Organic Metal with a High Oxidation State (+5/3), (TTM–TTP)$(I_3)_{5/3}$

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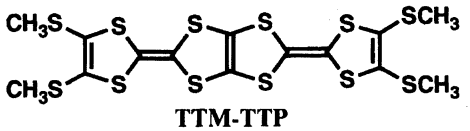
The crystal structure of the title compound, where TTM–TTP is 2,5-bis [4,5-bis(methylthio)-1,3-dithiol-2-ylidene] -1,3,4,6-tetrathiapentalene, has been determined by X-ray analysis. The donors form a uniform stack, which is responsible for metallic conduction down to $T_{MI} = 20$ K. The anions are composed of discrete I_3^- and an infinite chain of I_3^-. Each donor has anomalously large positive charge of +5/3.

Since the discovery of superconductivity in organic conductors,[1] a large number of organic metals have been prepared. Many of them are radical cation salts of TTF (tetrathiafulvalene) derivatives, and most of the highly conducting salts have a donor : anion = 2 : 1 composition. Recently a high oxidation state (+2) of the donor has been reported in such a salt as (BEDT–TTF)$(ClO_4)_2$,[2] yet this salt is an electrical insulator. As far as we know, no metallic conductor with an oxidation state exceeding +1 has been reported.

Recently Misaki et al. have prepared a number of donors with a bis-fussed TTF skeleton.[3] Since these donors have a tetrathiapentalene (TTP) unit at their central part, these donors are called TTP-series donors. Although the TTP-series donors have a strong tendency to stabilize metallic states down to low temperatures,[4] their tetrakismethylthio derivative, TTM–TTP (Scheme 1), makes electrically insulating radical cation salts with various counter anions.[5] The only exception is the iodine salts; we have obtained three different phases of the iodine salts: (TTM–TTP)I_3, α-(TTM–TTP)$_2I_3$, and "β-(TTM–TTP)$_2I_3$".[6] Despite the 1 : 1 composition, (TTM–TTP)I_3 exhibits a high conductivity $\sigma_{rt} = 700$ S cm^{-1} and retains the metallic conductivity down to 160 K, below which this salt becomes a Mott insulator.[7] This salt has a highly one-dimensional uniform column of the donors. The 1 : 1 composition, together with the uniformity of the column, results in a half-filled energy band, which is responsible for the Mott insulating state at low temperatures. Another salt, α-(TTM–TTP)$_2I_3$, is an insulator ($\sigma_{rt} = 0.03$ S cm^{-1}), and is composed of trimerized columns and complicated anion sheets which involve one-quarter of the donor molecules.



TTM-TTP

Scheme 1.

The third phase, reported as "β-(TTM–TTP)$_2I_3$", exhibits high conductivity $\sigma_{rt} = 200$ S cm^{-1} and remains metallic down to 20 K, at which it undergoes a metal-insulator (M-I) transition. This phase is easily distinguished from the other phases because the crystals have characteristic copper luster. The crystal structure analysis was not successful, owing to its small lattice volume (high symmetry) and the disorder. However, we have recently reinvestigated the crystal structure by using the imaging plate and succeeded in solving the structure. The resulting composition is (TTM–TTP)$(I_3)_{5/3}$, which is different from the initially reported 2 : 1 composition determined by the energy dispersion spectroscopy (EDS). In the present paper, we will report the crystal structure of this compound.

Experimental

Crystals were grown by the electrochemical method in 1,1,2-trichloroethane. Intensity data were collected by the Rigaku Raxis II area detector with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71070$ Å) at room temperature. Crystal data: (TTM–TTP)-I_5, $C_{14}H_{12}S_{12}I_5$, *F.W.* 1199.49, orthorhombic, space group *Cmmm*, $a = 6.247(4)$, $b = 18.68(2)$, $c = 12.804(7)$ Å, $V = 1491(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.666$ g cm^{-3}, and μ(Mo $K\alpha$) = 59.80 cm^{-1}. The present lattice constants are able to be transformed to the monoclinic lattice of the previous report as $a' = -a/2 + b/2 = 9.84$ Å, $b' = c$, $c' = a$, $\beta = 108.4°$ and $V = 747$ Å^3. The positions of all I and S atoms were determined from the Patterson map of the triclinic symmetry (space group C1); from the resulting symmetry, the above space group was concluded. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atomic scattering factors were taken from "International Tables".[8] The final cycle of full-matrix least-squares refinement ($w = 1/\sigma(F_o)^2$) converged to $R = 0.080$ and $R_w = 0.091$ based on 774 observed reflections ($2\theta < 60°$ and $I > 5\sigma(I)$).[9]

Results

The atomic coordinates and the equivalent isotropic thermal parameters are listed in Table 1. The atomic numbering scheme of the donor is shown in Fig. 1(a). The donor is

Table 1. Atomic Parameters

Atom	x	y	z	B_{eq}[a)]
I(1)	0	0	0	3.14
I(2)	0	0.1545(1)	0	4.41
I(3)	0	0.2512(1)	1/2	3.84
S(1)	−1/2	0.0839(3)	0.1626(5)	5.0
S(2)	−0.133(1)	0.0769(3)	0.2935(5)	2.8
S(3)	0.289(1)	0.0786(3)	0.4377(4)	2.2
C(1)	−1/2	0.172(1)	0.194(2)	3.7
C(2)	−0.331(3)	0.037(1)	0.231(2)	2.0
C(3)	0	0	0.334(2)	3.7
C(4)	0.161(5)	0	0.398(4)	2.7
C(5)	1/2	0.035(1)	1/2	1.7

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

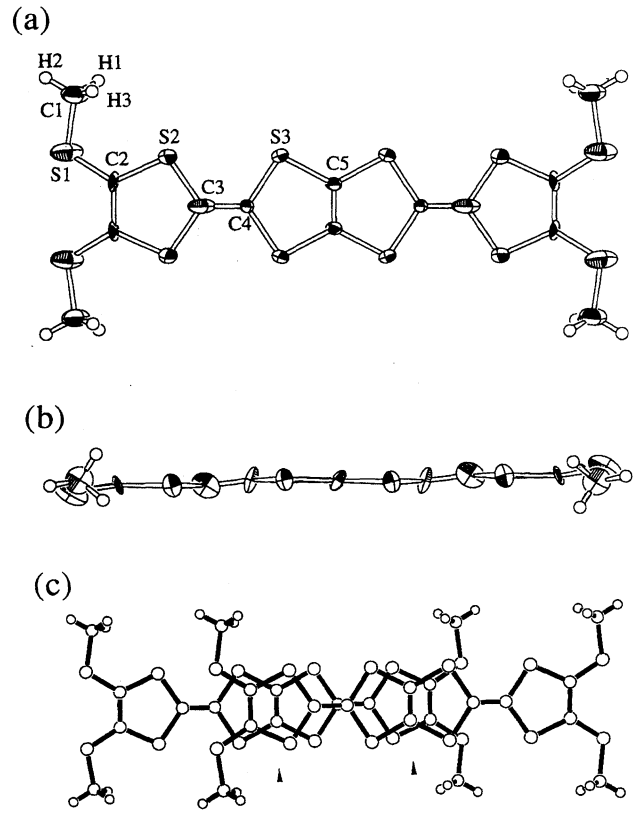


Fig. 1. (a) ORTEP drawing and atomic numbering scheme, (b) side view of the donor molecule, and (c) overlap mode of the intrachain donors.

located on a special position of mmm symmetry, so that one quarter of a donor is crystallographically independent. As shown in Fig. 2, the donors form a uniform stack along the *a* axis. On account of the *mmm* symmetry, two kinds of tilt coexist and the donor molecules are disordered; one is right down (Fig. 2(a)) and another is right up (Fig. 2(b)). Since the coexistence of these two patterns in a column is unlikely, one column is expected to be composed of only one pattern. We investigated other possibilities that are free from this disorder, by changing the space group, but according to the following logic, we have to conclude the existence of this disorder as far as the crystal has the C-center symmetry;

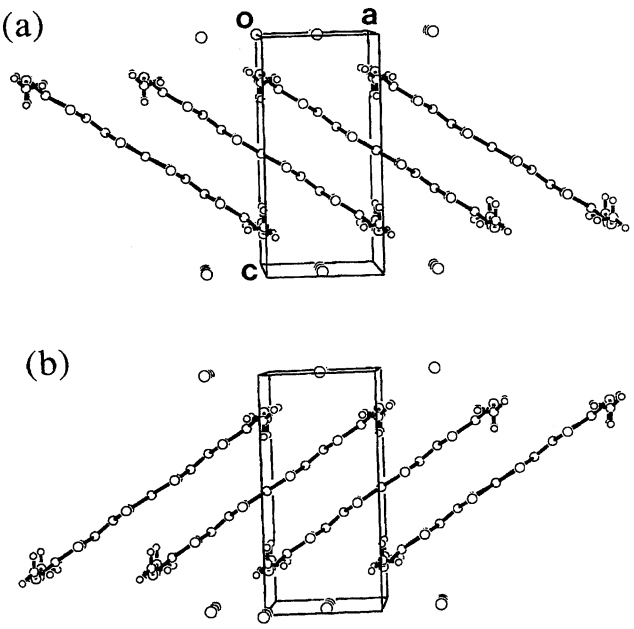


Fig. 2. (a) Projection along the *b* axis, and (b) another stacking pattern of the disordered donors. The infinite chain I(3) atoms are omitted for the sake of clarity.

a unit cell contains two donors belonging to two different columns. Since these two donors are connected by the C-center symmetry, these two are parallel to each other. So we cannot avoid the existence of the disorder, because the C-centered lattice is evident from the systematic absences.

From the present structure analysis it is not obvious whether the donor columns are arranged completely at random, or the neighboring columns have some tendency to be arranged parallel to each other, and the crystal consists of some domains of the same orientation. The latter might be distinguished by the investigation of scanning tunneling microscopy or a similar microscopic method. An alternating arrangement of the up and down patterns, or any other long-range order is unlikely, because we did not observe any superstructure reflections along *b* or *c* axes on the X-ray photographs.

The donor molecule, including the methyl carbon of the terminal methylthio part, holds complete planarity; the deviations from the least-squares plane are less than 0.24 Å (Fig. 1(b)). It has been observed that in neutral TTM–TTP the terminal C–S bonds extend out of the molecular plane,[3] whereas in an ionized donor D^+, the methyl carbons are located in the molecular plane.[6] So the planar structure of the present compound suggests a high oxidation state (+1 or larger).

The intramolecular bond lengths are listed in Table 2. Owing to the disorder, unfortunately the bond lengths are not accurate enough to estimate the amount of the positive charge located on each donor molecule.[6]

The interplanar distance of the neighboring donors in a stack in 3.39 Å. The overlap mode is depicted in Fig. 1(c); the donors are slipped by 5.3 Å along the long molecular axis. The slip in (TTM–TTP)I_3, which has a similar kind of

Table 2. Intramolecular Bond Length

I(1)–I(2)	2.885(3)	I(3)–I(3)	3.124(2)
S(1)–C(1)	1.70(2)	S(1)–C(2)	1.63(2)
S(2)–C(2)	1.65(3)	S(2)–C(3)	1.74(1)
S(3)–C(4)	1.74(2)	S(3)–C(5)	1.75(1)
C(2)–C(2)	1.39(5)	C(3)–C(4)	1.30(4)
C(5)–C(5)	1.31(5)		

uniform stack, is 4.8 Å.[6] Because the length of a dithiole ring is about 3.2 Å, the latter corresponds to one and half of the dithiole ring, resulting in the usual ring-over-bond type overlap. The slip of the present compound is somewhat larger than the latter, but still much shorter than two units of the dithiole rings, 3.2 Å×2=6.4 Å. Then, as a rough approximation, the overlap mode is regarded as ring-over-bond type. Anyway these slip distances are significantly large, and as shown in Fig. 1(c), one TTF part of a donor molecule is located near another TTF part of the adjacent molecule.

There exist two kinds of anions (Fig. 3). One is composed of I(1) and I(2), located on the origin with *mmm* symmetry, and extending along the *b* axis. The I(1)–I(2) distance, 2.885(3) Å, is typical of I_3^-.[10] Since the I(2)–I(2) distance between the neighboring I_3^- is as long as 4.75 Å, these anions are regarded as discrete I_3^-. In order to check the possibility of iodine deficiency, we have refined the population of the iodine atoms, but the resulting occupancy is very close to 1.0 (of course considering the multiplicity coming from the symmetry) for I(1), I(2), and I(3).

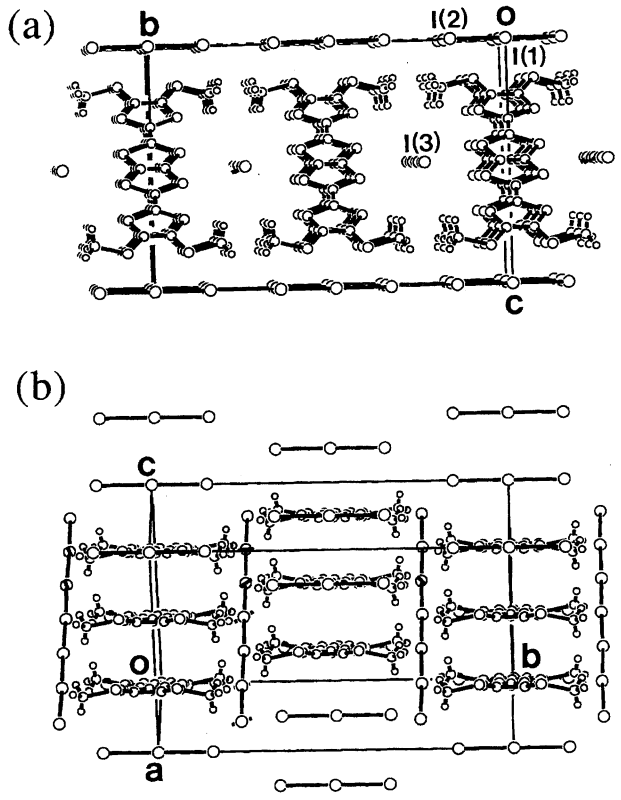


Fig. 3. (a) Projection along the *a* axis, and (b) view from the donor's molecular long axis.

Another anion site is I(3). Because the adjacent I(3)–I(3) distance is as short as $a/2=3.12$ Å, the I(3) atoms form an infinite chain along the *a* axis. Iodine anions frequently form infinite chains,[9] where the actual unit which constitutes the chain is I^-, I_3^-, or I_5^-, but what appears in such an average structure analysis as the present analysis, is an infinite chain with regular intervals. The average iodine spacing in the present compound, 3.12 Å, is typical of an infinite I_3^- or I_5^- chain. If I(3) is I^-, the distance should be larger than twice the ionic radii, 4.32 Å. In the present case, the oscillation photographs along the *a* axis showed a few spots at $a^*/3$. The repeating unit $3a=18.7$ Å is not only too long as a repeating unit of an I_5^- chain (typically 15.5 Å) but also contradicts the restriction that this unit should contain $2\times3=6$ iodine atoms. On the contrary this superstructure is reasonably interpreted by assuming the periodicity of $(3/2)a=9.37$ Å, which is the typical length of the repeating unit of the infinite I_3^- chain. The existence of the infinite iodine chain is probably associated with the characteristic copper luster.

From this perspective, we can conclude that the anion part is composed of discrete I_3^- and an infinite chain of I_3^-, both without any observable deficiency. This determines the accurate composition to be (TTM–TTP)$(I_3)(I_3)_{2/3}$ or simply (TTM–TTP)I_5, resulting in a +5/3 charge on a donor molecule. Even if the iodine species included in the infinite chain were entirely I_5^-, the formula should be the same (formally written as (TTM–TTP)$(I_3)(I_5)_{2/5}$), and the positive charge on a donor, +1.4, should be still large.

Since the previous EDS result was entirely incorrect, we reinvestigated EDS; the result is D : I = 1 : 4.78, in good agreement with the X-ray analysis. As far as we know, no such high oxidation state of the donor molecules realizing the metallic conduction on themselves has ever been found. Obviously this is associated with the molecular structure; a TTP-series donor is able to be oxidized to 4+, because it contains two TTF units in a molecule. If we naively take the TTF parts to be independent, each TTF is regarded to hold $+5/6=+0.833$; this is still large but not quite unusual because it is less than +1.

It should be worth nothing that the TTF analog of the present donor, namely TTM–TTF (tetrakis(methylthio)-tetrathiafulvalene) makes a similar iodine salt (TTM–TTF)-$I_{2.47}$; the anion is composed of an infinite chain of I_3^-, which is running in the same direction as the uniform chain of the TTM–TTF molecules.[11] Positive charge on each donor is $2.47/3=0.823$; this is almost the same as 0.833 of each TTF unit in (TTM–TTP)$(I_3)_{5/3}$.

The donor columns are separated by the two kinds of anions: along the *c* axis by the discrete I_3^- and along the *b* axis by the infinite I_3^- chain, so that a highly one-dimensional nature along the *a* axis is expected. In order to make a quantitative estimation, transfer integrals are calculated from the overlap of HOMO of the donor molecules.[12] The resulting transfer integrals are $t_a=0.157$ eV along the stack, $t_c=0.03$ eV, and $t_b=4\times10^{-4}$ eV (C-centered oblique interaction). It is reasonable that t_b is very small, because this interaction is interrupted not only by the infinite I_3^- chain but also by

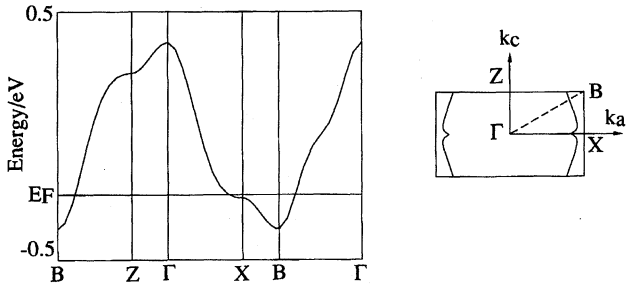


Fig. 4. Energy band structure and Fermi surface.[12]

the methyl groups of the donors themselves, which enlarge the S–S distances as long as 6.7 Å. On the other hand the unexpectedly large t_c, which amounts to one-fifth of the intracolumnar interaction t_a, is related to the comparatively short S(1)–S(1) distance 4.16 Å; although the interaction in this direction is basically blocked by the discrete I_3^-, there exists a short S–S contact through the small opening between the anions. As a result, the interchain interaction is relatively large ($t_c/t_a = 0.2$), in comparison with the very high one-dimensionality in (TTM–TTP)I_3 ($t_b/t_c = 0.03$). The relatively large interchain interaction may be related to the stabilization of the metallic state and the resulting comparatively low M-I transition temperature (20 K), though the mechanism of the M-I transition has not been elucidated.

Tight-binding energy band structure and Fermi surface, calculated from the above transfer integrals, are depicted in Fig. 4. Figure 4 consists of a single energy band, which can be regarded as an energy band of a single chain.[13] The bandwidth 0.6 eV is comparable to other organic metals, but somewhat smaller than 1.0 eV in (TTM–TTP)I_3, calculated by using the same parameters.[6] As a first approximation, the energy band is one-dimensional along the *a* axis, but on account of the considerable interchain interaction, the Fermi surface is significantly corrugated. It is worth nothing that the Fermi surface is located very close to the XB boundary; this is related to the high oxidation state of the donors. In other words, only a small part (one sixth) of the HOMO band is occupied by electrons. This leads to electron conduction, which is in agreement with the actually observed negative thermoelectric power ($-60\ \mu V\ K^{-1}$ at room temperature).[6]

In conclusion, we have described the crystal and electronic structures of the organic metal (TTM–TTP)I_5 with a high oxidation state. As a naive expectation, a high oxidation state with good conduction should be a characteristic of the TTP-series donor. Yet, as a matter of fact, many TTP salts take smaller donor-to-anion ratios (fewer oxidation states) than 2 : 1 that is most usual in the TTF-series salts.[4] Further efforts to make TTP-series salts with comparatively high oxidation states and the development of the means to control the oxidation states of the donors in radical–cation salts are strongly required to exploit the novel types of organic conductors.

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9) Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crysrallographic Data Center (CCDC).

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13) For the sake of clarity we regarded the unit cell as if it were primitive monoclinic with the unique axis *c*; this eliminates the inconvenience of handling the C-centered lattice, but does not make any alteration in Fig. 4, because the k_a–k_c plane is kept unchanged.