

## Crystal Structure and Properties of $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$ [TTF = tetrathiafulvalene and mnt = 1,2-dicyanoethylene-1,2-dithiolate(2–)]

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### Abstract

The title salt was obtained by a reaction of  $[\text{TTF}]_3[\text{BF}_4]_2$  (TTF = tetrathiafulvalene) with  $[\text{NMe}_4]_2[\text{V}(\text{mnt})_3]$  [mnt = 1,2-dicyanoethylene-1,2-dithiolate(2–)] in a mixture of 1,2-dichloroethane and acetonitrile (3:2 v/v). A single crystal X-ray analysis of it revealed a TTF columnar structure consisting of both  $\text{TTF}^0$  and the  $\text{TTF}^{+\cdot}$  radical cation and the distorted octahedral geometry of the  $[\text{V}(\text{mnt})_3]^{2-}$  anion. The salt crystallizes in a monoclinic system, space group  $C2/c$  with unit cell constants  $a = 25.428(3)$ ,  $b = 12.434(2)$ ,  $c = 25.477(3)$  Å,  $\beta = 92.428(3)^\circ$  and  $Z = 8$ . The structure was solved by the direct method and refined, on the basis of 3854  $[|F_o| > 3\sigma(F)]$  observed data, to an  $R$  value of 0.078. The salt exhibits electrical conductivity of  $1.7 \times 10^{-4}$  S  $\text{cm}^{-1}$  at 25 °C for a compacted pellet.

### Introduction

Electrical conductivities of tetrathiafulvalene radical cation ( $\text{TTF}^{+\cdot}$ ) salts depend on molecular packings of the radical cation molecules including some neutral TTF molecules in the crystal phase [1, 2]. Packing modes are greatly affected by formal charges and geometries of counter anions. We have clarified crystal structures and electrical properties of several TTF salts with  $[\text{SnR}_2\text{Cl}_4]^{2-}$  (R = Cl [3], Me [4], and Et [5]) and  $[\text{PtCl}_6]^{2-}$  anions [6]; they have two-dimensional TTF interactions through sulfur atoms, exhibiting high conductivities ( $10^{-3} \sim 10^{-2}$  S  $\text{cm}^{-1}$  at 25 °C). Recently we have obtained  $[\text{TTF}]_2\text{-}[\text{V}(\text{dmit})_3]$  [dmit = 4,5-dimercapto-1,3-dithiole-2-thionate(2–)] with a high conductivity ( $1.0 \times 10^{-2}$  S  $\text{cm}^{-1}$  at 25 °C) which seems to arise from electrical conduction pathways through two- or three-dimensional sulfur–sulfur interaction including TTF and dmit moieties [7]. On the other hand, TTF salts containing the  $[\text{V}(\text{mnt})_3]^{2-}$  [mnt = 1,2-dicyano-

ethylene-1,2-dithiolate(2–)] anion with an octahedral geometry are expected to contain a  $\text{TTF}/\text{TTF}^{+\cdot}$  columnar structure affecting an electrical conduction and little interaction among TTF and mnt moieties. In order to compare electrical and structural properties of a  $\text{TTF}\text{-}[\text{V}(\text{mnt})_3]^{2-}$  salt with those of  $[\text{TTF}]_2\text{-}[\text{V}(\text{dmit})_3]$ , we have prepared a  $\text{TTF}/\text{TTF}^{+\cdot}$  salt with the  $[\text{V}(\text{mnt})_3]^{2-}$  anion and clarified its X-ray crystal structure as well as its electrical conductivity.

### Experimental

#### Preparation of $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$

A 1,2-dichloroethane–acetonitrile (4:1 v/v) solution (5  $\text{cm}^3$ ) of  $[\text{NMe}_4]_2[\text{V}(\text{mnt})_3]$  [8] (6.9 mg, 10  $\mu\text{mol}$ ) was added to a 1,2-dichloroethane–acetonitrile (1:1 v/v) solution (10  $\text{cm}^3$ ) of  $[\text{TTF}]_3[\text{BF}_4]_2$  [9] (14.2 mg, 18  $\mu\text{mol}$ ) and the mixture was allowed to stand in a refrigerator overnight to yield dark green plates suitable for the X-ray analysis of  $[\text{TTF}]_{2.5}\text{-}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$  (yield 10%, based on  $[\text{NMe}_4]_2[\text{V}(\text{mnt})_3]$ ).

#### Physical Measurements

ESR [10] and Raman spectra [11] were measured in the solid state as described previously. Electrical resistivity was measured for a compacted pellet as described elsewhere [12]. Cyclic voltammetry of the salt was measured for its acetonitrile solution containing  $[\text{NBu}_4][\text{ClO}_4]$  as a supporting electrolyte, using a conventional cell consisting of two platinum plates as working and counter electrodes and a saturated calomel electrode (SCE) as reference.

#### X-ray Crystal Structure of $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$

Oscillation and Weissenberg photographs indicated a monoclinic system and possible space groups  $C2/c$  and  $Cc$ . The former was confirmed from the successful analysis. Accurate unit-cell parameters were determined by least-squares treatment of the angular coordinates of 25 independent reflections with  $2\theta$  in the range 17–25°, measured on a Rigaku four-circle

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diffractometer at the Crystallographic Research Center, Institute for Protein Research, Osaka University, with Mo K $\alpha$  ( $\lambda = 0.71069$  Å) radiation.

#### Crystal data

C<sub>28</sub>H<sub>12</sub>ClN<sub>6</sub>S<sub>16</sub>V,  $M = 1031.8$ , monoclinic, space group  $C2/c$ ,  $a = 25.248(3)$ ,  $b = 12.434(2)$ ,  $c = 25.477(3)$  Å,  $\beta = 92.237(9)^\circ$ ,  $U = 8049(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.703(1)$  g cm<sup>-3</sup>,  $F(000) = 4144.0$ , and  $\mu(\text{Mo K}\alpha) = 4.9$  cm<sup>-1</sup>.

Intensity data were collected for a specimen,  $0.09 \times 0.20 \times 0.26$  mm, by the  $\omega$ - $2\theta$  scan technique up to  $2\theta = 50^\circ$  with a scan rate of  $8^\circ \text{min}^{-1}$  in  $2\theta$ . The scan width in  $2\theta$  was  $(1.2 + 0.35 \tan \theta)^\circ$ . No significant intensity variation was observed throughout the data collection. The intensities were corrected for Lorentz and polarization effects, but no correction was made for absorption. Of 7622 independent reflections collected, 3854 [ $|F_o| > 3\sigma(F)$ ] were used for solving and refining the structure.

Coordinates of vanadium and sulfur atoms were found according to the direct (MULTAN) method [13]. By successive Fourier calculations, positions of all the non-hydrogen atoms were found. Positions of hydrogen atoms were omitted from the refinement. The salt contains 0.5 molar amount of 1,2-dichloroethane molecule with a disorder in the crystal. Block-diagonal least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to final residual indices  $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.078$  and  $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.077$  with the weighting scheme  $1/w = \sigma^2(F_o) + 0.0007F_o^2$ . Atomic scattering factors used throughout the refinement were taken from ref. 14. The final atomic positional parameters with standard deviations are given in Table 1. Calculations for the crystallographic analysis were performed on ACOS-930 Computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. Figures 3, 4 and 5 were drawn with a local version of ORTEP-II [15]. See also 'Supplementary Material'.

## Results and Discussion

### Redox and Spectroscopic Properties of the [V(mnt)<sub>3</sub>]<sup>2-</sup> Anion

Figure 1 shows a cyclic voltammogram of [NMe<sub>4</sub>]<sub>2</sub>[V(mnt)<sub>3</sub>] in acetonitrile. Two redox waves are observed at  $E_{1/2} = (E_{pc} + E_{pa})/2 = +0.60$  ( $\Delta E = E_{pc} - E_{pa} = 80$  mV) and  $-0.51$  V ( $\Delta E = 160$  mV) (versus SCE) which correspond to [V(mnt)<sub>3</sub>]<sup>2-</sup>/[V(mnt)<sub>3</sub>]<sup>-</sup> and [V(mnt)<sub>3</sub>]<sup>3-</sup>/[V(mnt)<sub>3</sub>]<sup>2-</sup> redox processes, respectively. Since the oxidation potential of the [V(mnt)<sub>3</sub>]<sup>2-</sup> anion is somewhat higher than that of TTF (0.33 V versus SCE) [16], the TTF<sup>•+</sup> radical cation formed in the reaction system of

TABLE 1. Atomic Coordinates ( $\times 10^4$ ) for [TTF]<sub>2</sub><sup>•+</sup>[V(mnt)<sub>3</sub>]<sup>2-</sup>·0.5CH<sub>2</sub>ClCH<sub>2</sub>Cl<sup>a</sup>

Atom	x	y	z
V	4366.9(8)	2177(2)	538.9(8)
S(1)	3615(1)	2803(3)	62(1)
S(2)	4497(1)	1098(3)	-205(1)
S(3)	4003(1)	3090(2)	1254(1)
S(4)	4012(1)	633(3)	950(2)
S(5)	5229(1)	1691(3)	818(1)
S(6)	4728(1)	3914(3)	434(1)
S(7)	3406(1)	7263(3)	2682(2)
S(8)	3835(1)	5164(3)	2444(2)
S(9)	4768(1)	6323(3)	1804(2)
S(10)	4314(2)	8404(3)	2032(2)
S(11)	2589(1)	7155(3)	1588(1)
S(12)	2950(1)	5000(3)	1385(1)
S(13)	3918(1)	5903(3)	759(1)
S(14)	3566(1)	8097(3)	920(1)
S(15)	1996(2)	8566(5)	435(2)
S(16)	2905(2)	9057(5)	-205(2)
N(1)	2755(5)	2332(10)	-1100(5)
N(2)	3893(5)	295(11)	-1505(5)
N(3)	2988(4)	2885(7)	2252(4)
N(4)	3032(5)	-223(9)	1898(5)
N(5)	6362(5)	2894(10)	1561(5)
N(6)	5774(5)	5629(9)	1052(5)
C(1)	3580(5)	2069(9)	-498(5)
C(2)	3951(4)	1321(9)	-619(4)
C(3)	3122(5)	2220(11)	-841(5)
C(4)	3921(5)	742(11)	-1112(5)
C(5)	3614(4)	2175(9)	1554(4)
C(6)	3622(5)	1123(10)	1420(5)
C(7)	3261(5)	2553(9)	1952(5)
C(8)	3298(5)	380(9)	1688(5)
C(9)	5524(5)	2901(10)	967(5)
C(10)	5304(4)	3862(10)	809(5)
C(11)	6001(5)	2887(11)	1293(5)
C(12)	5565(5)	4841(10)	935(5)
C(13)	3883(5)	6529(9)	2375(5)
C(14)	4280(5)	7033(11)	2102(5)
C(15)	5094(5)	7439(12)	1578(6)
C(16)	4892(6)	8423(13)	1689(6)
C(17)	3084(5)	6150(11)	2928(5)
C(18)	3278(5)	5178(12)	2824(5)
C(19)	3050(5)	6345(9)	1310(5)
C(20)	3469(5)	6751(9)	1032(5)
C(21)	4271(5)	6915(10)	478(5)
C(22)	4116(5)	7945(10)	542(5)
C(23)	2219(5)	6134(11)	1834(5)
C(24)	2391(4)	5109(10)	1741(5)
C(25)	2466(10)	8031(14)	50(9)
C(26)	2241(9)	9877(15)	456(8)
C(27)	2621(8)	10102(15)	138(8)
1,2-Dichloroethane molecule			
Cl(1)	4895(5)	3490(8)	2642(6)
Cl(2)	4613(4)	835(8)	2584(4)
C(28)	4764(16)	2073(51)	2682(16)
C(29)	4786(18)	1787(51)	2311(14)

<sup>a</sup>e.s.d.s given in parentheses.

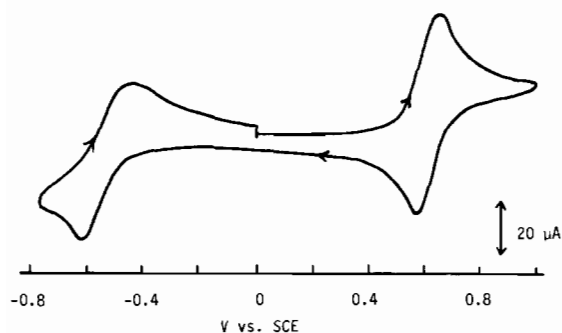


Fig. 1. Cyclic voltammogram of  $[\text{NMe}_4]_2[\text{V}(\text{mnt})_2]$  ( $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) in acetonitrile ( $0.1 \text{ mol dm}^{-3}$   $[\text{NBu}_4^+][\text{ClO}_4^-]$ ); scan rate,  $0.1 \text{ V s}^{-1}$ .

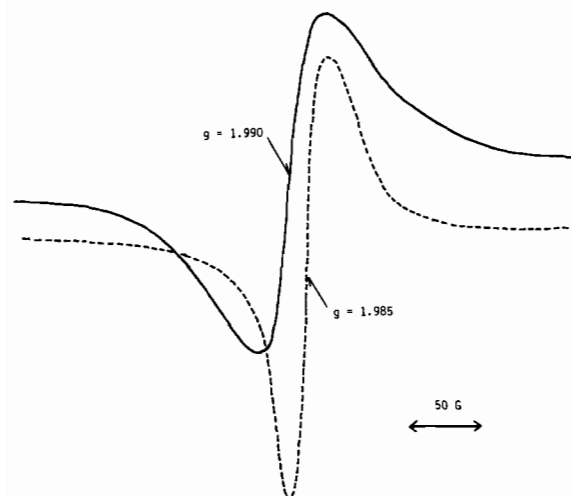


Fig. 2. Powder ESR spectra of  $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$  (—) and of  $[\text{NMe}_4]_2[\text{V}(\text{mnt})_3]$  (---) at room temperature.

$[\text{TTF}]_3[\text{BF}_4]_2/[\text{NMe}_4]_2[\text{V}(\text{mnt})_3]$  may not oxidize the  $[\text{V}(\text{mnt})_3]^{2-}$  anion. In fact, the salt obtained from the above reaction exhibits almost an isotropic, broad ESR signal due to the V(IV) state which is close to the signal of  $[\text{NMe}_4]_2[\text{V}(\text{mnt})_3]$ , as shown in Fig. 2. Thus, the present salt formally contains two molar  $\text{TTF}^{+\cdot}$  radical cations and 0.5 molar neutral  $\text{TTF}^0$  molecule with the divalent anion. The salt exhibits no ESR signal due to the  $\text{TTF}^{+\cdot}$  radical cation, as reported for  $[\text{TTF}]_2[\text{M}(\text{C}_2\text{O}_4)_3]$  ( $\text{M} = \text{Si}$  or  $\text{Ge}$ ) ( $g_{\text{max}} = 2.012$ ,  $g_{\text{int}} = 2.007$ ,  $g_{\text{min}} = 2.002$ ) [12] and  $[\text{TTF}][\text{Rh}(\text{CO})_2\text{Cl}_2]$  ( $g_{\text{max}} = 2.016$ ,  $g_{\text{int}} = 2.009$ ,  $g_{\text{min}} = 2.003$ ) [17]. This finding seems to arise from a spin-spin interaction due to the formation of a  $\text{TTF}^{+\cdot}$  radical cation dimer, as described later. Moreover, the Raman spectrum of the salt exhibits only a peak at  $1419 \text{ cm}^{-1}$  which is essentially attributable to the  $\nu_3$  mode of the  $\text{TTF}^{+\cdot}$  radical cation (a stretching of the central C-C bonding) [18].

### Crystal Structure of $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$ and Its Electrical Conductivity

Figure 3 shows the molecular geometry of the tris(mnt)vanadium anion with the atom-labelling scheme. Relevant bond lengths and angles of the anion are listed in Table 2 together with those of the TTF moieties. Six sulfur atoms are coordinated to the vanadium atom at the average distance of  $2.364 \text{ \AA}$ . The averaged S-V-S bite angle is  $84.3^\circ$  and the interligand S-V-S angles [S(1)-V-S(5), S(2)-V-S(3), and S(4)-V-S(6)] are averaged to  $163.3^\circ$ . This value deviates remarkably from that of a trigonal prism ( $136^\circ$ ) [19]. Thus, the  $\text{VS}_6$  core is considered to have a distorted octahedral symmetry. This geometry is close to the  $\text{VS}_6$  cores of  $[\text{NMe}_4]_2[\text{V}(\text{mnt})_3]$  (the pseudo-*trans* S-V-S angle,  $158.6^\circ$ ) [20],  $[\text{NBu}_4^+]_2[\text{V}(\text{mnt})_3]$  (dmt = 1,2-dithiole-3-thione-4,5-dithiolate; S-V-S,  $164.3^\circ$ ) [21], and  $[\text{NMP}]_2[\text{V}(\text{dmit})_3]$  (NMP = *N*-methylphenazinium; S-V-S,  $161.8^\circ$ ) [7].

Projections of TTF overlapping modes perpendicular to a TTF molecular plane are illustrated in Fig. 4, together with the atom-labelling scheme. TTF molecules are arranged to form a one-dimensional columnar structure, as displayed in Fig. 5. Moreover, no significant atom-atom contact between the TTF moieties and  $[\text{V}(\text{mnt})_3]^{2-}$  anions is observed in the solid state. The central C-C distances of molecules A and B [C(13)-C(14),  $1.397(18)$  and C(19)-C(20),  $1.398(16) \text{ \AA}$ ] are close to those of  $\text{TTF}^{+\cdot}$  radical cation salts, such as  $[\text{TTF}][\text{HgCl}_3]$  [ $1.41(1) \text{ \AA}$ ] [22] and  $[\text{TTF}][\text{ClO}_4]$  [ $1.400(13)$ ,  $1.407(14) \text{ \AA}$ ] [23]. For molecule C its central C-C distance [ $1.357(24) \text{ \AA}$ ] is appreciably shorter than those distances and is rather close to that of neutral TTF [ $1.349(3) \text{ \AA}$ ] [24]. Thus, molecules A and B seem to correspond to the  $\text{TTF}^{+\cdot}$  radical cation and molecule C to neutral TTF.

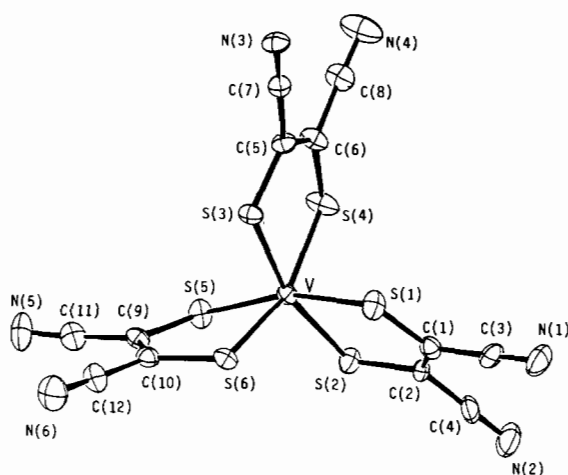


Fig. 3. Molecular geometry of the  $[\text{V}(\text{mnt})_3]^{2-}$  anion of  $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$  with the atom-labelling scheme.

TABLE 2 Selected Bond Distances (Å) and Bond Angles (°) for  $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$ <sup>a</sup>

V–S(1)	2.358(4)	S(15)–C(25)	1.711(24)
V–S(2)	2.356(4)	S(15)–C(26)	1.745(20)
V–S(3)	2.367(4)	S(16)–C(25)	1.831(22)
V–S(4)	2.381(4)	S(16)–C(27)	1.737(21)
V–S(5)	2.357(4)	N(1)–C(3)	1.130(17)
V–S(6)	2.365(4)	N(2)–C(4)	1.145(18)
S(1)–C(1)	1.693(12)	N(3)–C(7)	1.131(15)
S(2)–C(2)	1.734(11)	N(4)–C(8)	1.155(18)
S(3)–C(5)	1.707(12)	N(5)–C(11)	1.123(17)
S(4)–C(6)	1.698(14)	N(6)–C(12)	1.148(16)
S(5)–C(9)	1.717(12)	C(1)–C(2)	1.369(16)
S(6)–C(10)	1.720(11)	C(1)–C(3)	1.440(17)
S(7)–C(13)	1.729(13)	C(2)–C(4)	1.447(17)
S(7)–C(17)	1.738(14)	C(5)–C(6)	1.352(17)
S(8)–C(13)	1.711(12)	C(5)–C(7)	1.459(16)
S(8)–C(18)	1.746(14)	C(6)–C(8)	1.428(18)
S(9)–C(14)	1.724(14)	C(9)–C(10)	1.372(17)
S(9)–C(15)	1.726(15)	C(9)–C(11)	1.443(17)
S(10)–C(14)	1.716(14)	C(10)–C(12)	1.417(17)
S(10)–C(16)	1.739(15)	C(13)–C(14)	1.397(18)
S(11)–C(19)	1.720(12)	C(15)–C(16)	1.361(22)
S(11)–C(23)	1.712(14)	C(17)–C(18)	1.337(20)
S(12)–C(19)	1.703(11)	C(19)–C(20)	1.398(16)
S(12)–C(24)	1.722(12)	C(21)–C(22)	1.351(18)
S(13)–C(20)	1.719(12)	C(23)–C(24)	1.371(18)
S(13)–C(21)	1.718(13)	C(25)–C(25')	1.357(24)
S(14)–C(22)	1.739(13)		
S(1)–V–S(2)	84.9(1)	C(13)–S(7)–C(17)	95.3(6)
S(1)–V–S(3)	84.5(1)	C(13)–S(8)–C(18)	96.3(7)
S(1)–V–S(4)	100.3(1)	C(14)–S(9)–C(15)	95.6(7)
S(1)–V–S(5)	165.1(2)	C(14)–S(10)–C(16)	96.5(7)
S(1)–V–S(6)	87.2(1)	C(19)–S(11)–C(23)	96.2(6)
S(2)–V–S(3)	164.7(1)	C(19)–S(12)–C(24)	96.4(6)
S(2)–V–S(4)	87.9(1)	C(20)–S(13)–C(21)	94.9(6)
S(2)–V–S(5)	86.4(1)	C(20)–S(14)–C(22)	96.3(6)
S(2)–V–S(6)	111.2(1)	C(25)–S(15)–C(26)	97.1(10)
S(3)–V–S(4)	83.2(1)	C(25)–S(16)–C(27)	94.1(10)
S(3)–V–S(5)	106.1(1)	S(7)–C(13)–S(8)	115.1(7)
S(3)–V–S(6)	79.3(1)	S(9)–C(14)–S(10)	115.0(8)
S(4)–V–S(5)	91.5(1)	S(11)–C(19)–S(12)	115.0(7)
S(4)–V–S(6)	160.2(2)	S(13)–C(20)–S(14)	115.4(7)
S(5)–V–S(6)	84.7(1)	S(15)–C(25)–S(16)	112.4(10)
V–S(1)–C(1)	105.7(4)	N(1)–C(3)–C(1)	178.3(14)
V–S(2)–C(2)	105.3(4)	N(2)–C(4)–C(2)	179.1(14)
V–S(3)–C(5)	106.0(5)	N(3)–C(7)–C(5)	177.3(12)
V–S(4)–C(6)	105.3(5)	N(4)–C(8)–C(6)	179.1(14)
V–S(5)–C(9)	103.6(4)	N(5)–C(11)–C(9)	177.4(14)
V–S(6)–C(10)	103.2(4)	N(6)–C(12)–C(10)	178.1(14)
S(1)–C(1)–C(2)	122.8(9)	C(2)–C(1)–C(3)	120.0(11)
S(2)–C(2)–C(1)	121.0(9)	C(1)–C(2)–C(4)	121.3(10)
S(3)–C(5)–C(6)	121.2(9)	C(6)–C(5)–C(7)	120.2(11)
S(4)–C(6)–C(5)	122.6(10)	C(5)–C(6)–C(8)	119.4(12)
S(5)–C(9)–C(10)	121.9(9)	C(10)–C(9)–C(11)	120.2(11)
S(6)–C(10)–C(9)	121.6(9)	C(9)–C(10)–C(12)	120.0(10)

<sup>a</sup>e.s.d.s given in parentheses.

Molecules **A** and **B** are located almost parallel to each other (the dihedral angle, 1.0°) with an interplanar distance of 3.40 Å having an almost eclipsed

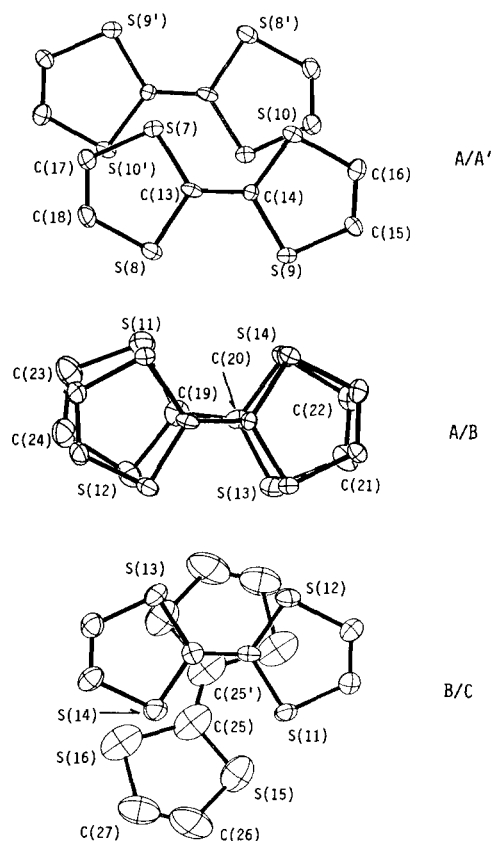


Fig. 4. Projections of TTF overlapping modes perpendicular to a TTF molecular plane, together with the atom-labelling scheme.

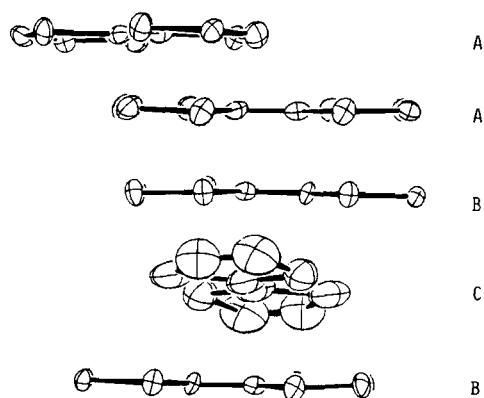


Fig. 5. One-dimensional TTF columnar structure of  $[\text{TTF}]_{2.5}[\text{V}(\text{mnt})_3] \cdot 0.5\text{CH}_2\text{ClCH}_2\text{Cl}$ .

overlap: S(7)–S(11), 3.417(49); S(8)–S(12), 3.455(51); S(9)–S(13), 3.405(50); S(10)–S(14), 3.373(52) Å. This suggests formation of a  $\text{TTF}^{+\cdot}$  radical cation dimer, which is close to the reported dimers;  $[\text{TTF}]\text{Br}$  (the interplanar distance, 3.34 Å) [25],  $[\text{TTF}][\text{DFTCNQ}]$  (DFTCNQ = 2,5-difluoro-7,7,8,8-tetracyano-*p*-quinodimethane) (3.34 Å) [26],

[TTF][ClO<sub>4</sub>] (3.42 Å) [23], [TTF][HgCl<sub>3</sub>] (3.43 Å) [22] and [TTF]<sub>2</sub>[Ni(S<sub>2</sub>C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>] (3.48 Å) [27]. These TTF<sup>•+</sup> radical cations seem to cause a significant spin-spin interaction, resulting in no ESR signals due to the TTF<sup>•+</sup> radical cation, as described above.

Molecule C lies on a center of symmetry and molecules A and A' are crystallographically equivalent. The overlap between A and A' seems to be insufficient. The dihedral angle between these molecular planes is 5.3° and the closest sulfur-sulfur contact is 3.695 Å [S(9)-S(9')]. Molecule C deviates significantly from the parallel arrangement against molecule B with the dihedral angle of 8.6°. The overlap between them, however, is relatively improved, with sulfur-sulfur contacts; S(11)-S(15), 3.693 Å and S(14)-S(16), 3.479 Å.

The salt behaves as a semiconductor with the electrical conductivity of  $1.7 \times 10^{-4}$  S cm<sup>-1</sup> at 25 °C and the activation energy  $E_a = 0.24$  eV for a compacted pellet. The electrical conduction may occur through the TTF<sup>•+</sup>/TTF<sup>•+</sup>/TTF<sup>0</sup> columnar structure described above, which is in a contrast to the conduction through pathways constructed with the interaction among TTF and dmit sulfur atoms expected for [TTF]<sub>2</sub>[V(dmit)<sub>3</sub>] [7].

### Supplementary Material

Atomic thermal parameters and observed and calculated structure factors are available from the authors on request.

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### References

- 1 A. F. Siedle, G. A. Candela, T. F. Finnegan, R. P. van Duyne, T. Cape, G. F. Kokoszka, P. M. Woyciesjes, J. A.

- Hashmall, M. Glick and W. Ilsley, *Ann. N.Y. Acad. Sci.*, **313** (1978) 1.
- 2 J. S. Miller (ed.), *Extended Linear Chain Compounds*, Vol. 2, Plenum, New York, 1982.
- 3 K. Kondo, G. Matsubayashi, T. Tanaka, H. Yoshioka and K. Nakatsu, *J. Chem. Soc., Dalton Trans.*, (1984) 379.
- 4 G. Matsubayashi, K. Ueyama and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, (1985) 465.
- 5 K. Ueyama, G. Matsubayashi, R. Shimizu and T. Tanaka, *Polyhedron*, **4** (1985) 1783.
- 6 K. Ueyama, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, **112** (1986) 135.
- 7 G. Matsubayashi, K. Akiba and T. Tanaka, *Inorg. Chem.*, in press.
- 8 A. Davison, N. Edelstein, R. H. Holm and A. H. Maki, *J. Am. Chem. Soc.*, **86** (1964) 2799.
- 9 F. Wudl, *J. Am. Chem. Soc.*, **97** (1975) 1962.
- 10 G. Matsubayashi, K. Kondo and T. Tanaka, *Inorg. Chim. Acta*, **69** (1983) 167.
- 11 G. Matsubayashi, Y. Sakamoto and T. Tanaka, *J. Chem. Soc., Perkin Trans. II*, (1985) 947.
- 12 K. Ueyama, G. Matsubayashi and T. Tanaka, *Inorg. Chim. Acta*, **87** (1984) 143.
- 13 M. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolson, *MULTAN 78*, a system of computer programs for the automatic solution of crystal structures for X-ray diffraction data, University of York, 1978.
- 14 *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.
- 15 C. K. Johnson, *ORTEP-II, Report ORNL 5138*, Oak Ridge National Laboratory, TN, 1976.
- 16 E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Clots and R. N. Compton, *J. Am. Chem. Soc.*, **97** (1975) 2921.
- 17 G. Matsubayashi, K. Yokoyama and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, (1988) 253.
- 18 R. Bozio, I. Zanon, A. Girlando and C. Pecile, *J. Chem. Phys.*, **71** (1979) 2282.
- 19 M. Cowie and M. J. Bennett, *Inorg. Chem.*, **15** (1976) 1595.
- 20 E. I. Stiefel, Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **89** (1967) 3353.
- 21 R.-M. Oak, W. Dietzsch, R. Kirmse, J. Stach and E. Hoyer, *Inorg. Chim. Acta*, **128** (1987) 251.
- 22 T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. van Duyne and A. R. Siedle, *Inorg. Chem.*, **19** (1980) 3604.
- 23 K. Yakushi, S. Nishimura, T. Sugano, H. Kuroda and I. Ikemoto, *Acta Crystallogr., Sect. B*, **36** (1980) 358.
- 24 B. A. Scott, S. J. La Placa, J. B. Torrance, B. D. Silverman and B. Webster, *J. Am. Chem. Soc.*, **99** (1977) 6631.
- 25 T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, (1973) 471.
- 26 T. J. Emge, F. M. Wiygul, J. P. Ferraris and T. J. Kistenmacher, *Mol. Cryst. Liq. Cryst.*, **78** (1981) 295.
- 27 J. S. Kasper, L. V. Interrante and C. A. Secaur, *J. Am. Chem. Soc.*, **97** (1975) 890.