

Fig. 2. Stereoscopic view of the crystal packing. H atoms have been omitted. Hydrogen bonds are indicated by broken lines.

essential link. The ribose...phosphate backbone reported for cytidinium dihydrogenphosphate does not include the 2'-hydroxyl group (Jaskólski, 1989) and therefore can be preserved in identical form in 2'-deoxycytidinium dihydrogenphosphate (Jaskólski, 1991). *a*-Translated sugar units within the present sugar...phosphate chains are linked through a direct O(3')H...O(5') hydrogen bond. This bond is the only intermolecular interaction in which the nucleoside cation plays the role of the acceptor. The hydrogen-bond network described above extends in three dimensions. The ethenocytosinium system does not form any stacking pattern in the crystal.

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## Structure of 1,5-Diselenoniabicyclo[3.3.0]octane Bis(tetrafluoroborate) Acetonitrile Solvate

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**Abstract.**  $C_6H_{12}Se_2^{2+} \cdot 2BF_4^- \cdot CH_3CN$ ,  $M_r = 456.74$ , monoclinic,  $P2_1/a$ ,  $a = 24.053(6)$ ,  $b = 6.955(2)$ ,  $c = 9.416(3)$  Å,  $\beta = 100.47(2)^\circ$ ,  $V = 1549.0(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.959$  Mg m<sup>-3</sup>,  $T = 295$  K,  $\lambda(Mo K\alpha) =$

0.71069 Å,  $\mu = 4.796$  mm<sup>-1</sup>,  $F(000) = 880$ ,  $R = 0.069$  for 1688 observed reflections. The Se<sup>+</sup>—Se<sup>+</sup> distance is 2.382(2) Å. The conformation of the eight-membered ring is a chair-boat form, while that in 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) is a distorted chair-chair form.

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The X-ray analysis reveals that the crystal has one acetonitrile molecule as a crystal solvent in an asymmetric unit. Very short contacts are observed between the Se atom of the dication and the F atoms of counter anions and the N atom of CH<sub>3</sub>CN. The coordination around Se is a roughly distorted octahedron with F, N and two C atoms in a plane and apical Se and F atoms.

**Introduction.** Some sulfur-bonded 1-thionia-5-thiacyclooctane salts and 1,5-dithiacyclooctanes have been found to have a relatively short transannular S...S contact in the range 3.121–3.271 Å owing to the hypervalency of the S atom (Johnson, Maier & Paul, 1970; Musker, Olmstead & Goodrow, 1983; Olmstead, Williams & Musker, 1982; Iwasaki & Furukawa, 1987). The existence of an S<sup>+</sup>—S<sup>+</sup> bond has also been confirmed in 1,5-dithionibicyclo[3.3.0]octane bis(trifluoromethanesulfonate) by the X-ray analysis, in which the length of the S<sup>+</sup>—S<sup>+</sup> bond is only slightly longer than the normal single bond (Iwasaki, Toyoda, Akaishi, Fujihara & Furukawa, 1988). In this crystal strong interactions have been observed between dications and anions. Recently, crystals of 1,5-diselenoniabicyclo[3.3.0]octane bis(tetrafluoroborate) have been isolated. The X-ray analysis was undertaken to elucidate the structural features of a diselenonia dication.

**Experimental.** Pale-yellow plate with dimensions 0.40 × 0.30 × 0.15 mm was sealed in a thin glass capillary because the crystals were unstable in air. Unit-cell parameters by least squares from 25 reflections ( $2\theta < 30^\circ$ ), Rigaku AFC-4 diffractometer with graphite monochromator,  $2 \leq 2\theta \leq 50^\circ$ ,  $h = -28 \rightarrow 28$ ,  $k = 0 \rightarrow 8$ ,  $l = 0 \rightarrow 11$ ,  $\omega$ - $2\theta$  scan, scan range  $(1.2 + 0.4 \tan \theta)^\circ$ , scan speed  $4^\circ \text{ min}^{-1}$  ( $2\theta < 30^\circ$ ) and  $8^\circ \text{ min}^{-1}$  ( $2\theta > 30^\circ$ ) in  $2\theta$ , 5 s background counts at both ends of the scan range for each reflection, three reflections monitored (002, 400,  $\bar{1}10$ ) every 50 reflections, of which intensities gradually decreased to 80%. Corrections were made for intensity variation. 3310 reflections measured, 2668 unique,  $R_{\text{int}} = 0.039$ , 1688 observed [ $|F_o| \geq 3\sigma(F)$ ]. Absorption corrections were applied experimentally ( $A_{\text{max}} - A_{\text{min}} = 0.980 - 0.739$ ).

The structure was solved by Patterson methods using SHELXS86 (Sheldrick, 1986) and successive Fourier and least-squares methods. From the Fourier map an acetonitrile molecule was located in the asymmetric unit as a crystal solvent. One of the BF<sub>4</sub><sup>-</sup> anions was rotationally disordered around the F(1)—B(1) bond. The occupancy factors were refined with SHELX76 (Sheldrick, 1976). The positional parameters of most of the H atoms were assumed from the calculation and included in the refinements. Block-diagonal least squares refinement with aniso-

tropic temperature factors for non-H and isotropic temperature factors for H atoms.  $\sum w(|F_c| - k^{-1}|F_o|)^2$  was minimized.  $w = 1/[\sigma(F)^2 + 0.13804|F_o| + 0.00002|F_o|^2]$ .  $\Delta\rho(\text{max.}) = 1.02 \text{ e \AA}^{-3}$ ,  $\Delta/\sigma(\text{max.}) = 0.05$  for non-H atoms, 0.13 for H atoms.  $R = 0.069$ ,  $wR = 0.077$ ,  $S = 1.14$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All computations were performed on a HITAC M260D and IBM ES3090-180S of the Information Processing Center of the University of Electro-Communications with SHELX76, SHELXS86, UNICSIII (Sakurai & Kobayashi, 1979) and ORTEPII (Johnson, 1976). The final atomic parameters are given in Table 1.\*

**Discussion.** *Structure of the dication.* The structure of the dication with the atom numbering is shown in Fig. 1, and the bond distances and angles are listed in Table 2. The Se(1)—Se(5) length is 2.382 (2) Å, which is only slightly longer than the normal Se—Se single bond (2.34 Å). In the case of 1,4-diphenylhexaselenium bis(hexafluoroarsenate), the average Se<sup>+</sup>—Se length is 2.416 Å (Faggiani, Gillespie & Kolis, 1987). Therefore, Se<sup>+</sup>—Se<sup>+</sup> bond formation is confirmed unequivocally, and the structure of the dication is not an open cyclooctane ring but a bicyclooctane. In 1,5-dithionibicyclooctane the S<sup>+</sup>—S<sup>+</sup> distance is 2.124 Å compared with the normal single-bond length of 2.08 Å. Examples of Se...Se transannular contacts less than the sum of the van der Waals radii (4.0 Å) are 3.415 Å in the 1,4-diphenylhexaselenium salt (Faggiani *et al.*, 1987) and 3.384 Å in nonaselenahexazacyclopentadecane (Roesky, Weber & Bats, 1984). The Se—C lengths are 1.95 (2)—1.98 (1) Å. These values are also slightly longer than the normal Se—C single-bond length (1.94 Å). The C—Se—C bond angles are 101.7 (6) and 102.2 (6)° and Se—Se—C are 90.7 (5)—92.6 (4)°. These values are slightly smaller than the corresponding values with the 1,5-dithionia dication. The torsion angles of the dication are also listed in Table 2. The conformation of the eight-membered ring is a chair-boat form, while that of 1,5-dithionibicyclooctane is a distorted chair-chair form. For eight-membered rings, such as 1-thionia-5-thiacyclooctanes and 1,5-dithiacyclooctanes, a chair-boat conformation is dominant.

*Crystal structure.* The crystal structure projected along the *b* axis is shown in Fig. 2. Fig. 3 shows the molecular contacts shorter than the sum of the van

\* Lists of structure factors, anisotropic temperature factors for non-H atoms, atomic parameters for H atoms, and bond lengths and angles for the BF<sub>4</sub><sup>-</sup> anions and H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53734 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ( $\times 10^5$  for Se,  $\times 10^4$  for other atoms) and *equivalent isotropic temperature factors* ( $\text{\AA}^2$ ) for non-H atoms

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Se(1)	8826 (5)	11119 (18)	8097 (13)	3.69 (4)
Se(5)	13396 (5)	1407 (17)	31592 (13)	3.60 (4)
C(2)	570 (5)	3436 (18)	1549 (13)	4.3 (4)
C(3)	940 (5)	3999 (18)	2991 (14)	4.5 (4)
C(4)	1028 (6)	2360 (22)	4015 (13)	5.4 (5)
C(6)	2078 (4)	1132 (17)	2833 (11)	3.3 (3)
C(7)	2085 (6)	1017 (18)	1247 (13)	4.4 (4)
C(8)	1595 (6)	2086 (19)	340 (14)	5.0 (4)
C(11)	-1102 (7)	3385 (22)	3145 (15)	6.2 (5)
C(12)	-1160 (6)	3081 (19)	1574 (16)	5.3 (5)
N(1)	-1205 (6)	2887 (19)	364 (13)	7.8 (5)
B(1)	-190 (7)	-1849 (23)	2835 (16)	4.8 (5)
B(2)	2682 (7)	-3909 (23)	3065 (16)	4.6 (5)
F(11)	36 (5)	-2731 (17)	4006 (9)	10.0 (4)
F(12)*	-740 (5)	-1469 (23)	2806 (16)	7.6 (5)
F(13)*	24 (8)	-105 (22)	2652 (21)	10.3 (7)
F(14)*	-144 (8)	-2880 (23)	1607 (13)	9.9 (7)
F(12B)†	-522 (18)	-524 (49)	3064 (33)	16.2 (18)
F(13B)†	184 (11)	-1098 (63)	2146 (29)	14.9 (14)
F(14B)†	-469 (12)	-3019 (40)	1867 (26)	10.0 (10)
F(21)	2990 (4)	-5136 (11)	4077 (8)	6.3 (3)
F(22)	2976 (3)	-2227 (10)	3025 (9)	6.4 (3)
F(23)	2622 (5)	-4819 (13)	1780 (9)	8.4 (4)
F(24)	2168 (4)	-3599 (13)	3430 (11)	8.3 (4)

\* Occupancy factor 0.6134.

† Occupancy factor 0.3866.

Table 2. *Bond lengths* ( $\text{\AA}$ ) and *angles* ( $^\circ$ ) of non-H atoms, and *torsion angles* ( $^\circ$ ) of the dication

Se(1)—Se(5)	2.382 (2)	C(2)—C(3)	1.534 (18)
Se(1)—C(2)	1.963 (13)	C(3)—C(4)	1.483 (20)
Se(1)—C(8)	1.967 (14)	C(6)—C(7)	1.499 (18)
Se(5)—C(4)	1.952 (16)	C(7)—C(8)	1.519 (20)
Se(5)—C(6)	1.981 (12)		
Se(5)—Se(1)—C(2)	92.6 (4)	Se(1)—C(2)—C(3)	109.0 (8)
Se(5)—Se(1)—C(8)	91.9 (4)	C(2)—C(3)—C(4)	111.7 (11)
C(2)—Se(1)—C(8)	101.7 (6)	Se(5)—C(4)—C(3)	111.1 (10)
Se(1)—Se(5)—C(4)	90.7 (5)	Se(5)—C(6)—C(7)	108.0 (8)
Se(1)—Se(5)—C(6)	91.9 (3)	C(6)—C(7)—C(8)	112.7 (11)
C(4)—Se(5)—C(6)	102.2 (6)	Se(1)—C(8)—C(7)	108.9 (9)
C(8)—Se(1)—C(2)—C(3)	-68.1 (8)	Se(1)—C(2)—C(3)—C(4)	-52 (1)
C(2)—Se(1)—C(8)—C(7)	118.8 (8)	Se(1)—C(8)—C(7)—C(6)	-55 (1)
C(6)—Se(5)—C(4)—C(3)	62.7 (9)	Se(5)—C(4)—C(3)—C(2)	55 (1)
C(4)—Se(5)—C(6)—C(7)	-119.9 (8)	Se(5)—C(6)—C(7)—C(8)	56 (1)
C(11)—C(12)	1.476 (22)	C(12)—N(1)	1.133 (21)
C(11)—C(12)—N(1)	178.6 (17)		
B(1)—F	1.29 (2)—1.38 (3)	B(2)—F	1.35 (2)—1.39 (2)
F—B(1)—F	102 (3)—115 (2)	F—B(2)—F	106 (1)—112 (1)

der Waals radii. Very strong interactions were observed between Se<sup>+</sup> of the dications and F(14<sup>i</sup>) [or F(14B<sup>i</sup>), (i) = -x, -y, -z] and F(21<sup>ii</sup>) [(ii) =  $\frac{1}{2} - x$ ,  $\frac{1}{2} + y$ , 1 - z] atoms of the counter anions. The Se...F distances are 2.89 (2) [or 2.86 (3)] and 2.807 (9)  $\text{\AA}$  for F(14<sup>i</sup>) [or F(14B<sup>i</sup>)] and F(21<sup>ii</sup>), respectively. These values are remarkably shorter than the van der Waals contact of 3.35  $\text{\AA}$ . Nearly collinear

F...Se—Se...F interactions are formed with angles of 164.6 (4) [167.7 (6)] and 166.1 (2) $^\circ$  for Se(5)—Se(1)...F(14<sup>i</sup>) [Se(5)—Se(1)...F(14B<sup>i</sup>)] and Se(5)—Se(1)...F(21<sup>ii</sup>), respectively.

Other short non-bonded interactions between dications and anions and the N atom of acetonitrile are also shown in Fig. 3. Se(1) has non-bonded

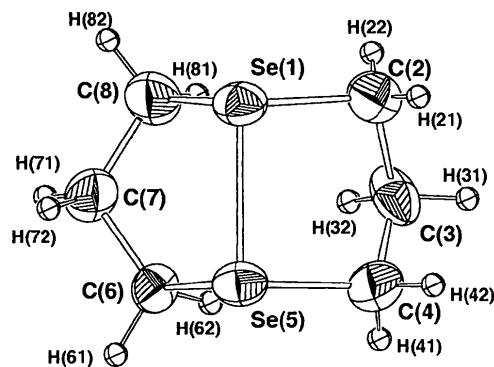


Fig. 1. The structure of dication with the atom numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

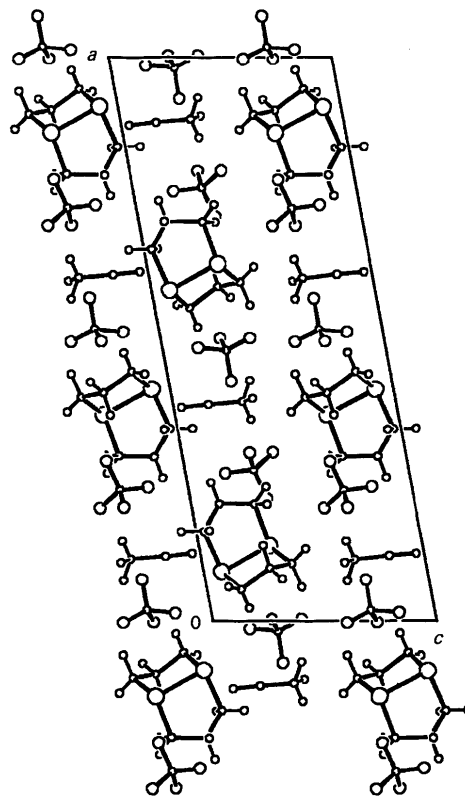


Fig. 2. The projection of the crystal structure viewed along the *b* axis. Disordered F atoms with smaller occupancy factors are omitted.

contacts to F(13) [or F(13*B*)] and N(1<sup>i</sup>) at the distances of 3.05 (2) [or 2.75 (4)] and 3.14 (2) Å, respectively. A similar situation is observed between Se(5) and F(13) [or F(13*B*)] and F(24). The distances S(5)···F(13) [F(13*B*)] and Se(5)···F(24) are 3.12 (2) [2.90 (4)] and 3.26 (1) Å, respectively. Thus the coordination around the Se atom is a roughly distorted octahedron with two C and F and N or F atoms in a plane and an apical Se—Se bond and Se···F contact. These structural features bear some resemblance those of 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate), in which strong linear O···S—S···O interactions and weak planar interactions between cations and anions also form a distorted octahedral coordination (Iwasaki *et al.*, 1988). Short Se···F contacts have been observed in 1,4-diphenylhexaselenium bis(hexafluoroarsenate) (average distance 3.16 Å). A linear X···S—S (X = O *etc.*) arrangement with short S···X distances (2.52–2.89 Å) is a typical feature of hypervalent sulfur compounds (Iwasaki, Toyoda & Yamazaki, 1989) (see Table 3). In the case of Se compounds, some lengths of short intra- and intermolecular Se···O

Table 3. Distances (Å) and angles (°) related to Se···X interactions

Y	X =	F(14 <sup>i</sup> )	F(13)	N(1 <sup>i</sup> )
Se(1)···X		2.89 (2)	3.05 (2)	3.14 (2)
Se(5)···Se(1)···X		164.6 (4)	68.8 (4)	88.5 (3)
C(2)—Se(1)···X		73.1 (5)	71.6 (5)	171.4 (5)
C(8)—Se(1)···X		96.5 (6)	158.7 (6)	86.8 (5)
N(1 <sup>i</sup> )	Y···Se(1)···X	104.8 (5)	101.0 (5)	
F(13)	Y···Se(1)···X	100.5 (5)		

Y	X =	F(21 <sup>ii</sup> )	F(13)	F(24)
Se(5)···X		2.81 (1)	3.12 (2)	3.26 (1)
Se(1)—Se(5)···X		166.1 (2)	65.7 (4)	118.1 (2)
C(4)—Se(5)···X		82.6 (5)	69.6 (6)	150.9 (5)
C(6)—Se(5)···X		77.7 (4)	155.4 (5)	74.7 (4)
F(24)	Y···Se(5)···X	68.5 (3)	123.9 (4)	
F(13)	Y···Se(5)···X	122.3 (4)		

contacts are: 2.622 and 2.657 Å in 5,5',12,12'-bis(triseleno)bis(naphthacene-6,11-quinone) (intramolecular; Shibaeva, Kaminskii, Kostyuchenko & Yagubskii, 1984), 3.224 Å in bis(*p*-nitrophenyl) diselenide (intermolecular; Morris & Einstein, 1986) and 3.092 Å in bis(phenylsulfonyl) diselane (intermolecular; Foss, Kvammen & Maroy, 1985).

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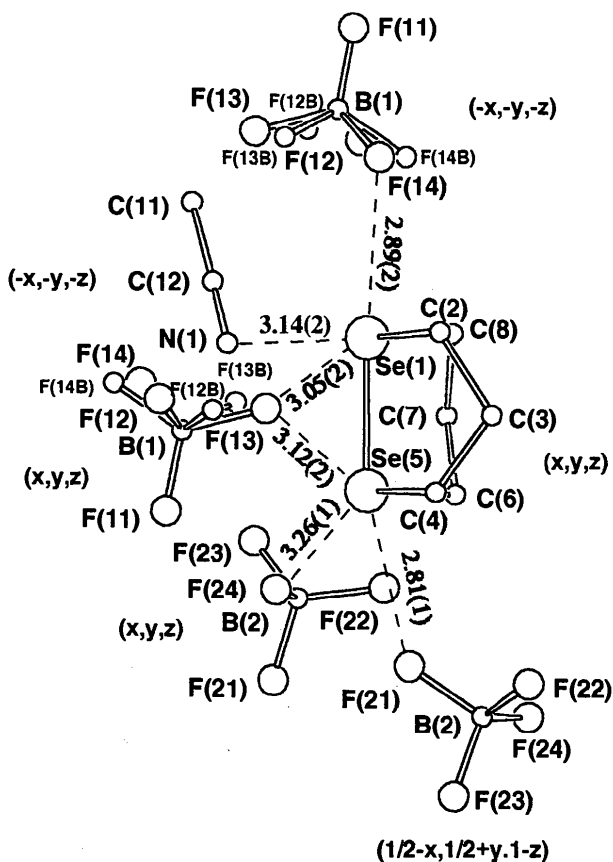


Fig. 3. Short contacts (Å) between dications and anions.