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The Structure of Di(3,3′,4,4′-tetramethyl-2,2′,5,5′-tetraselenafulvalenium) Pentafluorosilicate,* $(C_{10}H_{12}Se_4)_2SiF_5$ at 293 and 125 K

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Abstract. $(TMTSF)_2SiF_5$: $M_r = 1019{\cdot}18$, triclinic, $P\bar{1}$, $Z = 1$, $F(000) = 475$. At 293 K: $a = 7{\cdot}289\,(2)$, $b = 7{\cdot}715\,(2)$, $c = 13{\cdot}548\,(4)$ Å, $\alpha = 83{\cdot}53\,(2)$, $\beta = 86{\cdot}20\,(3)$, $\gamma = 70{\cdot}84\,(2)^\circ$, $V = 714{\cdot}1\,(4)$ Å^3, $D_x = 2{\cdot}370$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 102{\cdot}1$ cm^{-1}, $R(F) = 0{\cdot}051$, $R_w = 0{\cdot}032$, $S = 1{\cdot}725$ for 2951 reflections. At 125 K: $a = 7{\cdot}122\,(2)$, $b = 7{\cdot}682\,(1)$, $c = 13{\cdot}495\,(3)$ Å, $\alpha = 83{\cdot}72\,(2)$, $\beta = 86{\cdot}90\,(2)$, $\gamma = 70{\cdot}03\,(2)^\circ$, $V = 690{\cdot}0\,(2)$ Å^3, $D_x = 2{\cdot}452$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 105{\cdot}8$ cm^{-1}, $R(F) = 0{\cdot}045$, $R_w = 0{\cdot}024$, $S = 1{\cdot}640$ for 3969 reflections. No structural phase transition is observed between room temperature and 125 K. The structure is isomorphous with other highly electrically conducting $(TMTSF)_2X$ (X = monovalent anion) salts. The SiF_5^- ion is disordered at both temperatures. This report represents the first structural study of a 2:1 TMTSF salt containing an anion that has a geometry intermediate between octahedral and tetrahedral.

Introduction. A considerable number of structures of electrically conducting and superconducting TMTSF salts (TMTSF = tetramethyltetraselenafulvalene) have been reported in the literature. Many of these have been of the type $(TMTSF)_2{}^+.MX_6{}^-$ ($MX_6{}^- = PF_6{}^-$, $AsF_6{}^-$, $TaF_6{}^-$) and $(TMTSF)_2{}^+.MX_4{}^-$ ($MX_4{}^- = BF_4{}^-$, $ClO_4{}^-$, $BrO_4{}^-$, $ReO_4{}^-$, $FSO_3{}^-$) (Thorup, Rindorf, Soling, Johannsen, Mortensen & Bechgaard, 1983), and all these structures are isomorphous, containing positively charged TMTSF sheets that are interconnected through short Se—Se contacts, with the anions located between the sheets. No salts containing an $MX_5{}^-$ anion have been reported thus far. Since the pentafluorosilicate ($SiF_5{}^-$) salt has a geometry intermediate between $MX_4{}^-$ and $MX_6{}^-$ it was decided to determine the crystal structure at both room and low temperature. The electrical properties are, as yet, unknown and the structure is described below.

Experimental. Crystals prepared by electrolytic oxidation of TMTSF in 1,1,2-trichloroethane solution, in presence of (n-Bu_4N)(SiF_5). Syntex $P2_1$ automated diffractometer with graphite monochromator and a cold-stream device that allows crystal to be cooled to 125 K. At room temperature 4497 reflections including 230 Friedel pairs and at 125 K 7055 reflections including 2033 Friedel pairs. Unit-cell dimensions, in both cases, determined from least-squares refinement of setting angles of 25 reflections in 2θ range 15–20°. Further information about data collection and crystal parameters are given in Table 1. Intensities corrected for Lorentz and polarization factors and absorption. Latter correction used measured crystal dimensions and eight faces that bounded the crystal. Intensities of equivalent reflections averaged, $R_{\text{int}} = 0{\cdot}015$. A starting model was easily obtained by taking the parameters for the four Se

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* Alternative nomenclature: di(4,4′,5,5′-tetramethyl-2,2′-bi-1,3-diselenolyliden)ium pentafluorosilicate.

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Table 1. *Data collection and crystal parameters*

Crystal size (mm)	0·045 × 0·08 × 0·42	
Scan range (°)	2·4	
Scan rate (°min^{-1})	1·95–11·72	
Total background/scan time	0·5	
Range of 2θ (°)	3–60 (293 K); 3–65 (125 K)	
Check reflections; decay	$1\bar{1}\bar{4}$, $11\bar{5}$, 133; none	
Frequency of checks	After every 45 reflections	
Function minimized in least-squares refinement	$\sum w(\lvert F_o - F_c \rvert)$, $w = 1/\sigma(F_o)$	
T (K)	293 (1)	125 (3)
Range of h, k, l	$h = 0$–10	$h = 0$–10
	$k = -9$–10	$k = -10$–11
	$l = -18$–19	$l = -20$–20
Number of unique reflections measured	4267	5022
Number of reflections with $I > 2\sigma(I)$	2951	3969
Max. transmission coefficient	0·7797	0·7763
Min. transmission coefficient	0·6969	0·6902

and ten C atoms from the $(TMTSF)_2BF_4$ structure (Kobayashi, Kobayashi, Saito & Inokuchi, 1983), all the $(TMTSF)_2X$ structures being isomorphous. Si is located at 0,0,0 in analogy with B of BF_4. This model worked so well, in fact, that it converged after only a few cycles of least-squares refinement with isotropic thermal parameters to $R_w = 0{\cdot}12$ (293 K) and 0·10 (125 K), although none of the atoms of interest, *viz* fluorine and hydrogen, had been included. Successive difference electron density maps and full-matrix least-squares refinement cycles led to locations for all atoms including hydrogen. $\sigma(F_o) = 1/(2F_o)[\sigma_o(F_o^2) + (0{\cdot}02 \times F_o^2)^2]^{1/2}$ with $\sigma_o(F_o^2)$ based on counting statistics. Anisotropic parameters for all non-hydrogen atoms, hydrogens isotropic ($B = 1{\cdot}9$ Å^2 at 125 K, $B = 6{\cdot}0$ Å^2 at 293 K). At 125 K highest peak in final difference map 1·07 e Å^{-3} located near C(9). At 293 K highest residual peak (1·09 e Å^{-3}) located near Se(1). Lowest values in difference maps $-1{\cdot}0$ e Å^{-3} at both temperatures. Largest Δ/σ for non-hydrogen atoms 0·10 at 125 K, 0·39 at 293 K. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final positional parameters (non-hydrogen atoms) for the structure at 125 K are listed in Table 2, and relevant bond distances and angles are given in Table 3. The arrangement and the numbering of the atoms in TMTSF is shown in Fig. 1.*

Discussion. The final model used to describe the disorder of the anion is important and is described as follows: the SiF_5^- ion lies on an inversion center and since the ion is not centrosymmetric – its ideal symmetry is a trigonal bipyramid – it must be

Table 2. *Atomic parameters for* $(TMTSF)_2SiF_5$, $T = 125$ K

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2 × 10^4)
Se(1)	0·69849 (5)	0·66278 (4)	0·38529 (2)	146 (1)
Se(2)	0·83967 (5)	0·25042 (4)	0·48807 (2)	141 (1)
Se(3)	0·77220 (5)	0·41519 (4)	0·71650 (2)	138 (1)
Se(4)	0·62264 (5)	0·82785 (4)	0·61275 (2)	140 (1)
C(1)	0·7480 (5)	0·5052 (4)	0·5055 (2)	140 (10)
C(2)	0·7761 (5)	0·4636 (4)	0·3029 (2)	162 (11)
C(3)	0·8381 (5)	0·2888 (4)	0·3462 (2)	145 (10)
C(4)	0·7645 (6)	0·5233 (5)	0·1921 (3)	201 (13)
C(5)	0·9061 (6)	0·1124 (5)	0·2962 (3)	194 (13)
C(6)	0·7173 (5)	0·5722 (4)	0·5963 (2)	136 (10)
C(7)	0·6888 (5)	0·6151 (4)	0·7982 (2)	173 (11)
C(8)	0·6235 (5)	0·7905 (4)	0·7548 (2)	162 (10)
C(9)	0·6990 (7)	0·5596 (6)	0·9093 (2)	231 (13)
C(10)	0·5496 (7)	0·9647 (5)	0·8069 (3)	226 (13)
Si(1)	0·0000	0·0000	0·0000	282 (5)
F(1)	0·0512 (6)	−0·1195 (4)	0·1084 (2)	819 (15)
F(2)	0·0307 (10)	0·1714 (6)	0·0477 (3)	489 (22)
F(3)	0·1909 (10)	−0·1484 (7)	−0·0498 (4)	546 (24)
F(4)	−0·2029 (14)	−0·0173 (22)	0·0115 (6)	2127 (77)

Table 3. *Bond distances* (Å) *and angles* (°)

	293 K	125 K		293 K	125 K
Se(1)–C(1)	1·883 (6)	1·889 (6)	C(6)–C(1)–Se(1)	122·0 (4)	122·4 (2)
–C(2)	1·895 (6)	1·900 (3)	–Se(2)	124·4 (4)	123·5 (2)
Se(2)–C(1)	1·878 (6)	1·878 (3)	C(1)–Se(1)–C(2)	94·5 (3)	94·3 (1)
–C(3)	1·893 (5)	1·905 (3)	Se(1)–C(2)–C(3)	118·6 (4)	118·7 (4)
Se(3)–C(6)	1·902 (6)	1·887 (3)	–C(4)	115·4 (5)	114·7 (2)
–C(7)	1·892 (6)	1·898 (3)	C(3)–C(2)–C(4)	126·0 (6)	126·6 (3)
Se(4)–C(6)	1·877 (6)	1·880 (3)	C(2)–C(3)–Se(2)	118·3 (4)	118·5 (2)
–C(8)	1·907 (6)	1·907 (3)	–C(5)	126·3 (6)	127·6 (3)
C(1)–C(6)	1·334 (7)	1·358 (4)	Se(2)–C(3)–C(5)	115·4 (5)	113·8 (2)
C(2)–C(3)	1·348 (8)	1·339 (4)	C(3)–Se(2)–C(1)	94·9 (2)	94·4 (1)
C(2)–C(4)	1·494 (9)	1·513 (4)	Se(2)–C(1)–Se(1)	113·6 (3)	114·1 (2)
C(3)–C(5)	1·491 (9)	1·497 (5)	C(1)–C(6)–Se(3)	122·2 (4)	122·5 (2)
C(7)–C(8)	1·351 (8)	1·343 (4)	–Se(4)	124·3 (4)	123·1 (2)
–C(9)	1·506 (9)	1·513 (4)	C(6)–Se(3)–C(7)	94·5 (2)	94·0 (1)
C(8)–C(10)	1·491 (9)	1·499 (4)	Se(3)–C(7)–C(8)	119·1 (4)	119·1 (2)
Si–F(1)	1·574 (5)	1·629 (2)	–C(9)	116·6 (5)	115·5 (2)
F(2)	1·60 (1)	1·610 (4)	C(8)–C(7)–C(9)	124·3 (6)	125·4 (3)
F(3)	1·65 (2)	1·615 (5)	C(7)–C(8)–Se(4)	117·8 (4)	118·2 (2)
F(4)	1·60 (2)	1·494 (8)	–C(10)	126·6 (6)	126·6 (3)
F(5)	1·54 (2)		Se(4)–C(8)–C(10)	115·6 (5)	115·2 (2)
			C(8)–Se(4)–C(6)	95·0 (2)	94·2 (1)
Se(1)–Se(2^{i})	4·053 (2)	3·981 (1)	Se(3)–C(6)–Se(4)	113·5 (3)	114·4 (2)
Se(1)–Se(3^{i})	4·037 (2)	3·941 (1)	F(1)–Si–F(2)	92·5 (4)	91·8 (2)
Se(1)–Se(3^{ii})	3·876 (2)	3·812 (1)	–F(3)	93·7 (6)	90·7 (2)
Se(1)–Se(2^{ii})	4·137 (2)	4·067 (1)	–F(4)	92·7 (6)	92·5 (4)
Se(2)–Se(4^{i})	3·972 (2)	3·882 (1)	–F(5)	102·2 (9)	
Se(2)–Se(4^{ii})	3·931 (2)	3·863 (1)	F(2)–Si–F(3)	78·8 (8)	118·7 (3)
Se(1)–Se(4^{iii})	3·924 (1)	3·801 (1)	–F(4)	45·2 (8)	116·8 (5)
Se(4)–Se(4^{iii})	3·965 (2)	3·869 (1)	–F(5)	47·1 (8)	
Se(2)–Se(2^{iv})	3·848 (2)	3·732 (1)	F(3)–Si–F(4)	33·9 (7)	124·4 (5)
Se(2)–Se(4^{v})	4·189 (1)	4·208 (1)	–F(5)	58·2 (9)	
Se(3)–F(1)	3·211 (6)	3·085 (3)	F(4)–Si–F(5)	89·1 (11)	
Si–C(5^{vi})	4·179 (8)	4·153 (4)			
Si–C(9^{vii})	4·260 (8)	4·173 (4)			
Si–C(10)	4·371 (8)	4·336 (4)			
F(2)–H(4*C*)	2·44 (9)				
F(4)–H(5*A*)	2·31 (9)				
F(4)–H(4*C*)	2·34 (9)				
F(1)–H(9*B*)		2·52 (4)			
F(2)–H(9*C*)		2·49 (5)			
F(2)–H(4*C*)		2·54 (5)			
F(3)–H(9*B*)		2·51 (5)			

Symmetry operations: (i) = $1-x, 1-y, 1-z$; (ii) = $2-x, 1-y, 1-z$; (iii) = $1-x, 2-y, 1-z$; (iv) = $2-x, -y, 1-z$; (v) = $x, -1+y, z$; (vi) = $1+x, y, z$; (vii) = $1+x, y, 1+z$.

The first nine Se–Se distances are in the sequence d_1–d_9. Se(3)–F(1) is d_{10}. The last Se–Se distance is d_{11}.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters at 125 K, all atom parameters at 293 K and least-squares-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39469 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

disordered. For the room-temperature structure several models were tried, all of which resulted in the same values for the discrepancy factors, and all of which had in common two full axial F atoms [F(1) and F(1′)] and a more or less homogeneously distributed ring of electron density around Si in the equatorial plane. In the model reported here there are four fluorine atoms on this ring, for which the x, y and z coordinates and their multiplicity factors (M) were refined, but not the temperature factors (B), since simultaneous refinement of M and B led to high values for the correlation factors. The final multiplicities were 0·503 for F(2), 0·426 for F(3), 0·279 for F(4) and 0·337 for F(5). It should be noted that these multiplicities add to a value close to 1·5, as should ideally be the case. The low-temperature structure is much more well defined, the thermal motion of the atoms is much lower, as are the e.s.d.'s in distances and angles. In this case it was possible to refine the anion as a simple superposition of two orientations, as is the case for $(TMTSF)_2AsF_6$ (Williams, Beno, Sullivan, Banovetz, Braam, Blackman, Carlson, Greer, Loesing & Carneiro, 1983) which have a common axis F(1)—Si—F(1′) and which are rotated through an angle of 180°. The only unusual aspect of the anion is that F(4) displays very high thermal motion (see Fig. 2). A recent structure determination containing the SiF_5^- anion (Schomberg & Krebs, 1984) shows the same geometry for the anion and comparable Si—F distances.

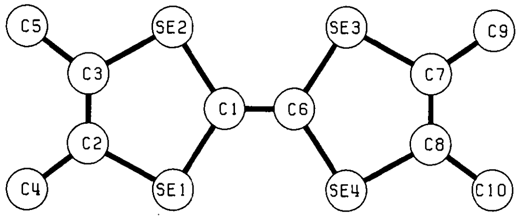

Fig. 1. Arrangement and numbering of atoms in the TMTSF donor.

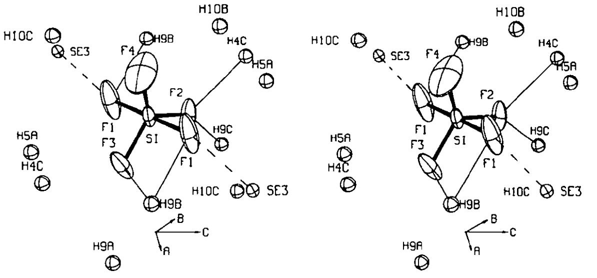

Fig. 2. The SiF_5^- anion in its cavity enclosed by methyl-group hydrogen atoms and a selenium atom.

The distances and angles for the low-temperature structure, especially those involving contacts between TMTSF and the anion, must be taken to be much more reliable than those at room temperature. The contacts between Se atoms that are responsible for forming the sheets of TMTSF molecules are very similar to those found in comparable $(TMTSF)_2X$ structures (Beno, Williams, Lee & Cowan, 1982). The short distance between Se(3) and F(1) is similarly found in these other structures (Beno, Williams, Lee & Cowan, 1982). In the present case it is 3·085 Å, much shorter than the sum of the van der Waals radii (1·9 Å for Se, 1·47 Å for F; Bondi, 1964). In addition there are some relatively short distances between methyl-group hydrogen atoms and fluorine atoms of the anion, which indicate the possibility of weak hydrogen-bond-like interactions (see Fig. 2). All these interactions together may be taken as being responsible for the unusual electrical properties often associated with anion-ordering transitions in this class of compounds. The mean separations between alternate TMTSF donors in the columns are: $D_1 = D_2 = 3{\cdot}560$ Å at 125 K, and $D_1 = 3{\cdot}644$, $D_2 = 3{\cdot}632$ Å at 293 K, indicating no dimerization.

The general conclusion of this determination is that the SiF_5^- anion yields a structure that is not significantly different, in terms of the correlations between anion size and the *intra*- and *inter*stack Se–Se distances (Williams, Beno, Sullivan, Banovetz, Braam, Blackman, Carlson, Greer & Loesing, 1983) from those containing MX_4^- or MX_6^- anions, and that the title compound does not exhibit a phase transition between room temperature and 125 K. The electrical properties are under investigation.

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