# Fluoride Crystal Structures. Part 27.[1] Seleninyl Difluoride at −35 °C

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The structure of the title compound (m.p. 15 °C) has been determined by the heavy-atom method from 184 diffractometer reflections, measured at −35 °C by use of a nitrogen-gas cooling device, and refined by full-matrix least-squares methods to *R* 0.082. Crystals are orthorhombic, space group $Pca2_1$, $a$ = 5.65(1), $b$ = 7.46(1), $c$ = 6.24(1) Å, $Z$ = 4. In the structure each selenium atom has one close oxygen (Se–O 1.62 Å) and two close fluorine neighbours (mean Se–F 1.70 Å) giving a pyramidal co-ordination. These units are then linked through two oxygen bridges (mean Se ··· O 2.76 Å) and one fluorine bridge (Se ··· F 3.03 Å) to form a layer arrangement perpendicular to [010], with a much distorted octahedral co-ordination around the selenium atom.

A COMPARISON of the physical properties of isovalent fluorides within a group of the *p*-block of the Periodic Table sometimes shows a marked discontinuity. In Group 4 there is an abrupt transition in melting point between $GeF_4$ (m.p. −37 °C) and $SnF_4$ (subl. 704 °C). This has been shown to be due to a change in structure from tetrahedrally co-ordinated molecular units in $GeF_4$ to octahedrally co-ordinated metal atoms linked into layers in $SnF_4$.[2]

There is a corresponding, but smaller, change for Group 5 trifluorides between $AsF_3$ (m.p. −8.5 °C) and $SbF_3$ (m.p. 292 °C) and we have attempted to determine the structure of $AsF_3$ at low temperature for comparison with that of $SbF_3$, where there are comparatively strong interactions between $SbF_3$ molecular units through fluorine bridges.[3] We have found that $AsF_3$ is isostructural with $SbF_3$, but as yet we have been unable to collect sufficiently good data to obtain definitive atom positions, owing to the high volatility of the crystals at −35 °C.

Seleninyl difluoride (m.p. 15 °C) is isoelectronic with $AsF_3$ and we determined its crystal structure (at −35 °C) in the expectation that the two compounds would be isostructural and direct comparisons could be made with $SbF_3$.

## EXPERIMENTAL

Small amounts of seleninyl difluoride, prepared by the action of selenium tetrafluoride on an excess of tellurium dioxide, were sealed into sections of Pyrex capillaries about 3.5 cm in length.

The cooling device, of similar design to that of Burbank[4] but constructed so as to consume considerably less liquid nitrogen, was set up on an Enraf Nonius Y 925 precession camera and run at −35 °C. A section of Pyrex capillary, containing a suitable amount of liquid $SeOF_2$, was mounted on a goniometer head and offset through the nitrogen-gas stream. A method of growing crystals suitable for *X*-ray work was evolved by trial and error. Crystals invariably grew as very thin plates with *b* as the plate normal, and in such a way that *a* could always be aligned as the rotation axis. Precession photographs of the zero and first layers of the two accessible zones were enough to deduce unit-cell and space-group data.

The cooling device was then re-assembled on a Stoe two-circle diffractometer. A crystal was grown as before, and by trial and error was aligned about the usual rotation axis. Unit-cell parameters were refined at −35 °C by the usual method. Data collection (at −35 ± 1 °C) was complete in 10 h which was approximately the lifetime of each individual crystal.

*Crystal Data.*—$F_2OSe$, $M = 133$, Orthorhombic, $a = 5.65(1)$, $b = 7.46(1)$, $c = 6.24(1)$ Å, $U = 263$ Å$^3$, $Z = 4$, $D_c = 3.36$ g cm$^{-3}$, $F(000) = 240$. Space group $Pca2_1$ ($C_{2v}^5$, No. 29) or $Pcam$ ($D_{2h}^{11}$, No. 57, in a non-standard setting) from systematic absences; $0kl$ when $l \neq 2n$ and $h0l$ when $h \neq 2n$; the former was confirmed by the successful structure refinement. Mo-$K_\alpha$ radiation ($\lambda = 0.7107$ Å; $\mu$(Mo-$K_\alpha$) = 151 cm$^{-1}$). Single-crystal precession photographs and diffractometer data.

*Structure Determination.*—Intensity data were collected about the *a* axis (layers 0—$5kl$) with a Stoe two-circle computer-controlled diffractometer, by use of graphite monochromated Mo-$K_\alpha$ radiation. The stationary-counter–moving-crystal method was used, with an ω-scan range of 1.2° on the lower levels, counting for 1 s at 0.02° intervals. For reflections on the second and higher layers ($\mu > 7°$) a variable range was scanned, with $\Delta\omega$ defined by $(A + B\sin\mu/\tan\nu)$ where $A = 1.0$ and $B = 0.5$. Stationary-background counts were measured at the extremities of each scan for 10 s. Within the range $0.1 < \sin\theta/\lambda \leqslant 0.65$, 347 independent reflections were scanned, of which 184, having $I > 3\sigma(I)$, were considered observed. The intensity of a check reflection (002), measured after each layer, varied by *ca.* ±4% from the mean. Data were corrected for Lorentz and polarization factors as well as for absorption.

The selenium atom co-ordinates were derived from a

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[1] Part 26, A. J. Edwards and K. O. Christe, *J.C.S. Dalton*, 1976, 175.

[2] R. Hoppe and W. Dähne, *Naturwiss.*, 1962, **49**, 254.

[3] A. J. Edwards, *J. Chem. Soc.* (*A*), 1970, 2751.

[4] R. D. Burbank, *J. Appl. Cryst.*, 1973, **6**, 437.

three-dimensional Patterson synthesis; the remaining atoms, located in a subsequent difference-Fourier map, could only be reasonably placed in the non-centrosymmetric space group. The oxygen atom could not be distinguished from the fluorine atoms by *X*-ray methods in the presence of the heavy selenium atom. It was assigned by consideration of the geometry of the molecular unit [by comparison with seleninyl difluoride vapour [5] and the adduct $\mathrm{SeOF_2{\cdot}NbF_5}$ (ref. 6) where the angle F–Se–F < F–Se–O]. Scattering factors used were those for the neutral atoms,[7] with corrections for the effects of anomalous dispersion [8] ($\Delta f'$ and $\Delta f''$) applied to those for selenium. Initial refinement was by full-matrix least-squares methods with layer scale factors refined separately, and all atoms vibrating isotropically. Refinement was continued with the layer scale factors held constant and with the introduction of anisotropic thermal parameters, for the selenium atom, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. In the final stages of refinement the weighting scheme $w = [\sigma^2(F_o) + (0.06|F_o|)^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing sin θ/λ and with increasing fractions of $|F_o|$. At convergence, no parameter shift was $>0.001\sigma$ and a final difference-Fourier map showed no significant features. The final *R* was 0.082 and *R'* 0.099 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ for the preferred hand. Most of the calculations were carried out on the ICL 1906A at the Birmingham University Computer Centre using SHELX-76.[9] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21858 (3 pp., 1 microfiche),* the final positional and thermal parameters with their estimated standard deviations in Table 1, and interatomic distances and angles in Table 2.

TABLE 1

(*a*) Atomic positional and isotropic thermal parameters (× $10^2$) with least-squares estimated standard deviations in parentheses

| Atom | *x/a* | *y/b* | *z/c* | *U* |
|---|---|---|---|---|
| Se | 0.038 0(5) | 0.191 7(5) | 0.25 | |
| O | 0.246(5) | 0.095(3) | 0.115(5) | 2.7(5) |
| F(1) | 0.150(3) | 0.399(3) | 0.283(7) | 4.8(7) |
| F(2) | −0.117(5) | 0.273(4) | 0.034(5) | 5.0(7) |

(*b*) Anisotropic thermal parameters (× $10^3$)

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Se | 32(2) | 32(2) | 31(2) | 11(4) | −1(6) | 1(2) |

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

| | | | |
|---|---|---|---|
| Se–O | 1.62(3) | $\mathrm{O \cdots F(2^{III})}$ | 2.89(4) |
| Se–F(1) | 1.68(2) | $\mathrm{O^{VIII} \cdots F(1^{I})}$ | 3.13(4) |
| Se–F(2) | 1.72(3) | $\mathrm{F(1) \cdots F(2)}$ | 2.36(4) |
| $\mathrm{Se \cdots O^{I}}$ | 2.68(3) | $\mathrm{F(1) \cdots F(1^{I})}$ | 3.32(6) |
| $\mathrm{Se \cdots F(2^{II})}$ | 3.03(3) | $\mathrm{F(1) \cdots F(2^{I})}$ | 3.21(4) |
| $\mathrm{Se \cdots O^{VI}}$ | 2.83(3) | $\mathrm{F(1) \cdots F(1^{IV})}$ | 3.20(3) |
| $\mathrm{O \cdots F(1)}$ | 2.56(4) | $\mathrm{F(1) \cdots F(1^{V})}$ | 3.20(3) |
| $\mathrm{O \cdots F(2)}$ | 2.50(4) | $\mathrm{F(1) \cdots F(2^{IV})}$ | 3.18(4) |
| $\mathrm{O \cdots O^{I}}$ | 3.12(4) | $\mathrm{F(1) \cdots F(2^{VII})}$ | 2.91(4) |
| $\mathrm{O \cdots O^{III}}$ | 3.16(4) | $\mathrm{F(2) \cdots F(2^{II})}$ | 3.46(4) |

(*b*) Angles

| | | | |
|---|---|---|---|
| O–Se–F(1) | 101.7(1.3) | $\mathrm{F(2){-}Se{-}F(2^{II})}$ | 89.3(1.1) |
| O–Se–F(2) | 96.9(1.4) | $\mathrm{F(2){-}Se{-}O^{VI}}$ | 74.7(1.1) |
| $\mathrm{O{-}Se{-}O^{I}}$ | 89.5(1.3) | $\mathrm{O^{I}{-}Se{-}F(2^{II})}$ | 85.1(0.9) |
| $\mathrm{O{-}Se{-}F(2^{II})}$ | 165.0(1.0) | $\mathrm{O^{I}{-}Se{-}O^{VI}}$ | 108.3(0.8) |
| $\mathrm{O{-}Se{-}O^{VI}}$ | 86.0(1.1) | $\mathrm{F(2^{II}){-}Se{-}O^{VI}}$ | 82.5(0.8) |
| F(1)–Se–F(2) | 87.9(1.5) | $\mathrm{Se{-}O{-}Se^{IX}}$ | 130.7(1.3) |
| F(1)–Se–O(1) | 88.4(1.4) | $\mathrm{Se{-}O{-}Se^{III}}$ | 127.3(1.5) |
| $\mathrm{F(1){-}Se{-}F(2^{II})}$ | 92.2(1.1) | $\mathrm{Se^{IX}{-}O{-}Se^{III}}$ | 101.1(0.9) |
| $\mathrm{F(1){-}Se{-}O^{VI}}$ | 161.8(1.1) | $\mathrm{Se{-}F(2){-}Se^{X}}$ | 142.0(1.4) |
| $\mathrm{F(2){-}Se{-}O^{I}}$ | 173.2(1.1) | | |

Roman numeral superscripts refer to atoms in the following equivalent positions:

| | | | |
|---|---|---|---|
| I | $\frac{1}{2} - x, y, \frac{1}{2} + z$ | VI | $-\frac{1}{2} + x, -y, z$ |
| II | $-\frac{1}{2} - x, y, \frac{1}{2} + z$ | VII | $-x, 1 - y, \frac{1}{2} + z$ |
| III | $\frac{1}{2} + x, -y, z$ | VIII | $x, y, 1 + z$ |
| IV | $\frac{1}{2} + x, 1 - y, z$ | IX | $\frac{1}{2} - x, y, -\frac{1}{2} + z$ |
| V | $-\frac{1}{2} + x, 1 - y, z$ | X | $-\frac{1}{2} - x, y, -\frac{1}{2} + z$ |

## DISCUSSION

Seleninyl difluoride is not isostructural with $\mathrm{AsF_3}$ or $\mathrm{SbF_3}$. In the structure, pyramidal $\mathrm{SeOF_2}$ units are linked together by oxygen and fluorine bridges (Figure 1).

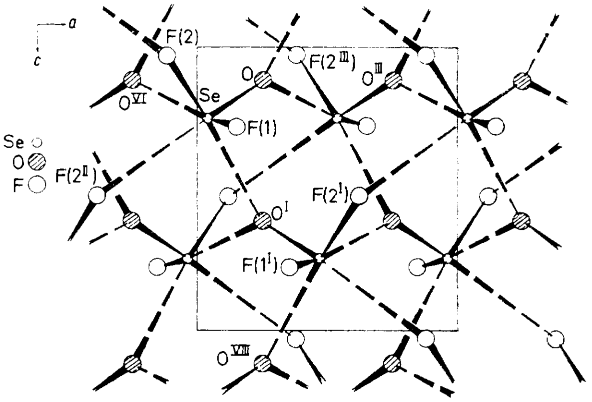

FIGURE 1 Projection of the structure down [010]

Each oxygen atom is engaged in one bonding and two bridging contacts to selenium atoms, F(2) has one bonding and one bridging contact, and F(1) has only one bonding contact. All atoms designated F(1) lie at the surfaces of the layers that compose the structure (Figure 2). The normal to these layers corresponds to the crystallographic *b* axis and can be correlated with the very thin plate-like habit exhibited by the crystals in which this axis is normal to the plate. Presumably there are only weak van der Waals interactions between adjacent layers in the structure.

The Se–O distance and general geometry of the $\mathrm{SeOF_2}$ molecule in the solid state is the same within experimental error as that in $\mathrm{SeOF_2}$(vapour) [5] and in the $\mathrm{SeOF_2{\cdot}NbF_5}$ adduct [6] (Table 3). The co-ordination about each selenium atom is a distorted octahedron comprising one close oxygen contact (1.62 Å) and two close fluorine contacts [F(1) 1.68, F(2) 1.72 Å], where the O–Se–F angles are 101.7 and 96.9° and F–Se–F is 87.9°, with two longer contacts to oxygen ($\mathrm{O^{I}}$ 2.68, $\mathrm{O^{VI}}$ 2.83 Å) and one long contact to fluorine [$\mathrm{F(2^{II})}$ 3.03 Å]. This arrangement can be described on VSEPR theory as

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

[5] J. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectroscopy*, 1967, **23**, 272.

[6] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1969, 2858.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] SHELX-76, Program for Crystal Structure Determination, G. M. Sheldrick, University of Cambridge, U.K., 1975.

being based on a distorted tetrahedral co-ordination of the three atoms forming the close bonding contacts to selenium, and the non-bonding pair of electrons. The three long bridging contacts are grouped around the non-bonding pair position to give an overall, distorted, seven-co-ordinate, monocapped octahedral geometry. The shape of this distorted octahedral arrangement is similar to those around selenium in $[SeF_3][Nb_2F_{11}]$ (ref. 10), $[SeF_3][NbF_6]$ (ref. 11), and $SeOF_2{\cdot}NbF_5$ (ref. 6) and to that around antimony in $SbF_3$.[3]

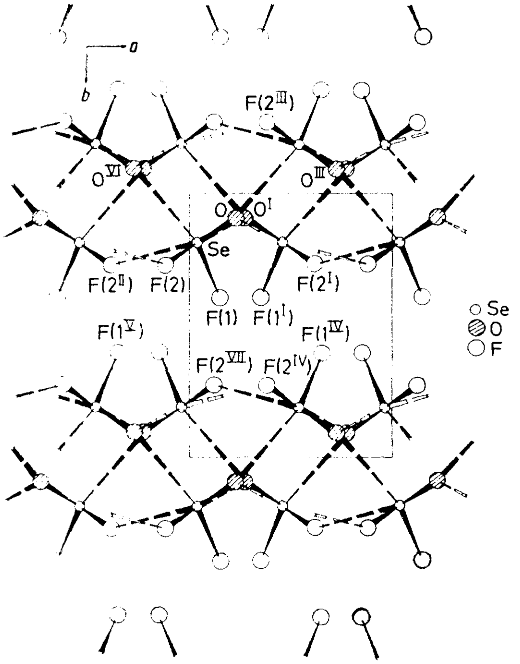

FIGURE 2 The packing arrangement seen in projection down [001]. Unfilled bonds represent contacts to or from atoms (not shown) at $x, y, 1 \pm z$

TABLE 3

Comparison of the geometry of seleninyl difluoride in the vapour and solid states and in the $SeOF_2{\cdot}NbF_5$ adduct

| | Vapour [a] | Solid [b] | Adduct [c] |
|---|---|---|---|
| Se–F | 1.727 Å | 1.68 Å | 1.70 Å |
| Se–O | 1.580 Å | 1.60 Å | 1.62 Å |
| F–Se–F | 92.4° | 92.6° | 89.5° |
| O–Se–F | 104.8° | 99.7° | 99.3° |

[a] Ref. 8. [b] This work. [c] Ref. 9.

The Se–F distances in the present compound are not significantly different from each other or from those in $[SeF_3][Nb_2F_{11}]$ (av. 1.66 Å), $[SeF_3][NbF_6]$ (av. 1.73 Å), $SeOF_2{\cdot}NbF_5$ (1.68 Å), and $SeOF_2$(vapour) (1.727 Å).[5] However, the bridging Se · · · O,F distances (av. 2.85 Å) are comparable with those in the adduct (av. 2.75 Å) but both are longer than those in $[SeF_3][Nb_2F_{11}]$ (av. 2.43 Å) and $[SeF_3][NbF_6]$ (av. 2.35 Å). The ratio of bonding to bridging distances is thus of the same order in the first two compounds (1.70, 1.77), as compared to the second two compounds where this ratio is 1.46 and 1.36, indicating weaker bridging interactions. The ratio in $SbF_3$ is also 1.36 and the $SbF_3$ molecular units are thus more closely linked than the $SeOF_2$ units. If this is also the case in $AsF_3$ then the lower melting point can be correlated with the weaker intermolecular interaction rather than with any change of structure.

The average F–Se–F angles in $[SeF_3][Nb_2F_{11}]$ and $[SeF_3][NbF_6]$ are respectively 94.2 and 94.9°. Substitution of an oxygen for a fluorine atom in the $[SeF_3]$ moiety is seen to result (Table 3) in an increase in the O–Se–F angles and a slight decrease in the F–Se–F angle although at the level of accuracy of the structures these differences are barely significant.

The formation of a layer structure in $SeOF_2$ compared to the three-dimensional network in $SbF_3$ (and $AsF_3$) appears to depend on the ability of the oxygen atom to attain a co-ordination number of three rather than the value of two for the fluorine atom. The co-ordination of the oxygen atom is distorted planar triangular, with the angles defined by the bonded atom (127 and 131°) larger than that defined by the two long contacts (101°)

We thank the S.R.C. for financial support.

[6/819 *Received, 27th April*, 1976]

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[10] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1491.

[11] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1891.