

**Di(4,4',5,5'-tetramethyl- $\Delta^{2,2'}$ -bi-1,3-diselenolyli-  
dium Trifluoromethanesulfonate,  
 $C_{21}H_{24}F_3O_3SSe_8$ , (TMTSF) $_2CF_3SO_3$**

BY HANS SOLING, GRETHE RINDORF AND NIELS THORUP

*Structural Chemistry Group, Chemistry Department B, Technical University of Denmark, DK-2800 Lyngby,  
Denmark*

(Received 23 November 1982; accepted 15 December 1982)

**Abstract.**  $M_r = 1045.2$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.333$  (3),  $b = 7.781$  (2),  $c = 13.799$  (3) Å,  $\alpha = 83.26$  (2),  $\beta = 85.72$  (3),  $\gamma = 71.18$  (3),  $Z = 1$ ,  $V = 739.5$  Å<sup>3</sup>,  $D_x = 2.35$ ,  $D_m = 2.34$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 9.86$  mm<sup>-1</sup>,  $F(000) = 489$ ,  $T = 295$  K. Final  $R = 0.054$  for 1040 unique reflections. A model with composite atoms (C,S) and (F,O) was refined for the  $CF_3SO_3$  molecule. There are no unusual distances or angles in the TMTSF molecule. Intermolecular distances are discussed.

**Introduction.** The physical properties of several members of the series (TMTSF) $_2X$ ,  $X = \text{ReO}_4$ ,  $\text{ClO}_4$ ,  $\text{BF}_4$ ,  $\text{PF}_6$ ,  $\text{AsF}_6$ , etc. have attracted much attention (Bechgaard, Jacobsen, Mortensen, Pedersen & Thorup, 1980; Bechgaard, 1982). This communication reports the results of a single-crystal X-ray study of the title compound [trivial name: di(2,3,6,7-tetramethyl-1,4,5,8-tetraselenafulvalenium) trifluoromethanesulfonate].

**Experimental.** Single crystals of (TMTSF) $_2CF_3SO_3$  provided by K. Bechgaard (Bechgaard, Carneiro, Rasmussen, Olsen, Rindorf, Jacobsen, Pedersen & Scott, 1981),  $D_m$  measured by flotation, crystal  $0.34 \times 0.020 \times 0.024$  mm, CAD-4 diffractometer, cell dimensions from 25 selected reflections,  $\omega$ -scan intensities ( $\Delta\omega = 1.00^\circ + 0.35^\circ \tan \theta$ ) of 7199 reflections  $0 < \theta < 28^\circ$ , control intensities checked every 4 h; Lp and absorption corrections (transmission 0.721 to 0.842); merging into a set of 3565 unique observations, ( $R_{\text{int}} = 0.030$ ), 1040 with  $|F_o|^2 > 3\sigma(|F_o|^2)$ ; space group  $P\bar{1}$  indicated by statistics; *SHELX* (Sheldrick, 1976), Fourier maps and full-matrix least-squares minimization of  $\sum w(\Delta F)^2$ ,  $\Delta F = |F_o| - |F_c|$ , treating  $CF_3SO_3$  as a composite (C,S) (F,O) $_3$  and ignoring H atoms; Se anisotropic, remainder isotropic; ultimate  $R = 0.054$ ,  $wR = 0.060$ ,  $w = 2.181/[\sigma^2(|F_o|) + 0.0004|F_o|^2]$ ; shift/error ratio  $< 0.02$ ; random extremes in final electron density map  $-1.0$  to  $1.4$  e Å<sup>-3</sup>; neutral-atom scattering factors and anomalous-dispersion corrections for Se from *International Tables for X-ray Crystallography* (1974), built-in values of *SHELX* for S, C, F and O; drawings made with *ORTEP* (Johnson, 1965).

**Discussion.** Fractional atomic coordinates and isotropic thermal parameters are given in Table 1.\*

The structure of (TMTSF) $_2CF_3SO_3$  is illustrated in Figs. 1 and 2. The bond lengths and angles are listed in Table 2. They are very similar to those found in other members of the isostructural series (Thorup, Rindorf, Soling & Bechgaard, 1981; Rindorf, Soling & Thorup, 1982; Soling, Rindorf & Thorup, 1982).

The overall symmetry of the TMTSF moiety is approximately *mmm*, the r.m.s. deviation of the non-H atoms from the TMTSF plane being 0.030 Å.

The cell volume of the present compound is the largest observed in any member of the series. The cell volume of (TMTSF) $_2X$  increases in the sequence  $X = \text{NO}_3$ ,  $\text{ClO}_4$ ,  $\text{ReO}_4$ ,  $\text{PF}_6$ ,  $\text{CF}_3\text{SO}_3$ , obviously in response to the spatial demands of  $X$ . The lengths of the intermolecular Se–Se contacts follow the same sequence except for Se(11,A)–Se(11,F) (Fig. 1). A closer inspection shows that the two other interstack

\* Lists of structure factors and anisotropic thermal parameters for Se have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38289 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ,  $\times 10^4$  for Se) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Se(1)	2887 (4)	3441 (4)	6138 (2)	425 (12)*
Se(2)	1711 (4)	7466 (4)	5120 (3)	416 (12)*
Se(11)	3637 (4)	1796 (4)	3930 (2)	423 (11)*
Se(12)	2410 (4)	5804 (4)	2894 (2)	409 (11)*
C(1)	2119 (29)	5419 (29)	6939 (15)	39 (5)
C(2)	1648 (28)	7103 (28)	6503 (14)	35 (5)
C(3)	2495 (26)	4956 (26)	4947 (14)	32 (5)
C(4)	1093 (36)	8875 (35)	7008 (19)	56 (9)
C(5)	2259 (37)	4782 (37)	8021 (20)	65 (10)
C(11)	3677 (29)	2155 (28)	2557 (14)	34 (5)
C(12)	3193 (30)	3829 (30)	2107 (15)	42 (6)
C(13)	2809 (26)	3298 (25)	4091 (14)	34 (5)
C(14)	3178 (33)	4418 (31)	1034 (17)	48 (7)
C(15)	4396 (38)	440 (38)	2055 (19)	66 (9)
C,S	788 (28)	572 (29)	-199 (15)	144 (6)
F,O(1)	531 (37)	2029 (35)	343 (18)	165 (9)
F,O(2)	206 (36)	1300 (35)	-1202 (19)	164 (10)
F,O(3)	2557 (44)	-948 (39)	-104 (20)	197 (11)

\* $U_{\text{eq}}$  (Hamilton, 1959).

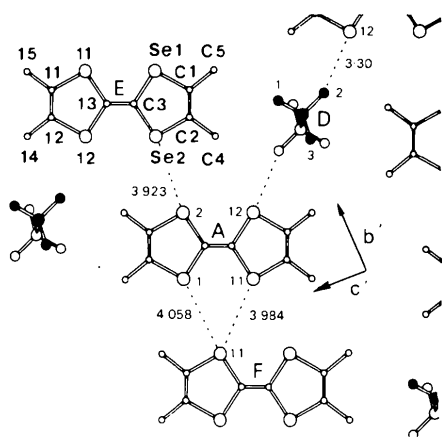


Fig. 1. View of the TMTSF molecule along the  $a$  axis with atom labels as in Tables 1 and 2.  $b'$  and  $c'$  are projections of the  $b$  and  $c$  axes. Intermolecular distances in Å; e.s.d.'s: Se–Se 0.008, Se–O 0.05 Å. The symmetry operations are:  $A(x,y,z)$ ,  $D$  (filled circles:  $x, 1+y, z$ ),  $E(-x, 2-y, 1-z)$  and  $F(1-x, -y, 1-z)$ .

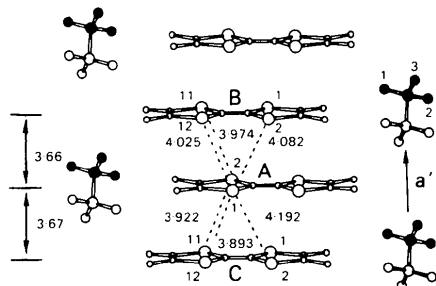


Fig. 2. Side view of stacks (tilted  $10^\circ$ ).  $a'$  is the projection of the  $a$  axis. Intermolecular Se–Se distances in Å; e.s.d.'s = 0.008 Å. The symmetry operations are:  $A(x,y,z)$ ,  $B(1-x, 1-y, 1-z)$  and  $C(-x, 1-y, 1-z)$ .

Table 2. Bond lengths (Å) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

The labelling of the atoms is shown in Fig. 1.

Se(1)–C(1)	1.912 (20)	Se(11)–C(11)	1.882 (18)	C(3)–C(13)	1.317 (21)
Se(1)–C(3)	1.890 (19)	Se(11)–C(13)	1.878 (18)	C(5)–C(1)–Se(1)	112.8 (16)
Se(2)–C(2)	1.895 (18)	Se(12)–C(12)	1.897 (20)	C(5)–C(1)–Se(1)	112.8 (16)
Se(2)–C(3)	1.889 (18)	Se(12)–C(13)	1.893 (18)	C(5)–C(1)–Se(1)	112.8 (16)
C(1)–C(2)	1.324 (25)	C(11)–C(12)	1.324 (24)	C(5)–C(1)–Se(1)	112.8 (16)
C(1)–C(5)	1.517 (32)	C(11)–C(15)	1.499 (31)	C(5)–C(1)–Se(1)	112.8 (16)
C(2)–C(4)	1.541 (30)	C(12)–C(14)	1.497 (29)	C(5)–C(1)–Se(1)	112.8 (16)
Se(2)–C(3)–C(13)	124.4 (13)	C(11)–C(12)–Se(12)	117.7 (15)	C(5)–C(1)–Se(1)	112.8 (16)
Se(1)–C(3)–C(13)	122.5 (12)	C(4)–C(2)–Se(2)	114.3 (16)	C(5)–C(1)–Se(1)	112.8 (16)
Se(11)–C(13)–C(3)	123.9 (13)	C(5)–C(1)–Se(1)	112.8 (16)	C(5)–C(1)–Se(1)	112.8 (16)
Se(12)–C(13)–C(3)	122.9 (13)	C(15)–C(11)–Se(11)	114.9 (19)	C(5)–C(1)–Se(1)	112.8 (16)
Se(1)–C(3)–Se(2)	113.1 (9)	C(14)–C(12)–Se(12)	113.5 (15)	C(5)–C(1)–Se(1)	112.8 (16)
Se(11)–C(13)–Se(12)	113.2 (9)	C(1)–C(2)–C(4)	126.5 (19)	C(5)–C(1)–Se(1)	112.8 (16)
C(2)–Se(2)–C(3)	94.8 (8)	C(2)–C(1)–C(5)	129.0 (20)	C(5)–C(1)–Se(1)	112.8 (16)
C(1)–Se(1)–C(3)	94.7 (8)	C(12)–C(11)–C(15)	124.9 (19)	C(5)–C(1)–Se(1)	112.8 (16)
C(11)–Se(11)–C(13)	94.4 (8)	C(11)–C(12)–C(14)	128.8 (19)	C(5)–C(1)–Se(1)	112.8 (16)
C(12)–Se(12)–C(13)	94.6 (8)	F,O(1)–C,S–F,O(2)	108.3 (20)	C(5)–C(1)–Se(1)	112.8 (16)
C(1)–C(2)–Se(2)	119.2 (15)	F,O(1)–C,S–F,O(3)	118.5 (22)	C(5)–C(1)–Se(1)	112.8 (16)
C(2)–C(1)–Se(1)	118.2 (15)	F,O(2)–C,S–F,O(3)	116.2 (20)	C(5)–C(1)–Se(1)	112.8 (16)
C(12)–C(11)–Se(11)	120.1 (15)			C(5)–C(1)–Se(1)	112.8 (16)

contacts shown are, by far, more strongly connected with the cell volume than the intrastack Se–Se contacts, shown in Fig. 2.

Since the staggered  $\text{CF}_3\text{SO}_3^-$  ion must be placed in the cavity between the  $\text{TMTSF}^{1/2+}$  ions with its pseudocenter at or very near the crystallographic center of inversion it is not possible to resolve the  $\text{CF}_3\text{SO}_3$  group into eight individual atoms. Only a model with composite atoms (C,S) and (F,O) refined properly. The (C,S)–(C,S) distance, 1.698 (34) Å, given in Table 2, is the distance between the center of gravity of one composite (C,S) atom and its centrosymmetrically related mate. Studies of a series of hydrated trifluoromethanesulfonic acids (Spencer & Lundgren, 1973; Delaplane, Lundgren & Olovsson, 1975*a, b*) give an average C–S bond length of 1.819 (8) Å. The significantly shorter (C,S)–(C,S) distance found in the present work is explained by assuming that the S atom is slightly closer to the crystallographic center of inversion than the C atom. The large values of the thermal parameters of the composite atoms support this interpretation. The distances (C,S)–(F,O) and the angles (F,O)–(C,S)–(F,O)' have the same average values, 1.44 (4) Å and  $114 (5)^\circ$ , as found in the  $\text{SO}_3$  group of the trifluoromethanesulfonic acid hydrates mentioned above.

This work has been supported by The Danish Natural Science Research Council.

## References

- BECHGAARD, K. (1982). *Mol. Cryst. Liq. Cryst.* **79**, 1–13.
- BECHGAARD, K., CARNEIRO, K., RASMUSSEN, F. B., OLSEN, M., RINDORF, G., JACOBSEN, C. S., PEDERSEN, H. J. & SCOTT, J. C. (1981). *J. Am. Chem. Soc.* **103**, 2440–2442.
- BECHGAARD, K., JACOBSEN, C. S., MORTENSEN, K., PEDERSEN, H. J. & THORUP, N. (1980). *Solid State Commun.* **33**, 1119–1125.
- DELAPLANE, R. G., LUNDGREN, J.-O. & OLOVSSON, I. (1975*a*). *Acta Cryst.* **B31**, 2202–2207.
- DELAPLANE, R. G., LUNDGREN, J.-O. & OLOVSSON, I. (1975*b*). *Acta Cryst.* **B31**, 2208–2213.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- RINDORF, G., SOLING, H. & THORUP, N. (1982). *Acta Cryst.* **B38**, 2805–2808.
- SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SOLING, H., RINDORF, G. & THORUP, N. (1982). *Cryst. Struct. Commun.* In the press.
- SPENCER, J. B. & LUNDGREN, J.-O. (1973). *Acta Cryst.* **B29**, 1923–1928.
- THORUP, N., RINDORF, G., SOLING, H. & BECHGAARD, K. (1981). *Acta Cryst.* **B37**, 1236–1240.