Crystal Structures of Highly Conducting Iodine Complexes of TTM-TTP

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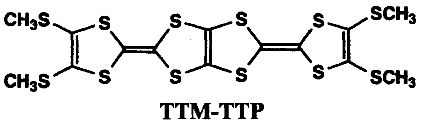
Methylthio substituted bis-fused tetrathiafulvalene, TTM-TTP (2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiaphentalene) makes three phases of iodine complexes: (TTM-TTP)I_3, α-(TTM-TTP)$_2I_3$, and β-(TTM-TTP)$_2I_3$. The 1:1 complex exhibits high conductivity, 700 S cm^{-1} at room temperature, and is metallic down to about $T_{MI}=160$ K. This complex has uniform columns of the donor molecules. In the semiconducting α-(TTM-TTP)$_2I_3$, one quarter of the donors is incorporated in the anion sheet, and the sides of the other trimeric donors are blocked by the anion sheets. β-(TTM-TTP)$_2I_3$ shows metallic conductivity down to $T_{MI}=20$ K.

Radical cation salts of tetrathiafulvalene (TTF) derivatives have been attracted a great deal of attention because they show high electrical conductivity and sometimes even superconductivity. Recently Misaki et al. have developed a general synthetic route to bis-fused TTF's,[1] where two TTF molecules are fused, or in other words a tetrathiapentalene (TTP) unit is inserted into the central double bond of a TTF molecule. These bis-fused TTF's are promising donor molecules for making highly conducting salts, because they have "ladder-like" array of sulfur atoms, which is an indispensable requirement for constructing two-dimensional network of the donor molecules in a crystal. In the present paper, we report three phases of iodine complexes of the tetrakis(methylthio) derivative, TTM-TTP (2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene) (Scheme 1). Though other anions do not give metallic salts with TTM-TTP, two of the iodine complexes show metallic conductivity at room temperature.

Experimental

Crystals of the 1:1 salt and β-(TTM-TTP)$_2I_3$ were grown by the electrochemical method in 1,1,2-trichloroethane (TCE) or THF. Though, when TCE is the solvent, two kinds of phases were obtained in the same lot, β-(TTM-TTP)$_2I_3$ was easily distinguished due to its characteristic copper color. When THF is the solvent, only the 1:1 phase was obtained. Alternatively interdiffusion of the donor and iodine in TCE/THF/EtOH mixed solvent (4.5:4.5:1) gave the 1:1 and the α-salts. The compositions were determined by the energy dispersion spectroscopy. Crystallographic data are listed in Table 1.

Intensity data were measured by the ω–2θ scan technique on a Rigaku automated four-circle diffractometer AFC-5R with graphite monochromatized Mo $K\alpha$ radiation ($2\theta<60°$). After absoption correction, the structure was solved by the direct method (SHELEX86[2]) and was refined by the block-diagonal least-squares procedure (UNICS III).[3] The atomic scattering factors were taken from the "International Tables for X-Ray Crystallography."[4] Anisotropic thermal parameters were adopted for all non-hydrogen atoms. The hydrogen atoms were refined isotropically for (TTM-TT)I_3, but not included for α-(TTM-TTP)$_2I_3$.[5]



TTM-TTP

Scheme 1.

Results

(TTM-TTP)I_3: The atomic coordinates and the equivalent isotropic thermal parameters are listed in Table 2. Because the donor molecule is located on an inversion center, the atomic numbering scheme corresponds to the left half of Fig. 1(a). As shown in Fig. 2-(a), the anions exist in the form of isolated I_3. The population analysis of the iodine atoms indicates that the defect of iodine is less than a few %, then we can regard this complex as almost exactly 1:1.

The donor molecule is almost completely planar; the deviations from the least-squares plane are less than 0.1 Å except the terminal carbons. Even the terminal C–S bonds extend basically in the molecular plane; the deviations from the least-squares plane are as small as 0.08(1) and 0.61(2) Å for C(1) and C(2), respectively. Such a flat molecular structure is consistent with the expected +1 charge; it has been observed in uncapped tetrathiafulvalenes that the terminal C–S bonds are out of the molecular plane in the neutral molecules, whereas those tend to be in the molecular plane in the ionic molecules.[6,7] In the present donor, the terminal carbons of the neutral molecule are also out of the molecular plane.[1]

Intramolecular bond lengths (averaged so as to have hypothetical *mmm* symmetry) are listed in Table 3. In comparison with the neutral TTM-TTP, all C=C bonds become longer, and all C–S bonds become shorter. This is consistent with the symmetry of the HOMO, which has nodes on all C–S bonds. The differences of the bond lengths between D^0 and D^+ are, however, as small as 0.01—0.03 Å; these values are about half of the cor-

Table 1. Crystallographic Data

	(TTM-TTP)I_3	α-(TTM-TTP)$_2$$I_3$	β-(TTM-TTP)$_2$$I_3$
Chemical formula	$(C_{14}H_{12}S_{12})I_3$	$(C_{14}H_{12}S_{12})_2I_3$	$(C_{14}H_{12}S_{12})_2I_3$
Formula weight	945.68	1510.65	1510.65
Shape	Black rod	Black plate	Copper plate
Crystal system	Triclinic	Triclinic	(Monoclinic)
Space group	$P\bar{1}$	$P1$	($P2/m$)
a/ Å	11.225(3)	13.324(3)	9.98(2)
b/Å	11.867(3)	16.375(4)	12.81(2)
c/Å	5.788(1)	12.333(3)	6.26(1)
$\alpha/^\circ$	99.69(2)	110.59(2)	
$\beta/^\circ$	102.36(2)	99.93(2)	108.6(1)
$\gamma/^\circ$	112.22(2)	86.10(2)	
V/Å^3	670.2(3)	2481(1)	758(2)
Z	1	2	
ρ(calcd)/g cm^{-1}	2.343	2.022	
λ/Å	0.71073	0.71073	
Temperature /K	298	298	
μ(Mo $K\alpha$) /cm^{-1}	43.67	28.68	
R	0.047	0.097	
$R_w^{a)}$	0.057	0.105	
Reflections used	1851	3050	
σ(rt) /S cm^{-1}	700	0.03	200
T_{MI}/K	160	(E_a=0.3 eV)	20

a) $w=[\sigma(F_o)^2+(0.015F_o)^2]^{-1}$.

Table 2. Atomic Parameters ($\times 10^4$) of (TTM-TTP)I_3

Atom	x	y	z	B_{eq}/Å
I(1)	0	0	0	7.0
I(2)	547(1)	1920(1)	−2718(2)	7.0
S(1)	5147(2)	9142(2)	12487(4)	3.0
S(2)	2059(2)	7126(3)	10328(4)	3.6
S(3)	5611(2)	7865(2)	7954(4)	2.3
S(4)	2764(2)	6010(2)	6010(4)	2.5
S(5)	6203(2)	6553(2)	3220(3)	2.1
S(6)	3316(2)	4643(2)	1393(3)	2.2
C(1)	6901(9)	10027(9)	12861(18)	4.0
C(2)	559(12)	6290(17)	7956(28)	10.2
C(3)	4542(7)	7998(7)	9689(13)	1.9
C(4)	3230(8)	7151(7)	8786(13)	2.1
C(5)	4361(7)	6577(7)	5619(13)	1.9
C(6)	4606(7)	5980(7)	3632(13)	1.8
C(7)	4339(7)	4572(7)	−416(13)	1.9

$B_{eq}=4/3(\sum_i\sum_j B_{ij}\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

responding changes in the TTF series, 0.02—0.07 Å.[8] This is reasonable because the HOMO of the present molecule spreads on the larger molecule. Since the change of each bond length is small, estimation of the charge transfer from the bond lengths is expected to be more difficult in the TTP series.

The donor molecules form a uniform stack along the c axis (Fig. 2(b)). The overlap mode in this stack (Fig. 1-(b)) is ring-over-bond type, though slip along the molecular long axis is large (4.8 Å). The interplanar distance is 3.453(6) Å. Along c, there are many S–S contacts shorter than the van der Waals distance.

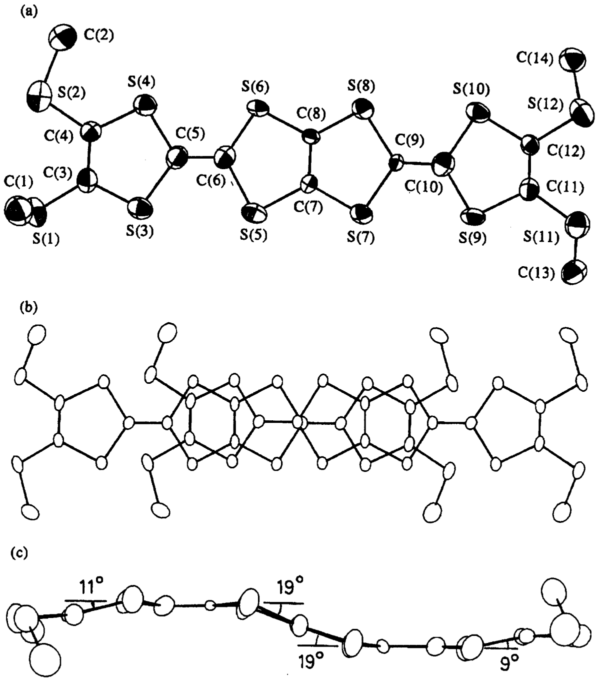


Fig. 1. (a) ORTEP drawing and atomic numbering scheme of the molecule A of α-(TTM-TTP)$_2$$I_3$, (b) overlap mode of intrastack donors in (TTM-TTP)-I_3, and (c) side view of the molecule D of α-(TTM-TTP)$_2$$I_3$.

As for the interstack interaction, short S–S contacts are found along [013] ($d_{S(1)-S(1)}$=3.412(4) Å) and along [012] ($d_{S(1)-S(1)}$=3.824(4) Å, $d_{S(1)-S(3)}$=3.987(4) Å). These are interactions from the terminal of a molecule

Table 3. Intramolecular Bond Lengths (Å) of TTM-TTP Averaged by Assuming *mmm* Symmetry

Compound	C(7)–C(8)	S(5)–C(7) S(6)–C(8) S(7)–C(7) S(8)–C(8)	S(5)–C(6) S(6)–C(6) S(7)–C(9) S(8)–C(9)	C(5)–C(6) C(9)–C(10)	S(3)–C(5) S(4)–C(5) S(9)–C(10) S(10)–C(10)	S(3)–C(3) S(4)–C(4) S(9)–C(11) S(10)–C(12)	C(3)–C(4) C(11)–C(12)
TTM-TTP[1)]	1.346(7)	1.743(4)	1.764(4)	1.348(6)	1.752(4)	1.754(4)	1.339(4)
α-$(\text{TTM-TTP})_2\text{I}_3$							
A	1.34(7)	1.73(6)	1.77(6)	1.35(10)	1.76(7)	1.73(7)	1.34(8)
B	1.33(8)	1.72(7)	1.77(7)	1.33(10)	1.74(6)	1.74(7)	1.37(8)
C	1.29(7)	1.75(7)	1.76(6)	1.37(9)	1.75(6)	1.74(7)	1.27(8)
D	1.22(8)	1.78(7)	1.76(6)	1.37(9)	1.75(7)	1.76(7)	1.34(8)
$(\text{TTM-TTP})\text{I}_3$	1.362(9)	1.732(9)	1.748(6)	1.38(1)	1.737(8)	1.752(8)	1.351(9)

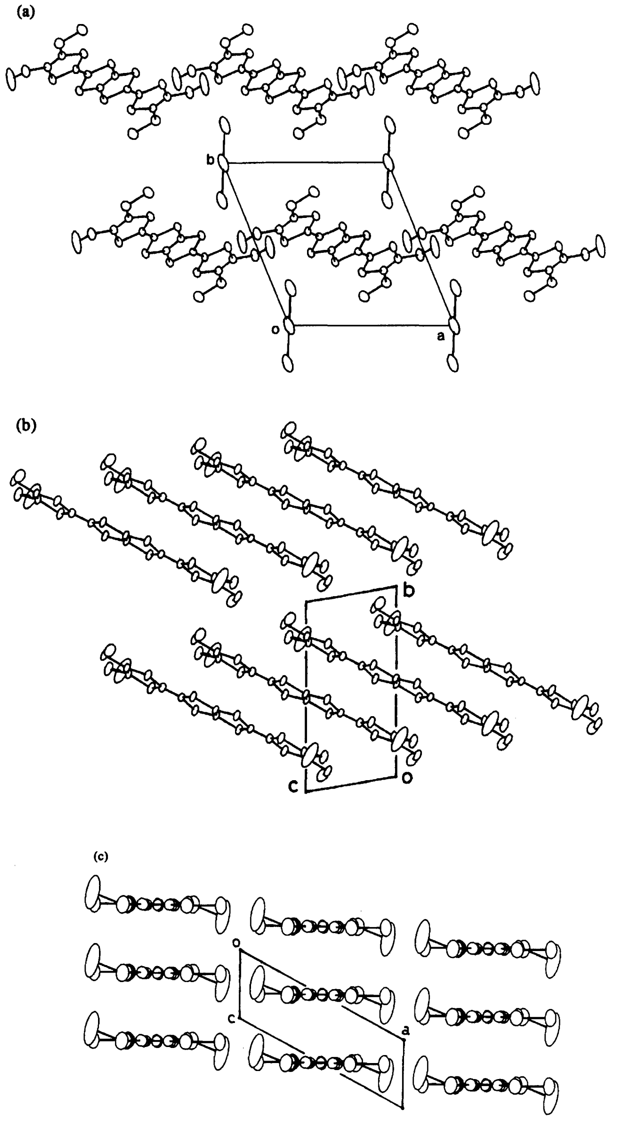


Fig. 2. Crystal structure of $(\text{TTM-TTP})\text{I}_3$. (a) Projection onto the *ab* plane, (b) projection onto the *bc* plane, and (c) view along the molecular long axis.

to the terminal of another molecule (Fig. 2(b)). Because the HOMO population is not large on the terminal sulfurs (S(1) and S(2)), these terminal-to-terminal interactions do not give large interstack interaction effective to the electron conduction.

Calculated intermolecular overlap integrals of the HOMO are listed in Table 4.[9)] The intrastack overlap $S=-26.1\times10^{-3}$ correspond to a bandwidth $4t=1$ eV. This comparatively large bandwidth is related to the high room-temperature conductivity (700 S cm^{-1}). The interstack interactions along [013] and [012] are less than 1/20 of the intrastack interactions. The "side-by-side" interactions along $[10\bar{1}]$ and $[10\bar{2}]$ are about the same order; in these directions the molecules cannot approach close each other because of the steric hindrance of the terminal methyl groups (Fig. 2(c)). This situation has a close resemblance to the corresponding TTF complexes.[7)] Therefore the electronic structure of the present compound is regarded as highly one-dimensional.

The conductivity is as high as 700 S cm^{-1} at room temperature, and basically constant down to about 160 K, below which it becomes a semiconductor (Fig. 3). It seems to be surprising that a 1 : 1 complex shows such a high conductivity. The present complex, however, has only one molecule in a unit cell, then there exists only one (half-fileed) energy band, which may result in metallic conduction. A similar situation has been observed in $(\text{BO})\text{ClH}_2\text{O}$ (BO : bis(ethylenedioxy)-TTF),[10)] which exhibits metallic conductivity down to liquid-helium temperatures. Conventional explanation tells us that a 1 : 1 complex has a general tendency to become semiconductivg because of the effect of the onsite Coulomb repulsion, U. The present donor is, how-

Table 4. Intermolecular Overlap Integrals, S ($\times10^3$) of HOMO of $(\text{TTM-TTP})\text{I}_3$

Direction	S	Direction	S
[001]	−26.1	[100]	0.1
[012]	−0.9	$[10\bar{1}]$	−0.5
[013]	0.6	$[10\bar{2}]$	0.9

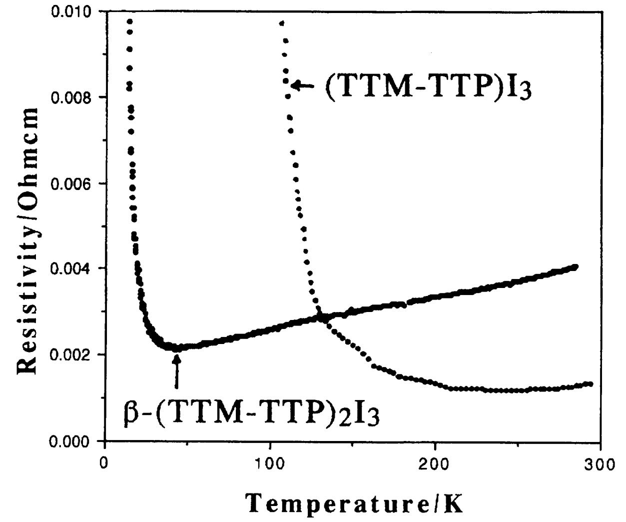


Fig. 3. Electrical resistivity of $(TTM-TTP)I_3$ (//*c*) and β-$(TTM-TTP)_2I_3$ (//*c*).

ever, expected to have comparatively small *U* due to its large molecular size; the difference of the first and the second redox potentials $\Delta E = E_2 - E_1$ is about two thirds of the corresponding TTF.[1] This small *U* together with the uniform molecular arrangements is considered to be the origin of the metallic conduction.

Thermoelectric power (Seebeck coefficient) in Fig. 4 affords another evidence that the present complex has a simple half-filled band. Thermoelectic power of one-dimensional tight-binding band is expressed as:

$$S = -\frac{\pi^2 k_B^2 T}{6et}\,\frac{\cos\left(\frac{1}{2}\pi\rho\right)}{1-\cos^2\left(\frac{1}{2}\pi\rho\right)}. \qquad (1)$$

In a 1 : 1 complex,the degree of charge transfer $\rho=1$ gives $S=0$. The observed *S* is very close to zero in the metallic temperature region.

The metal-semiconductor transition of the present complex around 160 K is probably due to the formation of charge density waves. In a preliminary X-ray investigation down to 120 K, however, we have not succeeded in finding the evidence of the modulated structure.

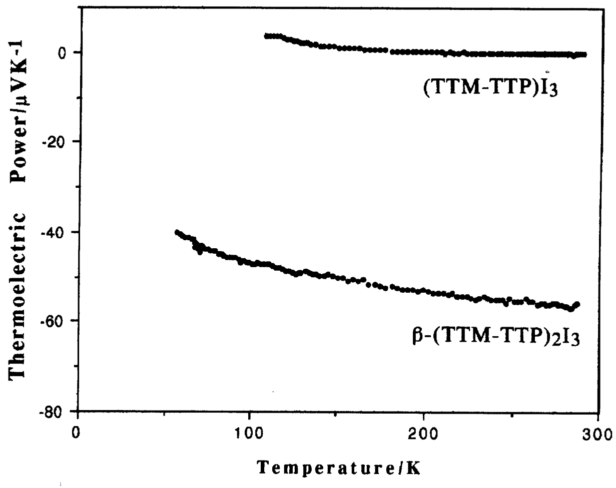


Fig. 4. Thermoelectric power of $(TTM-TTP)I_3$ (//*c*) and β-$(TTM-TTP)_2I_3$ (//*c*).

α-$(TTM-TTP)_2I_2$: The atomic coordinates are listed in Table 5. This crystal does not have an inversion center, and the space group is *P*1. The reason is recognized from Fig. 5(a); if one puts the donor molecules on inversion centers, the iodine atoms are deviated from the inversion centers. Then one unit cell contains four crystallographically independent donor molecules and two isolated I_3^- anions.

The donor molecules A, B, and C make a one-dimensional stack along the a axis (Fig. 5(b), (c)); the interplanar distances are 3.68(5), 3.34(5), and 3.48(4) Å for A–B, B–C, and C–A, respectively. In this stack, there are many S–S contacts shorter than the van der Waals distance. These donors are basically flat, but one or two terminal carbons are out of plane. This is similar to the corresponding TTF.[11]

The donor D is incorporated in the anion sheet (Fig. 5(a)). This molecule is not flat, but it bends at each dithiole sulfur, and the angles between the C_2S_4 units are 9—19° (Fig. 1(c)). This kind of "boat-like" form has been widely found in neutral uncapped TTF's,[6] though neutral TTM-TTP is almost flat.[1] The anion sheet spreads along the *ab* plane, and separates the donor columns. Therefore the interstack interactions of the donors exists only along the *b* axis (Fig. 5-(b)), and the interactions are again terminal-to-terminal type.

The intramolecular bond lengths of the present compound is not accurate enough to give conclusive information about the charge transfer (Table 3). The stacked donors, A, B, and C, make a trimer structure, and possibly there is some charge separation in the trimer. This charge separation as well as the trimeric structure is probably responsible for the low conductivity (0.03 S cm^{-1}) of the present compound.

β-$(TTM-TTP)_2I_3$: This compound has characteristic copper color, and exhibits metallic conductivity down to 20 K (Fig. 3). The unit cell is as small as the 1 : 1 salt, indicating that a unit cell contains only one molecule; X-ray photography did not show any longer periodicity. The lattice, however, seemed to be monoclinic, and the intensity data also showed apparent monoclinic symmetry. This suggests that there are two possible arrangements of the donor molecules, which are connected by the mirror or the two-fold axis of the monoclinic symmetry, and that the actual crystal is a random mixture of these two arrangements. This situation is the same as (TMET-TTP)-ClO_4 (TMET-TTP : 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene),[12] which shows apparent symmetry $P2_1$ as a convolution of $P2_1/n$ and $P2_1/a$. Therefore we could not carry out the structure analysis of this compound. The lattice constants, however, strongly suggest

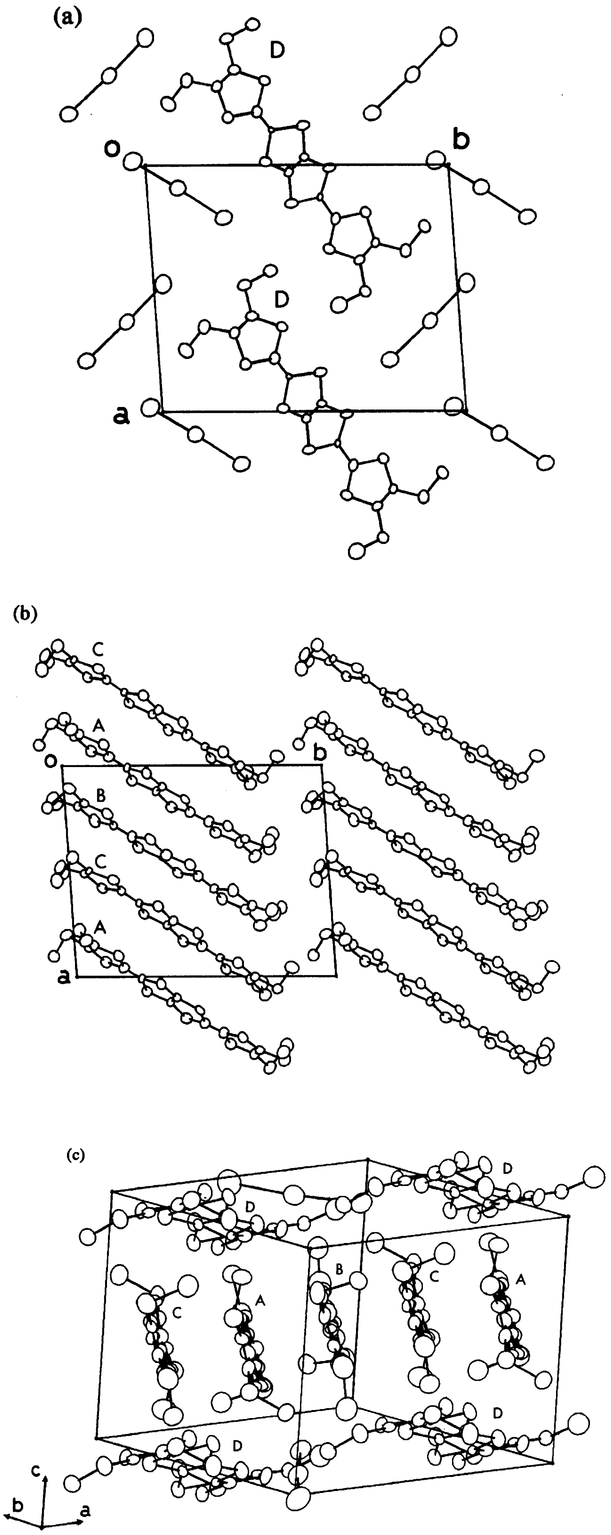


Fig. 5. Crystal structure of α-(TTM-TTP)$_2$I$_3$. (a) Anion sheet projected onto the *ab* plane, (b) donor arrangement projected onto the *ab* plane, and (c) view along the molecular long axis.

Table 5. Atomic Parameters ($\times 10^4$) of α-(TTM-TTP)$_2$I$_3$

Atom	x	y	z	B_{eq}/Å
I(1)	−183(5)	−415(5)	−26(6)	8.1
I(2)	979(5)	1134(4)	432(6)	5.8
I(3)	2254(4)	2693(4)	918(5)	5.8
I(4)	4769(6)	228(5)	−304(7)	8.5
I(5)	6249(5)	−1158(4)	−692(6)	5.6
I(6)	7785(5)	−2616(4)	−879(5)	6.1
SA(1)	4576(15)	7693(13)	1972(18)	5.0
SA(2)	4580(16)	8984(12)	4710(19)	5.3
SA(3)	3531(14)	6400(12)	2572(16)	3.5
SA(4)	3562(14)	7518(11)	5031(15)	3.2
SA(5)	2373(14)	4885(11)	3021(15)	3.3
SA(6)	2353(13)	6066(10)	5493(14)	2.1
SA(7)	1180(13)	3549(11)	3500(15)	2.9
SA(8)	1175(14)	4761(11)	5956(15)	2.9
SA(9)	−164(14)	2168(11)	3918(14)	3.1
SA(10)	−118(14)	3307(11)	6410(15)	3.1
SA(11)	−1421(14)	791(12)	4188(17)	4.4
SA(12)	−1268(16)	1996(14)	6904(18)	5.0
SB(1)	7963(16)	7872(15)	2666(20)	5.3
SB(2)	7765(20)	9189(15)	5432(23)	7.3
SB(3)	6775(16)	6623(12)	3205(17)	3.9
SB(4)	6703(16)	7692(12)	5633(18)	4.2
SB(5)	5574(15)	5087(12)	3591(16)	3.1
SB(6)	5538(15)	6233(12)	6079(16)	3.4
SB(7)	4400(15)	3718(12)	3954(16)	3.3
SB(8)	4376(15)	4849(11)	6434(15)	3.0
SB(9)	3196(17)	2232(12)	4392(18)	4.4
SB(10)	3211(15)	3369(12)	6850(17)	3.7
SB(11)	2194(18)	760(14)	4740(22)	6.5
SB(12)	2077(17)	2127(15)	7445(20)	5.4
SC(1)	5416(16)	2175(14)	7868(18)	5.2
SC(2)	5478(16)	959(12)	5105(19)	5.4
SC(3)	6428(14)	3560(11)	7380(15)	3.3
SC(4)	6477(13)	2478(10)	4919(14)	2.7
SC(5)	7625(13)	5101(10)	6934(14)	2.8
SC(6)	7651(13)	3899(10)	4484(14)	2.6
SC(7)	8850(14)	6449(10)	6509(15)	3.0
SC(8)	8864(14)	5226(11)	4020(15)	3.1
SC(9)	10192(14)	7797(10)	6045(15)	3.2
SC(10)	10138(14)	6676(11)	3573(15)	2.8
SC(11)	11395(14)	9188(11)	5796(16)	4.0
SC(12)	11298(15)	7986(12)	3037(17)	4.5
SD(1)	6825(15)	2047(12)	1906(17)	4.2
SD(2)	5014(14)	3258(12)	1097(17)	4.1
SD(3)	8313(13)	3279(11)	1752(15)	3.4
SD(4)	6709(12)	4364(11)	968(15)	2.9
SD(5)	10028(13)	4248(11)	1110(15)	3.2
SD(6)	8447(13)	5346(12)	274(15)	3.4
SD(7)	11528(13)	4642(11)	−283(15)	3.4
SD(8)	9970(12)	5772(11)	−1093(15)	3.0
SD(9)	13275(13)	5619(11)	−942(16)	3.2
SD(10)	11690(12)	6719(11)	−1712(15)	2.9
SD(11)	14972(13)	6655(11)	−1173(14)	2.9
SD(12)	13219(14)	7884(11)	−1935(16)	3.7

that the donors must show uniform stack just like the 1 : 1 salt.

Contrary to the 1 : 1 salt, this salt exhibits large negative thermoelectric power (Fig. 4). Large thermoelectric power generally means highly correlated system. In the

Table 5. (Continued)

Atom	x	y	z	B_{eq}/Å
CA(1)	3451(60)	8268(52)	1405(67)	5.8
CA(2)	4436(56)	9350(49)	6225(63)	5.2
CA(3)	4058(48)	7398(42)	2972(56)	3.4
CA(4)	4050(44)	7914(37)	4138(50)	2.6
CA(5)	3196(50)	6519(42)	3952(56)	3.6
CA(6)	2787(47)	5892(40)	4222(54)	3.3
CA(7)	1744(42)	4565(36)	3950(49)	2.2
CA(8)	1680(40)	5101(36)	5041(46)	1.9
CA(9)	749(41)	3734(35)	4844(46)	1.8
CA(10)	270(47)	3123(42)	5044(55)	3.4
CA(11)	−734(44)	1780(39)	4838(52)	3.0
CA(12)	−672(44)	2274(38)	5914(49)	2.6
CA(13)	−518(52)	53(44)	3411(59)	4.3
CA(14)	−578(53)	2585(47)	8318(60)	4.6
CB(1)	7076(55)	8694(46)	2375(63)	4.7
CB(2)	7801(61)	9446(53)	6828(71)	6.3
CB(3)	7345(49)	7619(43)	3655(55)	3.8
CB(4)	7311(46)	8181(39)	4797(51)	3.0
CB(5)	6476(43)	6712(38)	4616(49)	2.4
CB(6)	5887(49)	6144(41)	4669(54)	3.4
CB(7)	5013(34)	4728(30)	4437(39)	0.6
CB(8)	4999(52)	5199(45)	5559(57)	4.4
CB(9)	4078(49)	3861(41)	5298(55)	3.5
CB(10)	3587(40)	3238(34)	5530(44)	1.8
CB(11)	2640(42)	1844(37)	5280(50)	2.4
CB(12)	2638(45)	2394(39)	6385(52)	3.0
CB(13)	2185(67)	451(58)	3108(80)	7.4
CB(14)	3066(52)	1376(45)	7985(59)	4.3
CC(1)	6614(63)	1687(52)	8541(71)	6.1
CC(2)	5556(58)	690(49)	3629(67)	5.3
CC(3)	5915(40)	2494(35)	6805(46)	1.8
CC(4)	5896(43)	2053(37)	5757(50)	2.6
CC(5)	6761(43)	3491(37)	6021(50)	2.5
CC(6)	7326(39)	4103(34)	5881(44)	1.5
CC(7)	8192(45)	5412(39)	6024(51)	2.8
CC(8)	8253(40)	4899(36)	4970(47)	2.2
CC(9)	9265(48)	6219(42)	5121(55)	3.5
CC(10)	9787(40)	6834(35)	4941(46)	1.9
CC(11)	10734(45)	8187(39)	5178(53)	3.0
CC(12)	10702(45)	7720(40)	4080(51)	2.8
CC(13)	10486(57)	9995(51)	6560(67)	5.7
CC(14)	10586(67)	7466(61)	1676(75)	7.6
CD(1)	7679(59)	1213(51)	1207(70)	5.7
CD(2)	4334(50)	3940(44)	300(58)	4.0
CD(3)	7013(45)	2920(39)	1483(51)	2.7
CD(4)	6285(43)	3443(38)	1144(48)	2.4
CD(5)	7987(46)	4066(39)	1050(50)	2.6
CD(6)	8698(35)	4445(30)	849(39)	0.7
CD(7)	9662(38)	5200(35)	−184(45)	1.7
CD(8)	10309(41)	4734(36)	128(48)	2.2
CD(9)	11184(36)	5453(31)	−894(42)	1.1
CD(10)	12038(44)	5861(38)	−1110(49)	2.4
CD(11)	13695(40)	6545(36)	−1156(45)	1.9
CD(12)	12952(41)	7021(35)	−1497(47)	1.9
CD(13)	15623(63)	5927(55)	−507(71)	6.4
CD(14)	12331(50)	8742(44)	−1248(59)	3.9

limit of the large-U Hubbard model, S is given as:[13]

$$S = -\frac{k_B}{e}\ln\left[\frac{2(1-\rho)}{\rho}\right]. \tag{2}$$

The quarter-filled case $\rho=1/2$ results in $S=-(k_B/e)\times \ln 2=-58.9\ \mu\mathrm{V\,K^{-1}}$. The observed S is not strictly temperature-independent, but shows very weak temperature dependence, and seems to approach to the above constant limit at high temperatures. Therefore the present system is, though it is metallic down to a rather low temperature, not considered to have a simple metal band but considered to be highly correlated. Another important question about the thermoelectric power is that it is not positive by negative in spite of the donor conductor. We do not have any clear answer because we do not have detailed information about the crystal structure.

Discussion

From the viewpoint of the crystal structures, these TTM-TTP iodine complexes are regarded as highly one-dimensional. In the 1 : 1 complex, the terminal methyl groups block the "side-by-side" interactions. In α-(TTM-TTP)$_2$I$_3$, sides of each molecule are blocked by the anion sheets. β-(TTM-TTP)$_2$I$_3$ should have a uniform stack of the donors, which must be not much different from the 1 : 1 complex. Therefore we re-discover the old rule which had been proved in the corresponding TTF complexes:[7] The terminal methylthio groups are harmful to two-dimensional network of the donors.

Crystal structure of (TTM- TTP)(PF$_6$)$_{0.267}$-(THF)$_{0.60}$,[14] however, has two-dimensional array of the donors. The anions and the solvent molecules are located ends of the donors. This complex is semiconducting only because it makes pentamer structure. Unsymmetrical donors which have only *two* methylthio groups at one end even more tend to make two-dimensional networks.[12,15] Therefore we consider that the TTP skeleton itself prefers two-dimensional array, and that some methylthio groups are not fatal to realize conducting sheet of the donors.

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