

Radical Cation Salts of an Unsymmetrical BEDT-TTF Derivative: Molecular Structure and Physical Properties of (DIMET*)₂ClO₄ × THF

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Organic Metals, Electrocrystallization

4.5-Dimethyl-4'.5'-ethylenedithiotetrathiafulvalene (DIMET) was obtained by reacting 4.5-ethylenedithiolo-1.3-dithioliumtetrafluoroborate with 4.5-dimethyl-1.3-dithiolium-tetrafluoroborate in the presence of diisopropylethylamine or triethylamine. Electrocrystallization of this donor in different solvents like dichloromethane or tetrahydrofurane (THF) and with varying supporting electrolytes, like tetrabutylammonium hexafluorophosphate, triiodide, nitrate, perchlorate or perchlorate, results in a large number of well crystallizing compounds. The crystal and molecular structure of one of the isolated solids was elucidated by X-ray methods.

(C₁₀H₁₀S₆)₂ClO₄ × C₄H₈O, M_r = 816.66, is triclinic, P $\bar{1}$, $a = 6.731(5)$, $b = 7.632(3)$, $c = 33.32(3)$ Å, $\alpha = 96.53(5)$, $\beta = 92.99(6)$, $\gamma = 103.13(5)^\circ$, $V = 1650.7$ Å³, $Z = 2$, $d_c = 1.64$ g cm⁻³, final $R_w = 0.077$ for 1844 observed independent reflections. Sheets of cations with an average charge of 1/2+ are separated by sheets of anions and THF solvent molecules. Intermolecular S...S contacts result in two-dimensional physical properties. Electrical conductivity and thermopower measurements indicate two broad phase transitions at around 200 K and 80 K.

Introduction

BEDT-TTF** is at this time the most promising donor to prepare new highly conducting organic metals or even superconductors [1–7]. Furthermore it has been shown in earlier work [8, 9], that the unsymmetrically substituted donors of the TTF family with a C_{2v} molecular symmetry give TCNQ salts which show higher electrical conductivity than those with the more symmetrical TTF derivatives (D_{2h} symmetry). We, therefore, decided to test this interrelation using another member of the TTF donor family, BEDT-TTF. In the following we report the synthesis of the "unsymmetrical" (C_{2v}) TTF derivative 4.5-dimethyl-4'.5'-ethylenedithiotetrathiafulvalene (DIMET) which yields nicely crystallizing ion radical salts by electrocrystallization. The structure and the physical properties of one of the many isolated and characterized solids are described. A

TCNQ salt of this donor has been described very recently [10].

Experimental

Preparations

Donor synthesis

The donor DIMET was obtained by the reaction of 4.5-dimethyl-1.3-dithiolium-tetrafluoroborate (**1**) and 4.5-ethylenedithiolo-1.3-dithiolium-tetrafluoroborate (**2**) with diisopropylethylamine or triethylamine with reference to a similar procedure in the preparation of other unsymmetrical TTF donors [8]. **1** was prepared starting from 4.5-dimethyl-1.3-dithiol-2-thione [11] which was methylated [12], reduced with sodium borohydride in methanol and treated with tetrafluoroboric acid in acetic acid anhydride [13]. **2** was prepared in an analogous way starting from 4.5-ethylenedithiolo-1.3-dithiole-2-thione [14, 15]. This compound was methylated [16] using the stronger alkylating agent dimethoxycarbonium tetrafluoroborate as described earlier [17]. The reduction of this compound with sodium borohydride should be carried out at room temperature in acetonitrile instead of methanol as described in [13]. The resulting 2-S-methyl-1.3-dithiole was reacted with HBF₄ in acetic acid anhydride with a trace of diethyl-ether to yield **2**.

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* DIMET = 4.5-Dimethyl-4'.5'-ethylenedithiolo-tetrathiafulvalene = C₁₀H₁₀S₆.

** BEDT-TTF = Bis(4.5-ethylenedithiolo)tetrathiafulvalene = C₁₀H₈S₈.

DIMET

420 mg (1.9 mmol) of **1** and 540 mg (1.9 mmol) of **2** were dissolved in 10 ml dried acetonitrile. This solution was cooled to 0 °C and kept under nitrogen atmosphere. Then 4.6 ml diisopropylethylamine were added dropwise while the mixture was stirred. Stirring was continued for ten minutes after addition of the amine. 200 ml H₂O were added to the mixture after that time. The pink precipitate was filtered off and dried *in vacuo*. (Yield: 550 mg solid.)

The following procedure was successful in separating the three products BEDT-TTF, TMTTF, and DIMET contained in the pink solid: All of the pink solid (550 mg) was boiled twice with 45 ml and once with 30 ml CH₃CN and filtered off after each operation. The residue, a meat colored powder, turned out to consist mainly of BEDT-TTF. The filtrates were evaporated. The resulting solid (about 450 mg) was dissolved in a mixture of 20 ml dry CH₂Cl₂ and 20 ml dry *n*-hexane. The solution was run through a silica gel chromatography column (90 cm long, 4 cm diameter) using a 1:1 mixture of CH₂Cl₂ and *n*-hexane as solvent. The best velocity for this chromatographic procedure is about 5–7 ml/min. The first fraction consists mainly of TMTTF. After a short intermediate fraction the main part of the DIMET product is obtained. After another short intermediate a final (so far unidentified) yellow fraction can be collected. The DIMET obtained in this way was recrystallized from acetonitrile and used for the electrocrystallization.

Analyses: C₁₀H₁₀S₆, *M_r* = 322.57

Calcd C 37.24 H 3.12 S 59.64,

Found C 37.5 H 2.88 S 59.86.

The compound was finally identified by its ¹H NMR and mass spectra. It shows two reversible one electron redox steps at 0.44 V and 0.83 V and is oxidized irreversibly above 2.04 V.

Electrocrystallizations

The donor was electrocrystallized in different solvents using tetrabutylammonium salts of various anions as electrolytes. A U-shaped tube with a glass filter in the bottom bending of the tube was used as a cell for these preliminary crystallization experiments. Galvanostatic (current fixed between 12 and 40 μA, around 1 V) and potentiostatic (fixed potential between 1.7 and 1.9 V resulting in currents between 6–20 μA) have been used. The currents which result for certain potentials depend strongly on the cell and electrode arrangement, on the solvent used and mainly on the concentration and type of supporting electrolyte. Variations in these experimental para-

eters leads to the wide range of potential to current ratios observed during the electrocrystallizations. The following solids could be obtained under these conditions without any problems:

(DIMET)_x(PF₆)_y: black lustreous needles and platelets from CH₂Cl₂ after evaporation of the solvent in the anode compartment of the cell.

(DIMET)_x(PF₆)_y: from THF long black needles (8×0.1×0.1 mm³) (semiconductor).

(DIMET)_x(I₃)_y: small black lustreous platelets from THF.

(DIMET)_x(ReO₄)_y: long black needles (5×0.1×0.1 mm³) (metal).

(DIMET)_x(AsF₆)_y: black lustreous needles (semiconductor).

(DIMET)_x(NO₃)_y: black lustreous rhombic prisms (metal).

(DIMET)₂ClO₄×THF: black lustreous rhombic flat needles.

The larger crystals of (DIMET)₂ClO₄×THF used for the following investigations were obtained in an arrangement described earlier [18].

Physical investigations

The electrical conductivity was measured by the standard four probe method (dc and ac at 4–10 Hz) in the temperature range between 4.2 K and 300 K. Gold leads (0.015–0.025 mm diameter) were attached to the samples with silver or gold paint on previously evaporated gold pads, yielding contact resistencies of a few ohms. Thermopower measurements were performed in the temperature range between 20–300 K.

X-ray investigations

For the X-ray investigation a plate-like trunk of a crystal, 0.3×0.3×0.08 mm³, was mounted on top of a glass capillary. Lattice parameters were estimated from Weissenberg photographs and recalculated from the setting angles of 24 reflections (Syntex R3 diffractometer, monochromated MoK_α radiation). Data collection (ω -scans background-peak-background, $2\theta < 50^\circ$) yielded 1844 observed independent reflections with $I > \sigma 1.5(I)$. An empirical absorption correction ($\mu = 8.8 \text{ cm}^{-1}$) was applied using ψ -scans of 5 reflections with $8.4^\circ < 2\theta < 22.8^\circ$.

The structure was solved by direct methods and Fourier syntheses. H atoms were inserted at calculated positions and the methyl and methylene groups refined as rigid groups. Due to the unfavourable parameter to reflection ratio, only the perchlorate anion which was expected to show the largest thermal motion, was refined with anisotropic temperature factors. Final refinement of the 194 parameters

Table I. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$).

Atom	x	y	z	U
S(1)	8417(9)	3902(7)	426(2)	42(2)
S(2)	4268(8)	3503(7)	683(2)	42(2)
S(3)	6517(9)	2016(7)	- 480(2)	44(2)
S(4)	2414(9)	1608(7)	- 206(2)	41(2)
S(5)	10505(9)	5332(8)	1234(2)	52(2)
S(6)	5469(9)	4912(8)	1537(2)	49(2)
C(1)	5801(27)	3125(23)	287(5)	26(5)
C(2)	5014(29)	2342(25)	- 82(5)	33(5)
C(3)	8169(30)	4540(25)	930(5)	33(5)
C(4)	6284(30)	4381(26)	1057(5)	40(6)
C(5)	4470(28)	980(23)	- 838(5)	27(5)
C(6)	2633(29)	854(24)	- 706(5)	32(5)
C(7)	4985(29)	458(25)	-1250(5)	49(6)
C(8)	667(29)	- 14(26)	- 957(5)	54(7)
C(9)	9652(47)	5635(41)	1704(8)	135(13)
C(10)	7785(43)	5532(38)	1825(8)	128(12)
S(7)	7179(8)	2608(7)	4645(2)	34(1)
S(8)	11497(8)	3419(7)	4470(1)	34(1)
S(9)	8453(8)	1639(7)	5524(2)	35(1)
S(10)	12748(8)	2446(7)	5359(1)	30(1)
S(11)	5583(8)	3183(7)	3847(2)	38(2)
S(12)	10754(8)	4165(7)	3639(2)	38(2)
C(11)	9698(27)	2718(23)	4797(5)	29(5)
C(12)	10261(26)	2325(23)	5203(5)	25(5)
C(13)	7729(27)	3140(23)	4166(5)	25(5)
C(14)	9730(28)	3545(24)	4076(5)	29(5)
C(15)	10191(27)	1452(23)	5914(5)	23(5)
C(16)	12164(28)	1814(24)	5834(5)	28(5)
C(17)	9314(27)	926(24)	6290(5)	40(6)
C(18)	13993(27)	1721(24)	6115(5)	47(6)
C(19)	6620(29)	3002(25)	3377(5)	43(6)
C(20)	8536(28)	4401(25)	3342(5)	43(6)
Cl	4174(11)	6855(9)	2731(2)	61(3)*
O(1)	4770(29)	8628(22)	2939(4)	115(10)*
O(2)	3999(25)	6935(22)	2328(4)	91(9)*
O(3)	2317(38)	6044(27)	2854(6)	189(15)*
O(4)	5688(41)	5976(34)	2798(7)	197(18)*
O(5)	9379(25)	899(21)	1958(4)	80(5)

C(21)	8491(36)	757(33)	2345(6)	92(9)
C(22)	10107(40)	457(37)	2631(8)	112(11)
C(23)	11987(43)	1254(36)	2497(8)	112(11)
C(24)	11576(41)	1346(37)	2042(8)	115(11)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

by cascade matrix least squares based on F, with weights $w = 1/\sigma^2(F)$, converged with $R_w(R) = 0.077$ (0.092), a goodness of fit of 1.93, and a mean (max.) shift/error of 0.002 (0.009). Largest features in a final difference Fourier map were +0.94 and -0.75 electrons per \AA^3 .

Calculations were performed with the SHELXTL program package [19] on a Nova 3 computer using scattering factors, including anomalous dispersion, from International Tables for X-ray Crystallography [20]. Plots were done on a Tektronix plotter with SHELXTL.

Results and Discussion

Structure

Atom coordinates are listed in Table I*. The numbering scheme in the two crystallographically independent cations is shown in Fig. 1. Bond distances and angles are listed in Table II. The high tempera-

* Lists of anisotropic temperature factors of the ClO_4^- anion and observed and calculated structure factors as well as some further details of the X-ray investigations have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Copies may be obtained quoting the deposition number CSD 51659, the authors, and the journal reference.

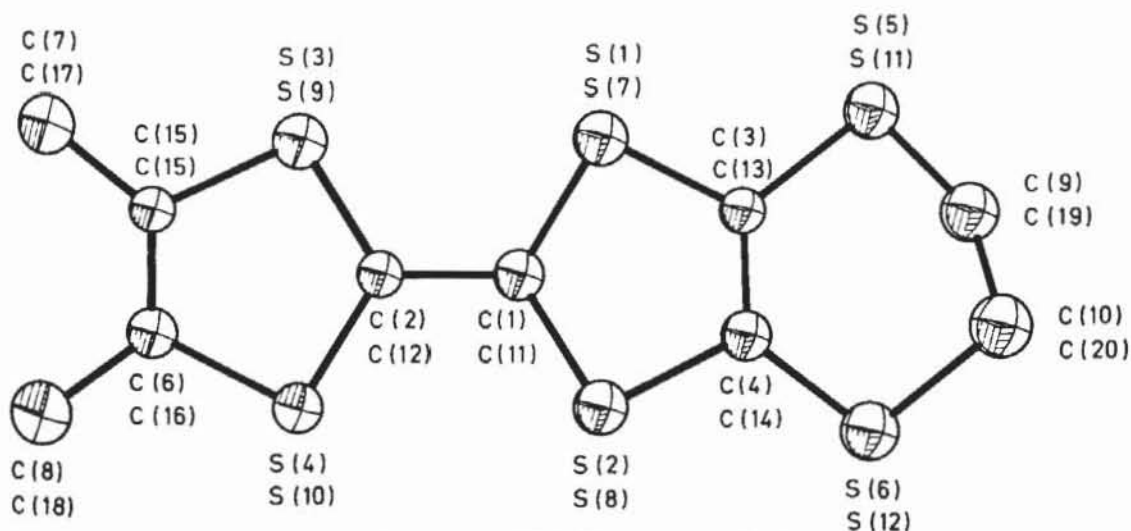


Fig. 1. Numbering scheme in the two $\text{DIMET}^{1/2+}$ cations. Upper numbers refer to species I, with the center of the tetrathiafulvalene core at 0.54, 0.27, 0.01, lower numbers to species II at 1.0, 0.25, 0.50. Isotropic thermal contours (at 50% probability) are drawn for species II.

Table II. Bond distances (Å) and angles (°).

S(1)–C(1)	1.745(18)	S(1)–C(3)	1.723(18)
S(2)–C(1)	1.755(18)	S(2)–C(4)	1.751(18)
S(3)–C(2)	1.739(19)	S(3)–C(5)	1.751(17)
S(4)–C(2)	1.724(19)	S(4)–C(6)	1.724(18)
S(5)–C(3)	1.768(19)	S(5)–C(9)	1.706(29)
S(6)–C(4)	1.750(20)	S(6)–C(10)	1.726(27)
C(1)–C(2)	1.331(22)	C(3)–C(4)	1.342(28)
C(5)–C(6)	1.322(27)	C(5)–C(7)	1.466(24)
C(6)–C(8)	1.500(24)	C(9)–C(10)	1.328(43)
S(7)–C(11)	1.725(19)	S(7)–C(13)	1.728(18)
S(8)–C(11)	1.707(18)	S(8)–C(14)	1.750(19)
S(9)–C(12)	1.696(18)	S(9)–C(15)	1.743(18)
S(10)–C(12)	1.706(19)	S(10)–C(16)	1.746(18)
S(11)–C(13)	1.757(19)	S(11)–C(19)	1.753(19)
S(12)–C(14)	1.713(18)	S(12)–C(20)	1.803(20)
C(11)–C(12)	1.467(25)	C(13)–C(14)	1.369(26)
C(15)–C(16)	1.341(26)	C(15)–C(17)	1.469(23)
C(16)–C(18)	1.526(26)	C(19)–C(20)	1.495(24)
Cl–O(1)	1.409(16)	Cl–O(2)	1.352(15)
Cl–O(3)	1.369(24)	Cl–O(4)	1.363(31)
O(5)–C(21)	1.453(27)	O(5)–C(24)	1.445(31)
C(21)–C(22)	1.484(36)	C(22)–C(23)	1.393(38)
C(23)–C(24)	1.541(38)		
C(1)–S(1)–C(3)	95.9(9)	C(1)–S(2)–C(4)	96.3(9)
C(2)–S(3)–C(5)	95.8(9)	C(2)–S(4)–C(6)	95.0(9)
C(3)–S(5)–C(9)	101.2(12)	C(4)–S(6)–C(10)	100.5(12)
S(1)–C(1)–S(2)	113.4(9)	S(1)–C(1)–C(2)	124.2(15)
S(2)–C(1)–C(2)	122.5(14)	S(3)–C(2)–S(4)	114.6(9)
S(3)–C(2)–C(1)	122.8(15)	S(4)–C(2)–C(1)	122.5(15)
S(1)–C(3)–S(5)	114.9(11)	S(1)–C(3)–C(4)	118.8(13)
S(5)–C(3)–C(4)	126.3(14)	S(2)–C(4)–S(6)	113.5(12)
S(2)–C(4)–C(3)	115.4(14)	S(6)–C(4)–C(3)	131.1(14)
S(3)–C(5)–C(9)	115.1(13)	S(3)–C(5)–C(7)	116.8(13)
C(6)–C(5)–C(7)	128.0(16)	S(4)–C(6)–C(5)	119.5(13)
S(4)–C(6)–C(8)	116.2(14)	C(5)–C(6)–C(8)	124.2(16)
S(5)–C(9)–C(10)	131.7(23)	S(6)–C(10)–C(9)	128.7(22)
C(11)–S(7)–C(13)	93.6(9)	C(11)–S(8)–C(14)	95.1(9)
C(12)–S(9)–C(15)	95.0(9)	C(12)–S(10)–C(16)	93.8(9)
C(13)–S(11)–C(19)	99.6(9)	C(14)–S(12)–C(20)	101.9(9)
S(7)–C(11)–S(8)	117.5(10)	S(7)–C(11)–C(12)	120.5(13)
S(8)–C(11)–C(12)	121.9(13)	S(9)–C(12)–S(10)	117.7(10)
S(9)–C(12)–C(11)	121.2(13)	S(10)–C(12)–C(11)	121.1(13)
S(7)–C(13)–S(11)	114.6(10)	S(7)–C(13)–C(14)	118.8(14)
S(11)–C(13)–C(14)	126.6(14)	S(8)–C(14)–S(12)	115.6(11)
S(8)–C(14)–C(13)	114.7(13)	S(12)–C(14)–C(13)	129.7(14)
S(9)–C(15)–C(17)	115.8(13)	S(9)–C(15)–C(16)	116.0(13)
C(16)–C(15)–C(17)	128.1(16)	S(10)–C(16)–C(15)	117.6(14)
S(10)–C(16)–C(18)	115.4(13)	C(15)–C(16)–C(18)	127.0(16)
S(11)–C(19)–C(20)	114.9(12)	S(12)–C(20)–C(19)	114.7(14)
O(1)–Cl–O(2)	109.4(10)	O(1)–Cl–O(3)	107.8(12)
O(2)–Cl–O(3)	109.7(12)	O(1)–Cl–O(4)	108.8(13)
O(2)–Cl–O(4)	106.5(13)	O(3)–Cl–O(4)	114.5(15)
C(21)–O(5)–C(24)	107.0(17)	O(5)–C(21)–C(22)	106.2(20)
C(21)–C(22)–C(23)	107.2(23)	C(22)–C(23)–C(24)	105.9(22)
O(5)–C(24)–C(23)	106.6(21)		

ture factors of the methylene C(9) and C(10) atoms indicate disorder.

As there are two independent DIMET species, it would be possible that one of them is always the

cation and the other one always neutral. But as there is no structural indication for this, we assume a fractional average charge for each species, as it is usual in molecular electronic conductors. The cations are ar-

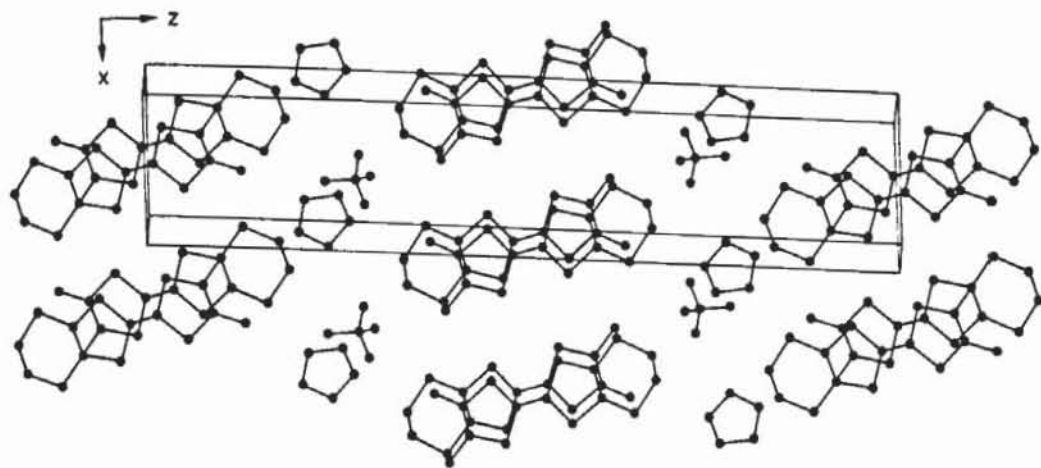


Fig. 2. Parallel projection of the crystal packing seen from a direction inclined at 10° to the y axis.

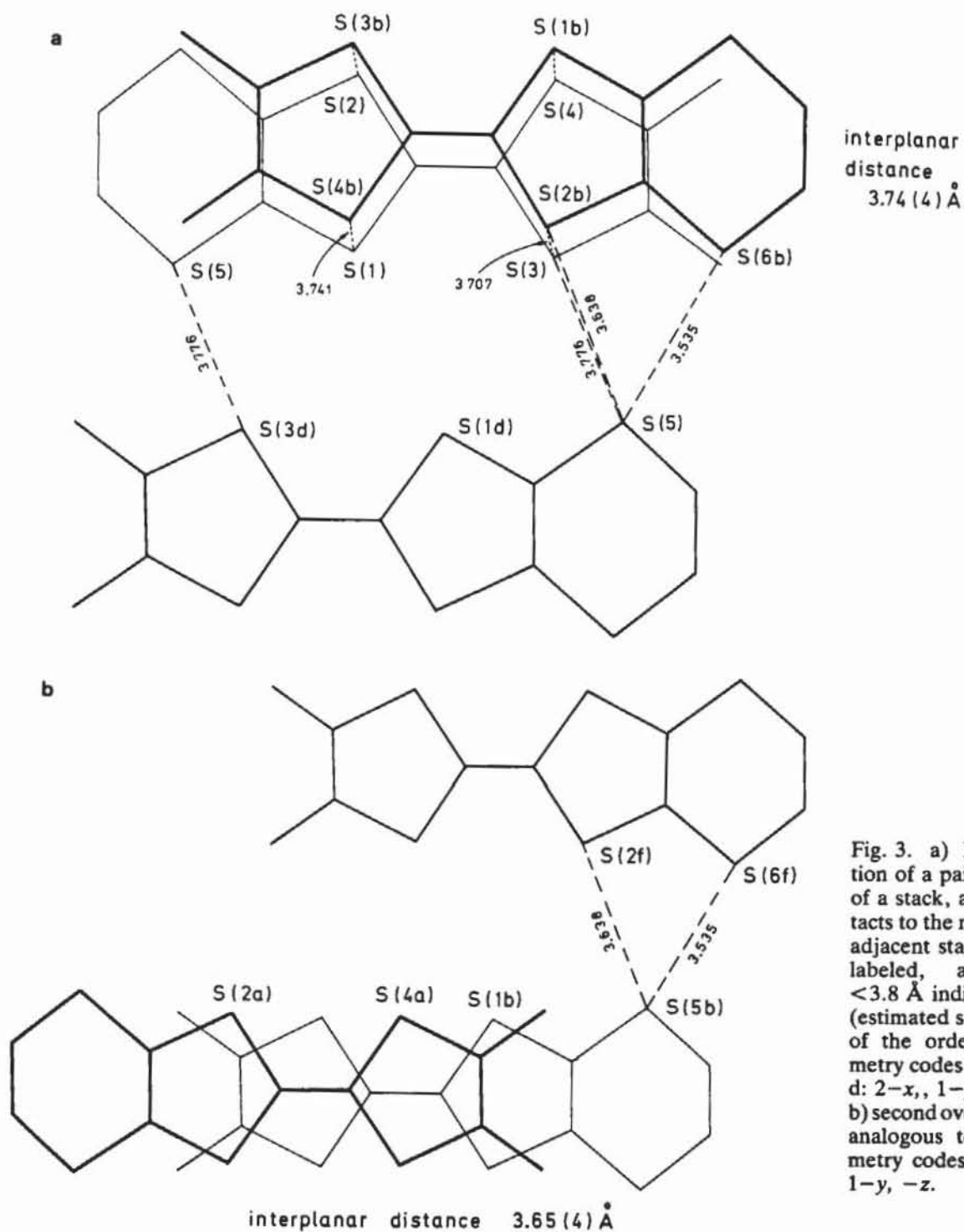


Fig. 3. a) Perpendicular projection of a pair of DIMET species I of a stack, and shortest $S \cdots S$ contacts to the nearest molecule of the adjacent stack. Some S atoms are labeled, and $S \cdots S$ contacts $< 3.8 \text{ \AA}$ indicated by broken lines (estimated standard deviations are of the order of 0.008 \AA). Symmetry codes are: b: $1-x, 1-y, -z$; d: $2-x, 1-y, -z$; f: $-x, 1-y, -z$.

ranged to stacks running along y which in turn are aligned in x direction to layers. There are two crystallographically different layers, each layer being composed of one of the two DIMET moieties. In z direction these layers are separated by sheets of anions and solvent molecules (Fig. 2).

Within each cation stack the molecules are parallel by symmetry (inversion centers midway between the molecules), but the cations of crystallographically

different stacks are inclined at $36(1)^\circ$ with respect to each other. (The molecular planes are defined as the least-squares planes through the four S and the six C atoms of the central tetrathiafulvalene core.)

Symmetry allows two different overlap patterns within each stack. These are indeed observed and they are also different in the two kinds of stacks (Figs 3 and 4). Figs 3 and 4 also contain the interplanar distances and the closest intermolecular S...S

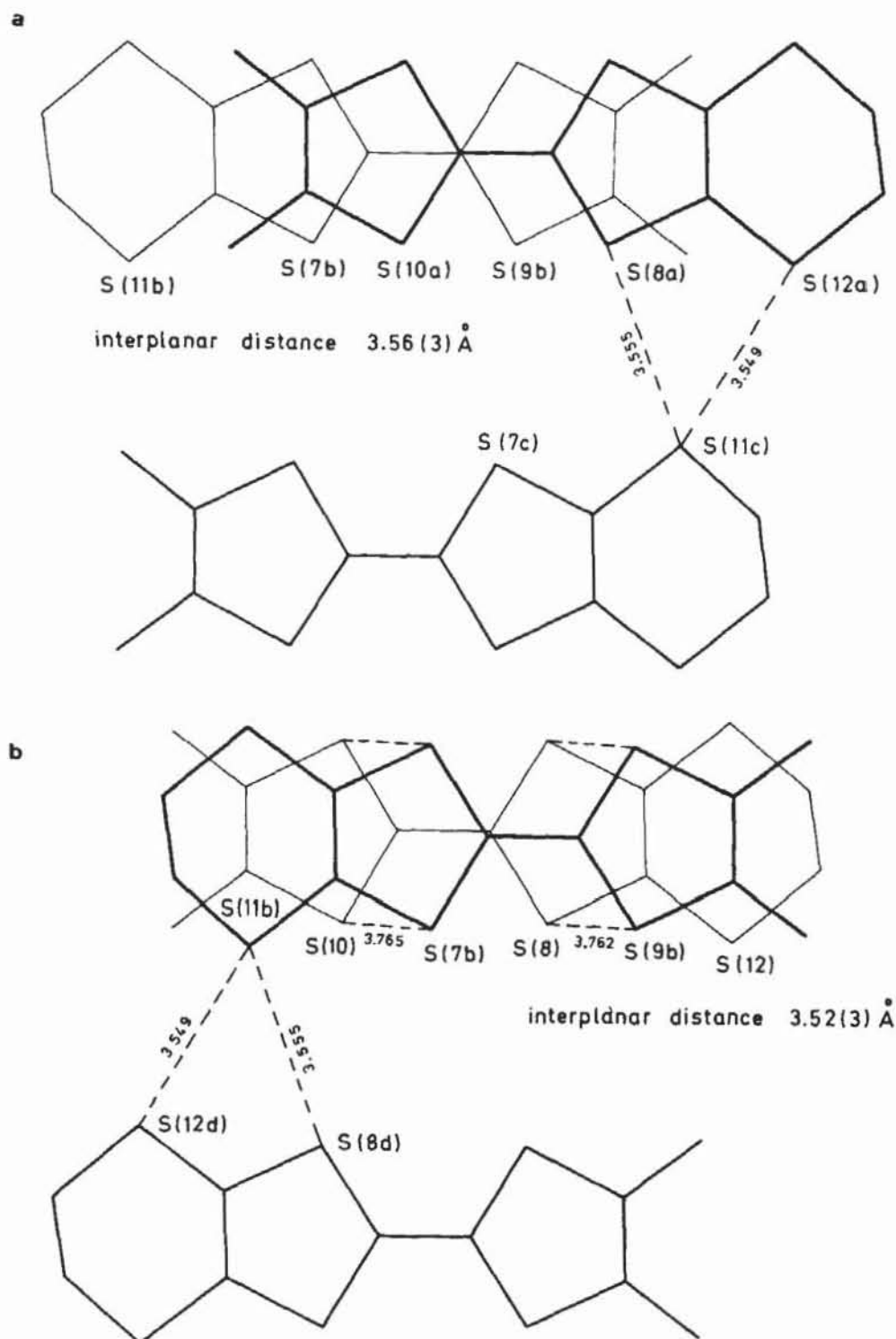


Fig. 4. a) Projection of a pair of molecules of stack II, analogous to Fig. 3a. Symmetry codes are: a: $x, 1+y, z$; b: $2-x, 1-y, 1-z$; c: $1+x, 1+y, z$; d: $3-x, 1-y, 1-z$.

contacts: Whereas the interplanar distances within the same stack are equal within their accuracy, they are shorter in stack II than in stack I. The different overlap patterns within a stack and the different interstack S...S contacts give the stacks a diadic character, despite the similar interplanar distances.

In the layers formed by the two kinds of stacks there are shorter S...S contacts between the stacks than within the stacks, resulting in the two-dimensional character of the solid. It is evident from Figs 3 and 4 that the S atoms of the six-membered rings are involved in the shortest contacts. So the presence of such rings is most important for creating a path for electronic conductivity, and the DIMET species is not as good a candidate for high conductivity as the BEDT-TTF donor, which has two such rings.

Physical results

The room temperature conductivity of needle shaped crystals of $(\text{DIMET})_2\text{ClO}_4 \times \text{THF}$ along the

needle axes ranges typically around $100 (\Omega \text{cm})^{-1}$. By lowering the temperature from room temperature a weak increase in conductivity is observed until 220 K, indicating a metallic regime (see Fig. 5). This is confirmed by the thermopower data (see Fig. 6) which show in this temperature region a weak linear temperature dependence. Around 200 K a broad phase transition might occur. Below 200 K a semi-conducting behaviour of the samples is observed as can be seen from the conductivity and thermopower data. Around 80 K the thermopower has a maximum of about $300 \mu\text{V/K}$. At lower temperatures the thermopower changes rapidly from positive to large negative values. This behaviour might indicate a second broad phase transition around 80–100 K in the semiconducting regime.

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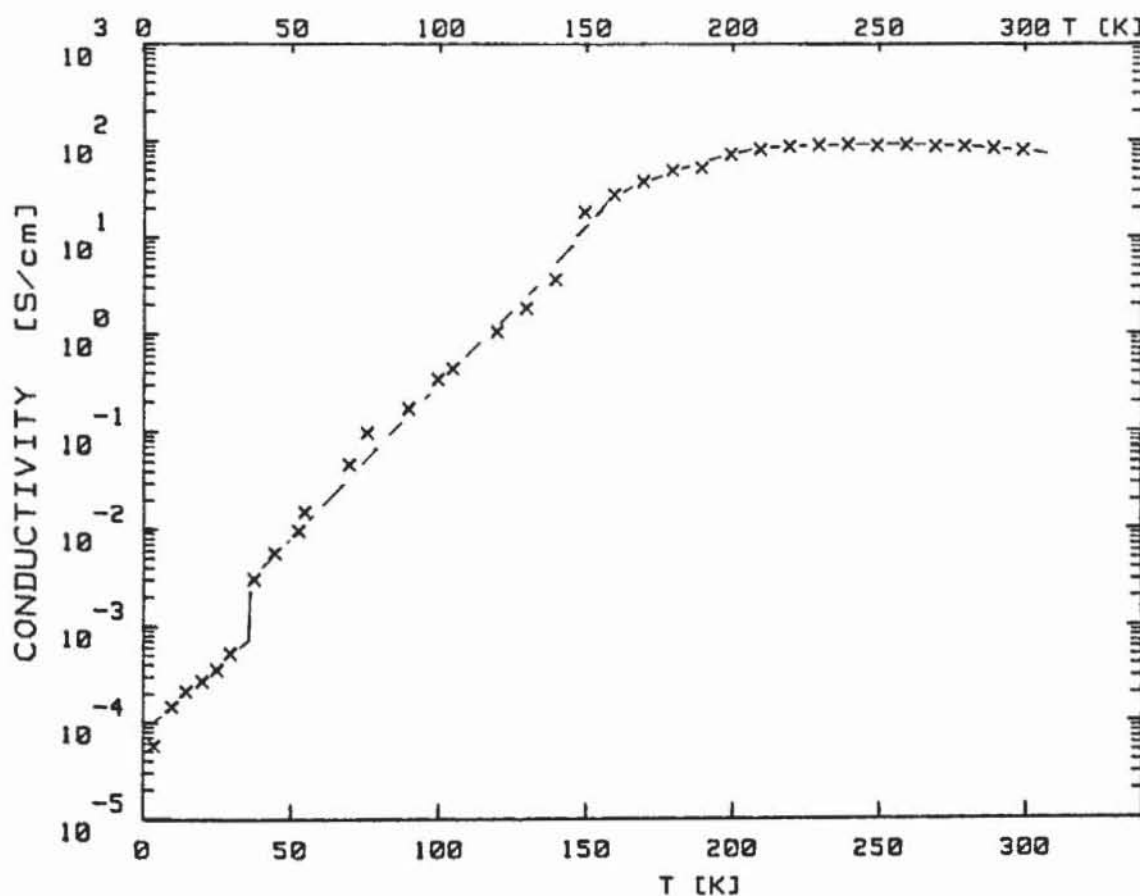


Fig. 5. Temperature dependence of the conductivity of $(\text{DIMET})_2\text{ClO}_4 \times \text{THF}$ measured along the needle axis.

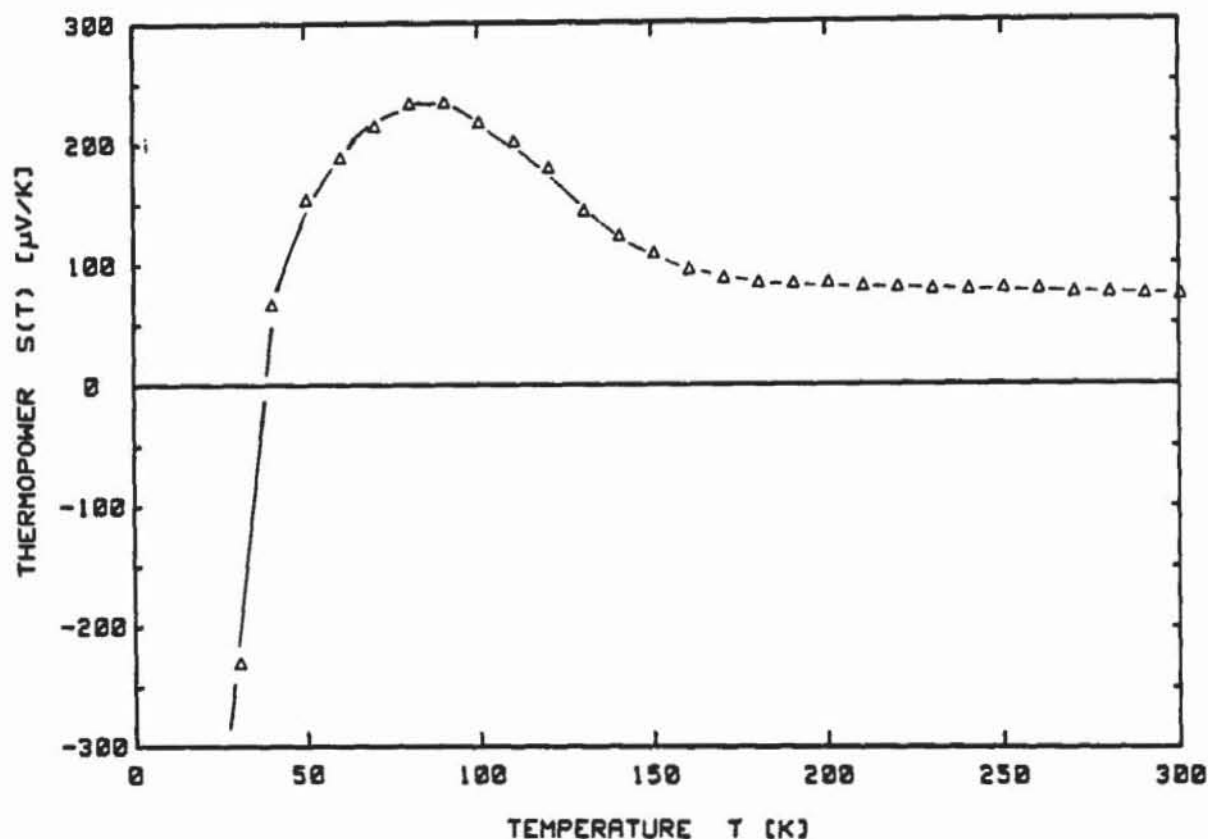


Fig. 6. Temperature dependence of the thermopower of $(\text{DIMET})_2\text{ClO}_4 \times \text{THF}$ crystals measured along the needle axis.

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