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**The Double-Stack Structure of Di(3,4-ethylenedithio-3',4'-dimethyl-2,2',5,5'-tetrathiafulvalenium) Perchlorate,\* (DIMET)<sub>2</sub>ClO<sub>4</sub>**

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**Abstract.**  $2\text{C}_{10}\text{H}_{10}\text{S}_6^{1/2+}.\text{ClO}_4^-$ ,  $M_r = 744.62$ , triclinic,  $P\bar{1}$ ,  $a = 7.000$  (2),  $b = 7.824$  (3),  $c = 27.010$  (14) Å,

$\alpha = 88.10$  (4),  $\beta = 89.02$  (4),  $\gamma = 74.58$  (3)°,  $V = 1425$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.73$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 10.1$  cm<sup>-1</sup>,  $F(000) = 762$ , room temperature, final  $R = 0.063$  for 3076 observed independent reflections. Two crystallographically independent

\* Alternative nomenclature: di(4,5-ethylenedithio-4',5'-dimethyl-2,2'-bi-1,3-dithiolylium) perchlorate.

DIMET molecules each with an average charge of  $\frac{1}{2}+$  form stacks, which run nearly perpendicularly to one another. Within each stack, two different interplanar spacings between adjacent parallel molecules are found. These overlap patterns are similar to those found in tetrahydrofuran solvate. The stacks are arranged side by side perpendicular to the long molecular axis to give a sheet-like arrangement.

**Introduction.** The electrochemical preparation of radical salts from the donor BEDT-TTF [bis(3,4-ethylenedithio)tetrathiafulvalene], which is not completely planar due to the tetrahedral methylene groups, often results in highly conducting materials. The electronic properties are quasi two-dimensional, owing to short S...S interstack contacts. In order to reduce the symmetry of the donor, the less-symmetrical TTF derivative DIMET (= 3',4'-dimethyl-3,4-ethylenedithiotetrathiafulvalene,  $C_{10}H_{10}S_6$ ) was synthesized (Heid, 1985; Heid, Endres, Keller, Gogu, Heinen, Bender & Schweitzer, 1985) and by other groups (Tatemitsu, Nishikawa, Sakata & Misumi, 1985; Aldoshina, Atovmyan, Goldenberg, Krasochka, Lubovskaya, Lubovskii, Merzhanov & Khidekel, 1985). This new donor was electrocrystallized in different solvents using tetrabutylammonium salts of various anions, such as  $ClO_4^-$ ,  $NO_3^-$ ,  $AsF_6^-$ ,  $PF_6^-$ ,  $ReO_4^-$ ,  $I_3^-$  as electrolytes (Heid *et al.*, 1985). Structural investigations on  $(DIMET)_2ClO_4 \cdot THF$ , which is a conductor down to low temperature, revealed short S...S interstack contacts, giving a two-dimensional character to the solid (Heid *et al.*, 1985). Recently investigated crystals of  $(DIMET)_2PF_6$ , however, showed only semiconducting properties (Aldoshina *et al.*, 1985).

In order to prevent the insertion of solvent molecules into the crystals, we prepared  $(DIMET)_2ClO_4$  electrochemically at room temperature from 1,1,1-trichloroethane and obtained the new type of structure described below.

**Experimental.** Prismatic crystal,  $0.05 \times 0.20 \times 0.31$  mm mounted on glass capillary. Lattice parameters from setting angles of 25 reflections centered on diffractometer (Syntex R3, monochromated Mo  $K\alpha$  radiation).  $\theta$ - $2\theta$  scans,  $2\theta \leq 50^\circ$ ,  $h, k, l$  range  $-8, -9, -32$  to  $0, 9, 32$ ; 3076 out of 5020 reflections observed with  $I > 2\sigma(I)$ . Empirical absorption correction using  $\psi$  scans of 7 reflections with  $9 < 2\theta < 48^\circ$ , min. transmission = 0.50 (max. = unity). Two check reflections at intervals of 98, intensity variation  $\pm 4.7\%$ ,  $R_{int} = 0.028$ . Structure solved by direct methods and completed by Fourier syntheses. Methyl and methylene groups refined as rigid groups with calculated H positions. Anisotropic temperature factors for non-H atoms, 334 variables. Cascade-matrix least-squares refinement based on  $F$

with weights  $w = 1/\sigma^2(F)$ ,  $\sigma$  from counting statistics,  $wR = 0.054$ ,  $R = 0.063$ ,  $S = 2.34$ ,  $(\Delta/\sigma)_{max} = 0.22$ ,  $\Delta\rho_{max}(\text{min.}) = 0.45 (-0.53) e \text{ \AA}^{-3}$ . SHELXTL program system (Sheldrick, 1983) on a Nova 3 computer, using scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous dispersion included. Plots on a Tektronix plotter with SHELXTL.

**Discussion.** Atomic coordinates are listed in Table 1, bond distances and angles in Table 2.\* The asymmetric unit consists of two DIMET molecules and one  $ClO_4^-$  anion. The numbering scheme in the DIMET donor molecules is given in Fig. 1. In analogy with other charge-transfer salts like the tetrahydrofuran solvate of the present compound (Heid *et al.*, 1985) it is assumed that the positive charge is equally distributed over the two DIMET molecules. The two DIMET molecules in this crystal are arranged in crystallographically inequivalent stacks running parallel to a [molecule II,

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43303 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
S(1)	3297 (3)	3771 (3)	657 (1)	39 (1)
S(2)	7552 (3)	2792 (3)	441 (1)	41 (1)
S(3)	2478 (3)	2343 (3)	-406 (1)	41 (1)
S(4)	6703 (3)	1363 (3)	-623 (1)	41 (1)
S(5)	3616 (3)	4857 (3)	1672 (1)	47 (1)
S(6)	8738 (3)	3695 (3)	1413 (1)	51 (1)
C(1)	5182 (10)	2863 (9)	236 (3)	35 (3)
C(2)	4818 (10)	2276 (9)	-201 (3)	34 (3)
C(3)	4876 (11)	4008 (9)	1133 (3)	35 (3)
C(4)	6814 (11)	3566 (9)	1032 (2)	34 (3)
C(5)	3211 (10)	1421 (9)	-977 (3)	35 (3)
C(6)	5121 (11)	994 (9)	-1083 (3)	38 (3)
C(7)	1580 (11)	1236 (10)	-1306 (3)	52 (3)
C(8)	6150 (11)	199 (10)	-1545 (3)	49 (3)
C(9)	5600 (12)	5295 (11)	2016 (3)	52 (4)
C(10)	7520 (12)	3885 (10)	2005 (3)	57 (4)
S(7)	3212 (3)	1878 (3)	4581 (1)	43 (1)
S(8)	2228 (3)	5248 (3)	4014 (1)	38 (1)
S(9)	2851 (3)	3988 (3)	5593 (1)	43 (1)
S(10)	1944 (3)	7355 (3)	5041 (1)	41 (1)
S(11)	3748 (4)	-376 (3)	3723 (1)	67 (1)
S(12)	2594 (4)	3648 (3)	3040 (1)	57 (1)
C(11)	2625 (10)	4218 (9)	4591 (3)	34 (3)
C(12)	2502 (10)	5047 (9)	5019 (3)	35 (3)
C(13)	3190 (10)	1797 (9)	3943 (3)	36 (3)
C(14)	2749 (10)	3301 (10)	3677 (3)	37 (3)
C(15)	2425 (10)	5917 (10)	5943 (3)	40 (3)
C(16)	2014 (11)	7435 (10)	5677 (3)	41 (3)
C(17)	2584 (11)	5614 (11)	6482 (3)	55 (4)
C(18)	1578 (11)	9270 (10)	5894 (3)	56 (4)
C(19)	3756 (20)	-3 (15)	3081 (4)	117 (7)
C(20)	2984 (32)	1475 (15)	2839 (4)	254 (14)
Cl	-603 (3)	8267 (3)	2700 (1)	52 (1)
O(1)	-210 (10)	7861 (8)	3204 (2)	79 (3)
O(2)	-1470 (11)	10115 (8)	2628 (3)	111 (4)
O(3)	1134 (11)	7749 (10)	2412 (3)	113 (4)
O(4)	-1989 (12)	7368 (10)	2546 (3)	119 (4)



S(7) to C(20)] and **b** [molecule I, S(1) to C(10)] (Fig. 2). This is an unusual feature for organic radical salts. Within each stack, adjacent molecules are related by inversion centers and two different molecular overlap patterns and interplanar separations between the parallel molecules are found. The overlap patterns are very similar to those in the THF solvate (Heid *et al.*, 1985), where all the stacks are parallel. Interplanar distances (taking the least-squares plane through the six S atoms as the molecular plane) in stack I are 3.59 (8) and 3.63 (8) Å; in stack II both distances are 3.49 (5) Å. The dihedral angle between the molecules of the two stacks is 81 (1)°.

Along each type of stack there are a few S...S contact distances of the order of the sum of the van der Waals radii (3.7 Å). The shortest contacts in stack II are 3.592 (5) and 3.632 (5) Å between one pair of molecules and 3.761 (5) Å between the second pair. In stack I the shortest contact is 3.799 (5) Å. As usually found in charge-transfer salts of thio-substituted tetra-thiafulvalene, the stacks are arranged side by side

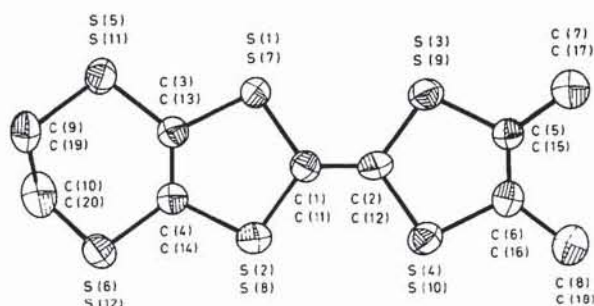


Fig. 1. The numbering scheme in the two independent DIMET molecules. Upper labels refer to species I, lower labels to species II. Thermal ellipsoids (50% probability) are drawn for I.

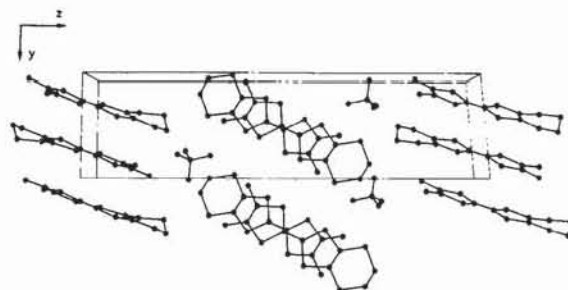


Fig. 2. Perspective projection of the structure along a ( $y = b \sin \alpha$ ,  $z = c \sin \beta$ ).

Table 2. Bond lengths (Å) and angles (°)

S(1)–C(1)	1.745 (7)	S(1)–C(3)	1.755 (8)
S(2)–C(1)	1.744 (8)	S(2)–C(4)	1.747 (7)
S(3)–C(2)	1.725 (8)	S(3)–C(5)	1.735 (7)
S(4)–C(2)	1.747 (7)	S(4)–C(6)	1.758 (8)
S(5)–C(3)	1.746 (7)	S(5)–C(9)	1.797 (9)
S(6)–C(4)	1.735 (8)	S(6)–C(10)	1.791 (8)
C(1)–C(2)	1.333 (10)	C(3)–C(4)	1.333 (10)
C(5)–C(6)	1.317 (10)	C(5)–C(7)	1.499 (11)
C(6)–C(8)	1.500 (9)	C(9)–C(10)	1.496 (10)
S(7)–C(11)	1.768 (7)	S(7)–C(13)	1.727 (7)
S(8)–C(11)	1.722 (7)	S(8)–C(14)	1.752 (8)
S(9)–C(12)	1.723 (7)	S(9)–C(15)	1.763 (8)
S(10)–C(12)	1.746 (7)	S(10)–C(16)	1.724 (8)
S(11)–C(13)	1.761 (7)	S(11)–C(19)	1.749 (11)
S(12)–C(14)	1.733 (7)	S(12)–C(20)	1.752 (12)
C(11)–C(12)	1.333 (10)	C(13)–C(14)	1.325 (10)
C(15)–C(16)	1.333 (11)	C(15)–C(17)	1.467 (10)
C(16)–C(18)	1.521 (11)	C(19)–C(20)	1.298 (16)
Cl–O(1)	1.405 (6)	Cl–O(2)	1.419 (6)
Cl–O(3)	1.404 (7)	Cl–O(4)	1.416 (9)
C(1)–S(1)–C(3)	95.8 (3)	C(1)–S(2)–C(4)	95.9 (3)
C(2)–S(3)–C(5)	96.6 (3)	C(2)–S(4)–C(6)	95.7 (3)
C(3)–S(5)–C(9)	100.6 (4)	C(4)–S(6)–C(10)	100.7 (4)
S(1)–C(1)–S(2)	114.0 (4)	S(1)–C(1)–C(2)	122.3 (6)
S(2)–C(1)–C(2)	123.7 (5)	S(3)–C(2)–S(4)	113.6 (4)
S(3)–C(2)–C(1)	124.0 (5)	S(4)–C(2)–C(1)	122.4 (6)
S(1)–C(3)–S(5)	113.4 (4)	S(1)–C(3)–C(4)	116.9 (5)
S(5)–C(3)–C(4)	129.7 (6)	S(2)–C(4)–S(6)	114.7 (4)
S(2)–C(4)–C(3)	117.2 (6)	S(6)–C(4)–C(3)	128.1 (5)
S(3)–C(5)–C(6)	117.4 (6)	S(3)–C(5)–C(7)	116.0 (5)
C(6)–C(5)–C(7)	126.6 (6)	S(4)–C(6)–C(5)	116.7 (5)
S(4)–C(6)–C(8)	114.8 (5)	C(5)–C(6)–C(8)	128.5 (7)
S(5)–C(9)–C(10)	115.6 (6)	S(6)–C(10)–C(9)	113.7 (5)
C(11)–S(7)–C(13)	94.7 (3)	C(11)–S(8)–C(14)	96.3 (3)
C(12)–S(9)–C(15)	96.7 (3)	C(12)–S(10)–C(16)	95.8 (4)
C(13)–S(11)–C(19)	102.1 (5)	C(14)–S(12)–C(20)	101.3 (5)
S(7)–C(11)–S(8)	114.0 (4)	S(7)–C(11)–C(12)	120.8 (6)
S(8)–C(11)–C(12)	125.2 (5)	S(9)–C(12)–S(10)	113.8 (4)
S(9)–C(12)–C(11)	124.4 (6)	S(10)–C(12)–C(11)	121.8 (6)
S(7)–C(13)–S(11)	113.5 (4)	S(7)–C(13)–C(14)	119.1 (6)
S(11)–C(13)–C(14)	127.3 (6)	S(8)–C(14)–S(12)	114.4 (4)
S(8)–C(14)–C(13)	115.8 (6)	S(12)–C(14)–C(13)	129.8 (6)
S(9)–C(15)–C(16)	114.9 (6)	S(9)–C(15)–C(17)	115.4 (6)
C(16)–C(15)–C(17)	129.7 (7)	S(10)–C(16)–C(15)	118.8 (6)
S(10)–C(16)–C(18)	116.4 (5)	C(15)–C(16)–C(18)	124.8 (7)
S(11)–C(19)–C(20)	127.1 (9)	S(12)–C(20)–C(19)	128.4 (11)
O(1)–C(1)–O(2)	109.9 (4)	O(1)–Cl–O(3)	111.2 (4)
O(2)–Cl–O(3)	109.7 (5)	O(1)–Cl–O(4)	108.5 (4)
O(2)–Cl–O(4)	107.8 (4)	O(3)–Cl–O(4)	109.6 (5)

perpendicular to the long molecular axis. Some short interstack S...S contacts result from this sheet-like arrangement, leading to a more or less two-dimensional character. In the present case the shortest interstack S...S contacts are 3.771 (5) Å in the sheet of molecules I and 3.647 (5) Å in the sheet of molecules II. Shorter contacts occur in the THF solvate (Heid *et al.*, 1985), the shortest one being 3.535 (8) Å.

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