K\alpha$ radiation using the ω–2θ scan technique ($2\theta<60°$). After absorption correction, the structure was solved by the direct method (SHELX86[21]) and was refined by full-matrix least squares analysis ($w=[\sigma(F_o)^2]^{-1}$). Anisotropic thermal parameters were used for all non-hydrogen atoms, whereas the hydrogen atoms were calculated geometrically. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

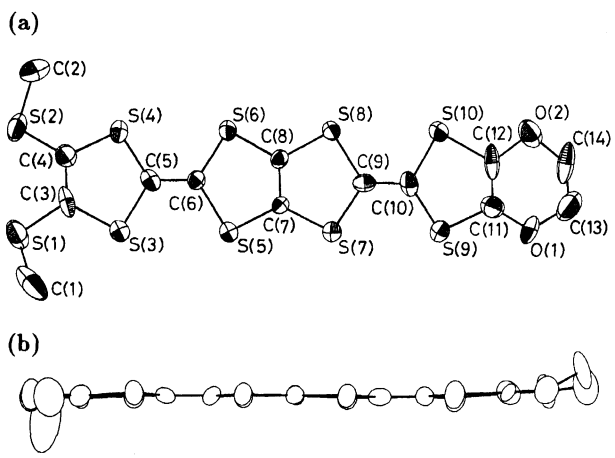


Fig. 3. (a) Molecular structure of TMEO-TTP in (TMEO-TTP)[$AuBr_2$]·THF, and (b) the side view.

(TMEO-TTP)[$AuBr_2$]·THF. Single crystals of (TMEO-TTP)[$ArBr_2$]·THF were obtained in the form of black needles by an electrochemical oxidation of TMEO-TTP in the presence of [Bu_4N][$AuBr_2$] in THF. This salt showed semiconducting behavior ($\sigma_{rt}=0.12$ S cm^{-1}, $E_a=0.1$ eV). Its crystallographic data are also listed in Table 1. In-

Table 3. Intramolecular Bond Distances of TMEO-TTP (Å)

S(1)–C(1)	1.79(2)	S(6)–C(6)	1.77(1)	O(1)–C(11)	1.34(2)
S(1)–C(3)	1.75(1)	S(6)–C(8)	1.74(2)	O(1)–C(13)	1.45(2)
S(2)–C(2)	1.76(2)	S(7)–C(7)	1.76(1)	O(2)–C(12)	1.36(2)
S(2)–C(4)	1.72(1)	S(7)–C(9)	1.77(1)	O(2)–C(14)	1.45(2)
S(3)–C(3)	1.81(1)	S(8)–C(8)	1.75(1)	C(3)–C(4)	1.30(2)
S(3)–C(5)	1.76(1)	S(8)–C(9)	1.77(1)	C(5)–C(6)	1.36(2)
S(4)–C(4)	1.78(1)	S(9)–C(10)	1.75(2)	C(7)–C(8)	1.31(2)
S(4)–C(5)	1.75(1)	S(9)–C(11)	1.75(2)	C(9)–C(10)	1.35(2)
S(5)–C(6)	1.75(1)	S(10)–C(10)	1.75(2)	C(11)–C(12)	1.34(2)
S(5)–C(7)	1.76(1)	S(10)–C(12)	1.77(1)	C(13)–C(14)	1.47(3)

Table 4. Atomic Parameters of (TMEO-TTP)-[$AuBr_2$]·THF

Atom	x	y	z	B_{eq}/Å^2
Au	0.8407	0.7555	0.1111	5.49
Br(1)	0.8822	0.6939	−0.1221	6.90
Br(2)	0.7994	0.8143	0.3439	8.34
S(1)	0.1251	0.6747	0.2203	5.49
S(2)	0.3665	0.8406	0.2753	5.23
S(3)	0.2440	0.5664	0.4418	3.51
S(4)	0.4690	0.7192	0.4887	3.56
S(5)	0.3587	0.4450	0.6742	3.14
S(6)	0.5865	0.6027	0.7255	3.00
S(7)	0.4688	0.3328	0.9008	3.13
S(8)	0.6960	0.4890	0.9507	3.02
S(9)	0.5866	0.2141	1.1335	3.92
S(10)	0.8117	0.3677	1.1786	3.85
O(1)	0.6926	0.1107	1.3108	5.56
O(2)	0.9101	0.2596	1.3623	5.04
C(1)	0.0083	0.6032	0.2779	16.84
C(2)	0.5113	0.9133	0.3526	7.21
C(3)	0.2497	0.6719	0.3486	4.10
C(4)	0.3546	0.7433	0.3683	3.44
C(5)	0.3909	0.6114	0.5357	2.72
C(6)	0.4398	0.5609	0.6343	2.54
C(7)	0.4744	0.4281	0.7985	2.37
C(8)	0.5778	0.5017	0.8231	2.39
C(9)	0.6135	0.3726	0.9954	2.85
C(10)	0.6607	0.3207	1.0899	3.22
C(11)	0.7023	0.1889	1.2471	3.87
C(12)	0.8035	0.2597	1.2710	4.33
C(13)	0.7929	0.0992	1.3965	6.97
C(14)	0.9022	0.1549	1.3745	8.34
O(S)	0.6400	0.9490	0.8161	8.79
C(S)(1)	0.6909	0.9736	0.9572	8.71
C(S)(2)	0.8224	1.0136	0.9535	10.41
C(S)(3)	0.8444	0.9774	0.8096	10.00
C(S)(4)	0.7269	0.9245	0.7390	9.10

tensities were measured by the ω–2θ scan technique on a Rigaku automated four-circle diffractometer AFC-5R with graphite monochromatized Mo $K\alpha$ radiation ($2\theta<55°$). After absorption correction, the structure was solved by the direct method (SHELX86[21]) and was refined by a block-diagonal least-squares procedure (UNICS III) ($w=[\sigma(F_o)^2+(0.015F_o)^2]^{-1}$).[22] The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[23] Anisotropic thermal parameters were adopted for all non-hydrogen atoms, whereas the hydrogen atoms were refined isotropically.

Results and Discussion

TMEO-TTP. The molecular structures are shown together with the atomic numbering scheme in Fig. 1, and atomic parameters and intramolecular bond distances are listed in Tables 2 and 3, respectively.[24] The terminal 1,3-dithiole ring, with the ethylenedioxy group substituted, and one of the 1,3-dithiole rings in the central tetrathiapentalene moiety (composed of S(7)–C(7)–C(8)–S(8)–C(9)) take envelope forms, in which C(5) and C(9) atoms are flapped in the opposite directions to each other. Thus, the BDT-TTP skeleton has a slightly flat chair conformation. The dihedral angles in the envelope 1,3-dithiole rings are 15° between the least square planes S(3)–C(3)–C(4)–S(4) and S(3)–C(5)–S(4), and 14° between those S(7)–C(7)–C(8)–S(8) and S(7)–C(9)–S(8), respectively. This result is in contrast with the fact that the BDT-TTP skeletons of tetrakis(methylthio) and 4,5-dimethyl-4′,5′-bis(methylthio) derivatives are almost planar.[13,19] On the other hand, the parent BDT-TTP also takes a chair conformation.[16] However both the envelope 1,3-dithioles are in the central tetrathiapentalene moiety in this case, and their dihedral angles (27.1 and 27.3°, respectively) are larger by 11—12° than those of TMEO-TTP.

Figure 2 shows crystal structures of TMEO-TTP. The crystal has a columnar structure, and TMEO-TTP molecules dimerize in a head-to-tail manner in the stack (Fig. 2(a)). There are several S···S contacts less than the sum of the van der Waals radii (3.70 Å) along the transverse direction, while there is no short S···S contact in the stack (Fig. 2(b)). The shortest one is 3.451 Å. This result suggests that cation radical salts of TMEO-TTP will have two-dimensional arrangement of donors.

(TMEO-TTP)[$AuBu_2$]·THF. Atomic parameters are listed in Table 4.[24] One TMEO-TTP molecule is crystallographically independent. Owing to the 1:1 composition, the charge on a donor molecule is expected to be +1. In contrast to the neutral molecule, the donor molecule is almost planar; the deviations from the optimal plane are less than 0.1 Å except for the terminal CH_3S groups and the terminal ethylenedioxy group (Fig. 3).[25]

Table 5. Intramolecular Bond Distances of (TMEO- TTP)-[$AuBr_2$]·THF (Å)

Au–Br(1)	2.388(5)	S(5)–C(6)	1.79(3)	S(10)–C(10)	1.79(3)
Au–Br(2)	2.369(6)	S(5)–C(7)	1.72(3)	S(10)–C(12)	1.81(3)
S(1)–C(1)	1.66(6)	S(6)–C(6)	1.74(3)	O(1)–C(11)	1.29(4)
S(1)–C(3)	1.76(3)	S(6)–C(8)	1.75(3)	O(1)–C(13)	1.37(5)
S(2)–C(2)	1.78(4)	S(7)–C(7)	1.71(3)	O(2)–C(12)	1.40(4)
S(2)–C(4)	1.68(3)	S(7)–C(9)	1.73(3)	O(2)–C(14)	1.50(5)
S(3)–C(3)	1.79(3)	S(8)–C(8)	1.74(3)	C(3)–C(4)	1.37(4)
S(3)–C(5)	1.76(3)	S(8)–C(9)	1.82(3)	C(5)–C(6)	1.35(4)
S(4)–C(4)	1.74(3)	S(9)–C(10)	1.67(3)	C(7)–C(8)	1.38(3)
S(4)–C(5)	1.71(3)	S(9)–C(11)	1.72(3)	C(9)–C(10)	1.34(4)
				C(11)–C(12)	1.34(4)

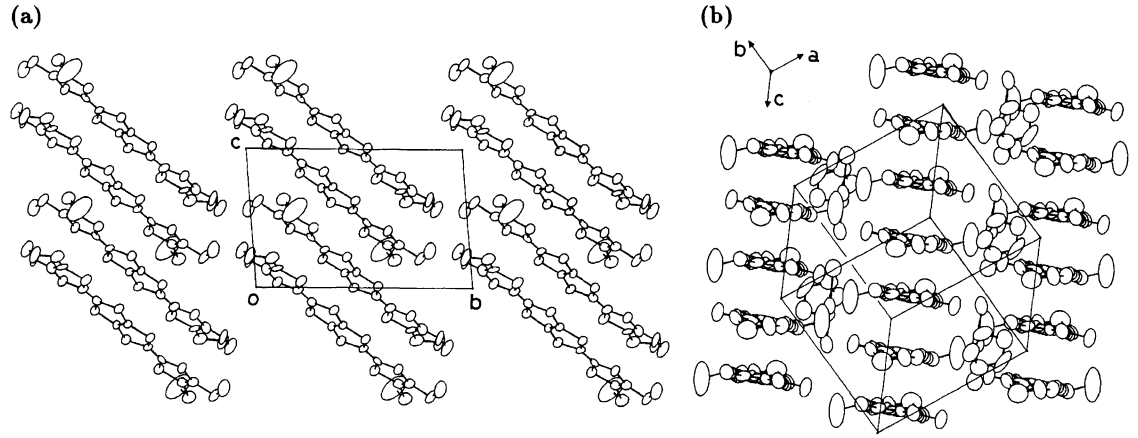


Fig. 4. Crystal structure of (TMEO-TTP)[$AuBr_2$]·THF. (a) Projection onto the *bc* plane and (b) viewed along the donor long axis.

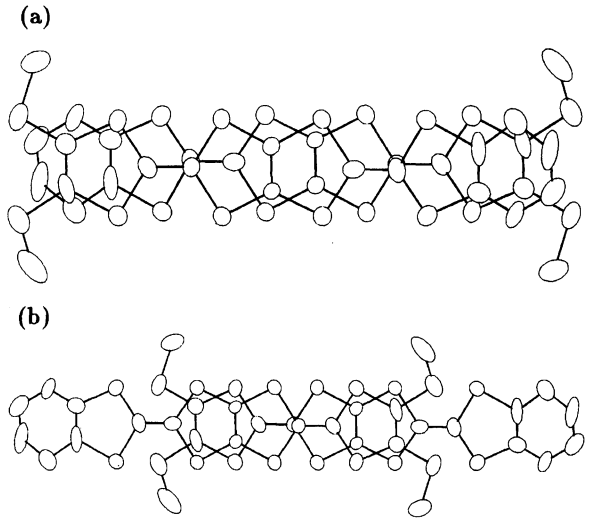


Fig. 5. Overlap modes of intrastack donors in (TMEO-TTP)[$AuBr_2$]·THF. (a) Projection onto the donor molecular plane in a dimer, and (b) between dimers.

The intramolecular bond distances are, however, not very sensitive to the charge transfer (Table 5). The central C(7)=C(8) bond length increases from 1.31(2) Å in neutral TMEO-TTP, 1.32(2) Å in (TMEO-TTP)$_2$[Au(CN)$_2$] to 1.38(3) Å in the present complex,[18] but other bond lengths show no systematic change. This is not very surprising because HOMO of the present donor spreads much more than that of the usual TTF-type molecule, even where the changes of the C–S bond lengths are not very large (0.2—0.3 Å).[26]

The donor molecules are stacked along the *c* axis (Fig. 4(a)). Though the overlap patterns in the stack are the usual ring-over-bond type (Fig. 5), the degree of overlap is alternatingly large, making dimerized units in the column. The $AuBr_2$ anions and the THF molecules are located at the sides of the donor molecules, and are separating each column (Fig. 4(b)). Therefore "side-by-side" interaction of the donors is prohibited, and the resulting electronic structure is expected to be one-dimensional. This type structure has been seen in (TTM-TTF)$I_{2.47}$,[27] and is probably associated with the steric effect of the CH_3S groups. Among the TTP series, this type structure has been found in semiconducting α-(TTM-TTP)$_2I_3$.[20] On the other hand, some other salts of the same donors, for example (TTM-TTP)$(PF_6)_{0.267}(THF)_{0.60}$[28] and (TMEO-TTP)$_2$[Au(CN)$_2$],[18] have the usual two-dimensional arrangements of the donors. It is interesting that the steric effect of the CH_3S groups is much reduced in the TTP series, probably because the TTP skeleton itself prefers two-dimensional packing, but it is *not* completely sup-

pressed, and occasionally results in the present type of semiconducting salt.

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