

## Structure of the Charge-Transfer Salt 2,2',5,5'-Tetraselenafulvalene–7,7,8,8-Tetracyano-*p*-quinodimethane (TSeF–TCNQ)

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### Abstract

2,2',5,5'-Tetraselenafulvalene–7,7,8,8-tetracyano-*p*-quinodimethane (1/1), TSeF–TCNQ, C<sub>6</sub>H<sub>4</sub>Se<sub>4</sub>·C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>,  $M_r = 596.13$ , monoclinic,  $P2_1/c$ ,  $a = 12.5048$  (4),  $b = 3.8724$  (2),  $c = 18.5041$  (7) Å,  $\beta = 104.131$  (3)°,  $V = 868.9$  Å<sup>3</sup>,  $T = 297$  K,  $Z = 2$ ,  $F(000) = 560$ ,  $D_x = 2.28$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 115.7$  cm<sup>-1</sup>,  $R(F) = 0.018$ ,  $wR(F) = 0.030$  for 1393 unique reflections with  $\sigma(F^2) > 3F^2$ . The crystals are isostructural with the corresponding tetrathiafulvalene salt, TTF–TCNQ, with both cations and anions arranged in segregated stacks parallel to **b**. There are Se···N distances of 3.17 and 3.18 Å along **a**, between cation and anion stacks, and H···H distances of 2.58 Å along **c**, between neighboring cation stacks, all shorter than the corresponding distances in TTF–TCNQ.

### 1. Introduction

The well known charge-transfer salt TTF–TCNQ, tetrathiafulvalene–tetracyano-*p*-quinodimethane, crystallizes in the segregated stack structure known to be necessary for conduction in organic salts (Kistenmacher, Phillips & Cowan, 1974). A variety of analogs have since been synthesized and studied by many workers, with a view to modifying the electronic properties while maintaining the segregated stack structure found in TTF–TCNQ. The crystal structure analysis of the simple selenium analog TSeF–TCNQ, which is presented here, was carried out in conjunction with early work in these laboratories which focused on the synthesis of TSeF–TCNQ and on the detailed study of physical properties of TSeF–TCNQ/TTF–TCNQ systems (Engler, Scott, Etemad, Penney & Patel, 1977; Etemad, Engler, Schultz, Penney & Scott, 1978).

### 2. Experimental

Crystals of the title compound, in the form of black needles elongated along **b**, were grown from hot

acetonitrile solutions and supplied to us by E. M. Engler and B. A. Scott. The majority of the crystals were twinned about a plane perpendicular to [100], with varying amounts of the two components present. However, a single crystal was selected, 0.232 mm long, and bounded by {001} faces at 0.012 mm, and by (100) and (10 $\bar{1}$ ) faces at 0.0255 mm from a central axis. Cell constants were determined by a least-squares procedure using the diffractometer coordinates of 25 reflections ( $130 < 2\theta < 140^\circ$ ), with  $\lambda(\text{Cu K}\alpha_1)$  taken as 1.54051 Å.  $2\theta_0$  was determined separately. The standard deviations quoted in the *Abstract* are those obtained from the inverse matrix in the least-squares method and are admittedly liable to be lower than the true uncertainties. Intensities of reflections to  $2\theta(\text{Cu}) = 154^\circ$  were measured by the  $\theta/2\theta$  scan technique on a CAD-4 diffractometer for the quadrant  $h, k, \pm l$ . Data from the  $-h, k, \pm l$  quadrant to  $2\theta(\text{Cu}) = 130^\circ$  were also measured. The standard CAD-4 data-collection algorithm was used, with scan width  $(2\theta) = (0.8 + \tan\theta)^\circ$ , initial scan speed =  $1^\circ(2\theta)\text{ min}^{-1}$ . Reflections with 20–5000 counts on the initial scan were rescanned with a scan rate chosen to give an integrated intensity of ~5000 counts. Data were corrected for absorption, with transmission factors 0.43–0.77, and for the decrease of intensity of the standard reflections (112,  $\bar{1}12$ ,  $\bar{1}1\bar{2}$ ) of ~1% for every 1000 reflections. A total of 3966 reflections, including duplicates, were measured, and on averaging equivalent reflections ( $R = 0.03$ ), 1393 of the 1810 unique intensities had  $I > 3\sigma(I)$  and were used in structure refinements.

Although this crystal is in fact isostructural with TTF–TCNQ, the structure was determined independently by heavy-atom methods. Local versions of the Brookhaven set of crystallographic programs were used. In the final refinements, H atoms were set initially in calculated positions, and their coordinates and isotropic temperature factors were allowed to vary. All other atoms were refined with anisotropic temperature factors. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , with weights  $w = 1/\sigma^2(F)$ , where  $\sigma(F) = \sigma(F^2)/2F$  and  $\sigma(F^2) = [\sigma_{\text{counting}}^2 + (0.06F^2)^2]$ . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). An isotropic secondary-extinction correction (Larson, 1970; Coppens & Hamilton, 1970) was

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Table 1. *Experimental details*

Crystal data	
Chemical formula	C <sub>6</sub> H <sub>4</sub> Se <sub>4</sub> .C <sub>12</sub> H <sub>4</sub> N <sub>4</sub>
Chemical formula weight	596.13
Cell setting	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	12.5048 (4)
<i>b</i> (Å)	3.8724 (2)
<i>c</i> (Å)	18.5041 (7)
$\beta$ (°)	104.131 (3)
<i>V</i> (Å <sup>3</sup> )	868.9
<i>Z</i>	2
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	2.28
Radiation type	Cu <i>K</i> $\alpha$
Wavelength (Å)	1.54184
No. of reflections for cell parameters	25
$\theta$ range (°)	65–70
$\mu$ (mm <sup>-1</sup> )	11.57
Temperature (K)	297
Crystal form	Needle
Crystal size (mm)	0.232 × 0.051 × 0.024
Crystal color	Black
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$
Absorption correction	Gaussian integration
<i>T</i> <sub>min</sub>	0.43
<i>T</i> <sub>max</sub>	0.77
No. of measured reflections	3966
No. of independent reflections	1810
No. of observed reflections	1393
Criterion for observed reflections	<i>I</i> > 3 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.03
$\theta$ <sub>max</sub> (°)	77
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 15 0 → <i>k</i> → 4 –22 → <i>l</i> → 22
No. of standard reflections	3
Frequency of standard reflections	1000 reflections
Intensity decay (%)	1
Refinement	
Refinement on	<i>F</i>
<i>R</i>	0.0176
<i>wR</i>	0.0296
<i>S</i>	0.83
No. of reflections used in refinement	1393
No. of parameters used	135
H-atom treatment	All parameters refined
Weighting scheme	$w = 1/\sigma^2(F)$
( $\Delta/\sigma$ ) <sub>max</sub>	0.2 $\sigma$
$\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.4
$\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	–
Extinction method	Secondary
Extinction coefficient	$g = 0.32(2) \times 10^4 \text{ rad}^{-1}$
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

included. The value of the extinction parameter *g* refined to 0.32(2) × 10<sup>4</sup> rad<sup>-1</sup>, with the largest extinction correction to *F*<sup>2</sup> being about 30% for the 002 and 012 reflections. The final agreement indices  $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$  and  $wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$  were 0.0176 and 0.0296, respectively, based on 1393 observations and 135 variable parameters. The maximum parameter shift in the final cycle was 0.2 $\sigma$ . The value of *R* in a calculation in which all 1810 reflections were included was 0.030. The most prominent

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)*

$B_{\text{eq}} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_i.a_j.$				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Se(1)	–0.10218 (2)	–0.19176 (9)	0.08120 (2)	1.95 (1)
Se(2)	0.15436 (2)	–0.18845 (10)	0.08874 (2)	1.96 (1)
N(1)	0.3871 (2)	0.5828 (10)	0.1897 (2)	3.26 (14)
N(2)	0.7429 (2)	0.6146 (9)	0.1872 (1)	2.83 (14)
C(1)	–0.0012 (3)	–0.3562 (9)	0.1667 (2)	2.28 (14)
C(2)	0.1049 (3)	–0.3555 (9)	0.1698 (2)	2.35 (14)
C(3)	0.0107 (2)	–0.0771 (9)	0.0342 (1)	1.74 (11)
C(4)	0.4591 (2)	0.5029 (8)	0.1650 (1)	1.96 (14)
C(5)	0.6545 (2)	0.5206 (8)	0.1645 (1)	2.01 (14)
C(6)	0.5442 (2)	0.4046 (9)	0.1309 (1)	1.67 (13)
C(7)	0.5229 (2)	0.2022 (8)	0.0661 (1)	1.51 (13)
C(8)	0.4132 (2)	0.0883 (8)	0.0315 (1)	1.71 (11)
C(9)	0.6083 (2)	0.1045 (8)	0.0311 (1)	1.73 (11)
H(1)	–0.036 (3)	–0.460 (11)	0.205 (2)	3.4 (1)
H(2)	0.164 (3)	–0.454 (12)	0.208 (2)	3.9 (1)
H(8)	0.358 (3)	0.130 (10)	0.056 (2)	2.5 (1)
H(9)	0.666 (3)	0.166 (11)	0.057 (2)	3.9 (1)

features in a final difference Fourier map were peaks of 0.3–0.4 e Å<sup>-3</sup> (30–40% of H) in most of the bonding regions between atoms.

Experimental details are summarized in Table 1. Final positional parameters, with *B* values equivalent to the anisotropic  $\beta$  values, are presented in Table 2.†

### 3. Discussion

Crystal packing viewed down [010] is shown in Fig. 1. For both TSeF–TCNQ and TTF–TCNQ, cations and anions each lie on crystallographic centers of symmetry and are arranged in separate stacks along the short **b** axis. The long axes of both cations and anions lie along **c**\*. On substitution of S by Se, the unit-cell dimensions increase by 0.20, 0.05 and 0.03 Å along **a**, **b** and **c**, respectively, while the  $\beta$  angle opens out by 0.3°. Contacts between like ions occur along the relatively constant **b** and **c** directions, while contacts along **a** occur between unlike ions.

The geometries of the TSeF cation and of the TCNQ anion are shown in Fig. 2. In Table 3 we compare structural features of TTF–TCNQ and TSeF–TCNQ. The geometry of the TSeF cation is very similar to that of TTF in TTF–TCNQ, the increase in chalcogen–carbon distances occurring without change in the X–C–X angle (X = S or Se), but with an increase in the X–C–C angle from 117.7 to 119.8°. The central C(3)–C(3') double-bond distance in the TSeF cation is 0.04 Å longer than the average distance for the corresponding bond in neutral TSeF (Weidenborner, La Placa & Engler, 1977), while the Se–C bond distances in the TSeF cation are on average 0.02 Å shorter than in

† Lists of structure factors and anisotropic thermal parameters have been deposited with the IUCr (Reference: CR0487). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

neutral TSeF. These differences are consistent with similar trends observed in TTF geometry as the charge on the molecule is increased (La Placa, Weidenborner, Scott & Corfield, 1975). The H atoms in the TSeF cation of the present structure lie in the best plane through the central part of the molecule and are bent 0.09 Å out of the plane through Se(1), Se(2), C(1) and C(2).

The TCNQ anion in the present study has a geometry indistinguishable from that in the TTF-TCNQ salt. Deviations of atoms from the best unweighted least-squares plane differ by no more than 0.006 Å from the corresponding distances in TTF-TCNQ.

Table 3 shows that substitution of Se for S in TTF-TCNQ hardly changes the tilt angles or the perpendicular distances of the molecular planes. However, in spite of the increase in chalcogen atomic radius, Se...N contacts between neighboring cation stacks and anion stacks are slightly shorter than S...N contacts in TTF-TCNQ and are much less than the sum of the van der Waals radii for Se and N, which is 3.45 Å (Bondi, 1964). Longer Se...N distances of 3.36 and of 3.48 Å are found in methylated TSeF-TCNQ derivatives (Bechgaard, Kistenmacher, Bloch & Cowan, 1977; Andersen, Bechgaard, Jacobsen, Rindorf, Soling & Thorup, 1978).

In the  $c^*$  direction the projected cation length increases by 0.28 Å on substitution of Se for S, yet the repeat distance  $c \sin \beta$  in TSeF-TCNQ is only 0.06 Å longer than in TTF-TCNQ. The closest contacts between cations are thus reduced by  $\sim 0.2$  Å on substitution of

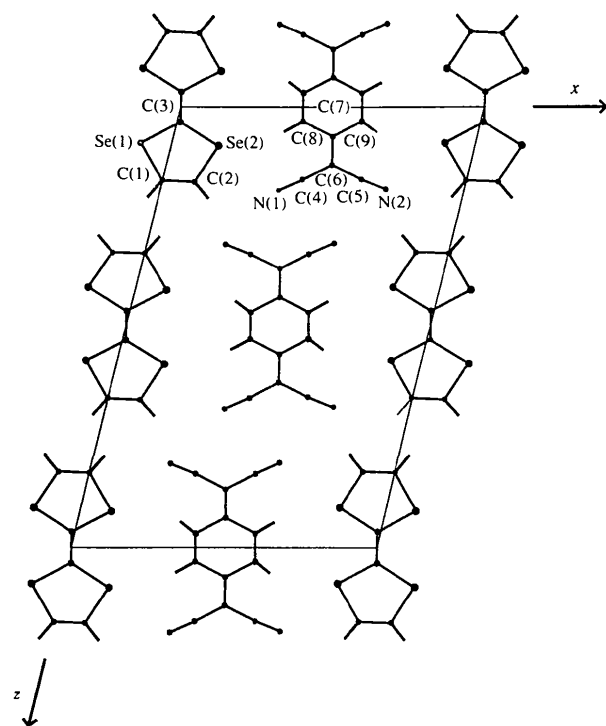


Fig. 1. Packing in TSeF-TCNQ; view normal to the  $ac$  plane.

Table 3. Comparison of structures of TTF-TCNQ and TSeF-TCNQ

Structural feature	TTF-TCNQ <sup>a</sup>	TSeF-TCNQ <sup>b</sup>
Cation tilt angle with $b$ axis ( $^\circ$ )	24.6	24.8
Anion tilt angle with $b$ axis ( $^\circ$ )	34.0	34.1
Interplanar stack distance (Å), cation	3.47	3.52 <sup>c</sup>
Interplanar stack distance (Å), anion	3.17	3.21
Angle between central and exterior planes in cation ( $^\circ$ )	2.2	2.5
Selected bond lengths (Å)		
C(3)-X	1.743 (3)	1.883 (2) <sup>d,e</sup>
C(1)-X	1.737 (3)	1.875 (3)
C(1)-C(2)	1.323 (4)	1.314 (4)
C(3)-C(3')	1.369 (4)	1.367 (5)
C(8)-C(9 <sup>iii</sup> )	1.356 (3)	1.350 (4)
C(7)-C(8), C(7)-C(9)	1.433 (3)	1.431 (3)
C(6)-C(7)	1.402 (3)	1.403 (4)
C(4)-C(6), C(5)-C(6)	1.423 (3)	1.428 (4)
N(1)-C(4), N(2)-C(5)	1.151 (4)	1.145 (4)
Selected bond angles ( $^\circ$ )		
X-C-X	114.7 (3)	115.1 (1)
C-X-C	94.9 (2)	92.7 (1)
X-C-C	117.7 (2)	119.8 (2)
C(7)-C(9)-C(8'), C(7)-C(8)-C(9')	121.4 (2)	121.4 (2)
C(8)-C(7)-C(9)	117.2 (2)	117.2 (2)
C(4)-C(6)-C(5)	117.8 (2)	117.9 (3)
Shortest interstack distances (Å)		
Cation-cation		
H(1)...H(1 <sup>iii</sup> )	2.78 <sup>f</sup>	2.58 (5)
C(1)...H(1 <sup>iii</sup> )	3.04	2.78 (4)
C(2)...H(1 <sup>iii</sup> )	3.36	3.08 (4)
C(1)...C(1 <sup>iii</sup> )	3.83	3.64 <sup>g</sup>
Anion-anion		
N(1)...C(4 <sup>iv</sup> )	3.28	3.32
N(1)...C(5 <sup>v</sup> )	3.29	3.33
Cation-anion		
X(1)...N(2 <sup>v</sup> )	3.25	3.17
X(2)...N(1 <sup>vi</sup> )	3.20	3.18
X(1)...H(9 <sup>vii</sup> )	2.99	3.14 (4)
X(2)...H(8 <sup>viii</sup> )	3.02	3.03 (3)
N(1)...H(2 <sup>ix</sup> )	2.81	2.90 (4)
N(2)...H(1 <sup>x</sup> )	2.59	2.72 (3)
N(2)...H(2 <sup>xi</sup> )	2.62	2.60 (4)
N(2)...H(2 <sup>v</sup> )	2.80	2.97 (4)
r.m.s. libration amplitudes ( $^\circ$ )		
Cation, axis $l$		
$l$	3.5 <sup>h</sup>	2.9
$m$	1.7	2.3
$n$	1.3	1.3
Anion, axis $l$		
$l$	3.2	4.5
$m$	1.2	1.7
$n$	0.8	0.6

Notes: (a) Kistenmacher, Phillips & Cowan (1974). (b) This work. (c) All atoms were given equal weight in least-squares planes calculations. H atoms not included. (d) Average values and standard deviations are quoted. (e) X refers to S in TTF-TCNQ and to Se in TSeF-TCNQ. (f) H parameters in the TTF-TCNQ structure were not refined. (g) Intermolecular distances not involving H atoms have e.s.d.'s averaging 0.004 Å. (h) At 100 K (Schultz, Stucky, Blessing & Coppens, 1976). Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $1-x, -y, -z$ ; (iii)  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iv)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (v)  $x-1, y-1, z$ ; (vi)  $x, y-1, z$ ; (vii)  $x-1, y, z$ ; (viii)  $x, y, z$ ; (ix)  $x, 1+y, z$ ; (x)  $1+x, 1+y, z$ ; (xi)  $1-x, \frac{3}{2}+y, \frac{1}{2}-z$ .

Se for S. The two shortest contacts along  $c^*$  between TCNQ anions increase by 0.04 Å, however, consistent with the slight increase in  $c$ . This suggests that in TTF-

TCNQ, packing in the  $c^*$  direction is dominated by contacts between the TCNQ anions, while in TSeF-TCNQ, contacts involving the TSeF cations become more important. Greater crowding in TSeF-TCNQ for

the cation rather than the anion is also suggested by the rigid-body r.m.s. libration amplitudes in Table 2. As expected, the room-temperature values for the TCNQ anion in TSeF-TCNQ are nearly 50% larger on average than values obtained at 100 K for the same anion in TTF-TCNQ. However, the room-temperature libration amplitudes for the TSeF cation are the same as for the TTF cation at 100 K.

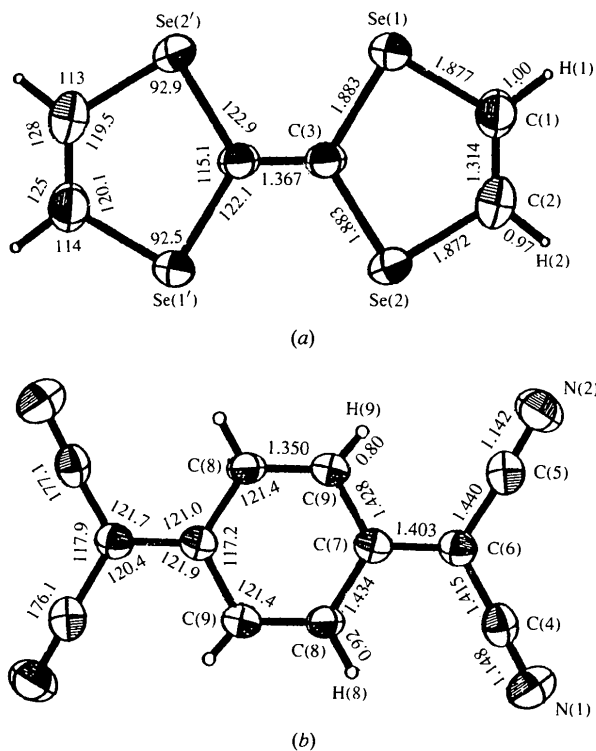


Fig. 2. TSeF-TCNQ with the atomic numbering scheme and bond lengths (Å) and angles ( $^{\circ}$ ), drawn by ORTEP (Johnson, 1976). Thermal ellipsoids are shown at the 75% probability level.

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