Crystal and Molecular Structure of Xenon Bis(oxopentafluoroselenate(VI)), Xe(OSeF$_5$)$_2$[1]

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Crystals of Xe(OSeF$_5$)$_2$ are rhombohedral, space group $R\bar{3}m$. At 23.5 °C the hexagonal axes are $a = b = 8.588$ (3) and $c = 11.918$ (3) Å; $Z = 3$, $d_{calcd} = 3.345$ g cm^{-3}, and $V = 761.23$ Å^3. The molecule lies on a threefold axis, and there is orientational disorder of the oxygen and fluorine positions. X-ray diffraction data obtained with an automatic diffractometer were analyzed on the basis of a molecular model with some constraints based on chemical considerations to reduce the number of independent parameters of the poorly resolved oxygen and fluorine atoms. For 122 unique reflections with $F^2 > \sigma(F^2)$ and with anisotropic thermal parameters, $R = 0.064$. Bond distances are Xe–O = 2.12 (5), Se–O = 1.53 (5), and Se–F = 1.70 (2) Å (uncorrected) and Se–F = 1.77 Å (corrected for thermal motion).

Introduction

The synthesis[3] of xenon(II) bis(oxopentafluoroselenate(VI)) had provided a xenon(II) compound of relatively high thermal stability and melting point. Several substitutional derivatives of xenon difluoride had previously been obtained,[4,5] but hitherto FXeOSO$_2$F was the sole compound for which a full crystal structure had been reported.[6] In this paper in which we describe the single-crystal x-ray diffraction analysis of Xe(OSeF$_5$)$_2$ we have the first description of Xe(II) bound symmetrically to two oxygen ligands.

Experimental Section

Xenon(II) bis(oxopentafluoroselenate(VI)) was prepared from xenon difluoride and pentafluoroselenic acid, HOSeF$_5$, as previously described.[3] Crystals were grown by sublimation in Teflon FEP tubing under dynamic vacuum. Raman spectra of the crystals studied established that they were representative of the bulk material.[7] The hydrolytically unstable crystals, which were pale yellow tablets, were loaded in a nitrogen-filled Vacuum Atmospheres Drilab, into 0.2-mm diameter thin-walled quartz capillaries. The capillaries were sealed in a small flame.

After preliminary study of several crystals by the precession method, diffractometer measurements were made of a crystal which did not have well-defined faces. Its dimensions were approximately 0.11 × 0.13 × 0.22 mm. Unit cell dimensions were determined from nine hand-centered reflections (36 < 2θ < 42°) measured with a Picker FACS-I automatic diffractometer which was equipped with a graphite monochromator and used molybdenum radiation (λ 0.709 26 Å for Kα$_1$). The same instrument was used to collect the intensity data. The integrated intensity of each reflection was measured using a θ–2θ scan technique with a scanning rate of 1°/min from 0.6° below the 2θ angle at which Kα$_1$ was diffracted to 0.6° above the 2θ angle at which Kα$_2$ was diffracted. Two 20-s background counts were taken with the apparatus stationary and offset 0.5° from each end of the scan. Three strong reflections (330, 404, 033) were checked every 100 reflections for crystal decomposition and/or instrument malfunction. There was no decay within the accuracy of the measurements. Reflections were collected in the hemisphere +h,±k,±l to 2θ of 45°. Of 723 reflections which were measured, 140 are unique. For 123 of them $F^2 > \sigma(F^2)$. The strongest reflection, 110, was calculated to be even stronger than observed and appeared to suffer from some unidentified experimental error; it was assigned zero weight in the refinement.

Absorption corrections calculated by an analytical integration[8] ranged from 2.337 to 4.602. Their validity was justified by multiple measurements of two reflections at various azimuthal angles.

Crystal Data

The crystals are rhombohedral, space group $R\bar{3}m$, with hexagonal unit cell dimensions at 23.5 ± 1 °C: $a = b = 8.588$ (3) Å, $c = 11.918$ (3) Å, $Z = 3$, $d_{calcd} = 3.345$ g cm^{-3}, $V = 761.23$ Å^3, mol wt 511.20, $\mu = 102.71$ cm^{-1}.

For the rhombohedral cell containing one molecule, $a = 6.354$ (2) Å and $\alpha = 85.04$ (2)°.

Structure Determination

The structure was solved by Fourier and least-squares methods. Scattering factors for neutral Xe, Se, O, and F were taken from Doyle

and Turner[9] and the anomalous dispersion correction was from Cromer and Liberman.[10] The Laue symmetry $\bar{3}m$ and the lack of systematic absences, other than those of the rhombohedral lattice, limit the choice of space groups to $R32$, $R3m$, and $R\bar{3}m$. The centric group $R\bar{3}m$ was adopted for reasons discussed later. The xenon atom is at the origin, and the positions of two selenium atoms above and below it on the threefold axis are obvious from the Patterson function. Electron density maps, phased by the heavy atoms, show the fluorine and oxygen atoms as peaks at the corners of an octahedron around each selenium atom, but because of the threefold symmetry no particular peak could be assigned to oxygen. On the basis of previous spectroscopic work[7] it was apparent that the oxygen atom of the OSeF$_5$ ligand was linked to the Xe atom. We made this assumption in the assignment of electron density peaks. We also assumed that in each orientation of the molecule the O–Xe–O angle was 180°. The molecules must have disorder among three orientations, with oxygen and fluorine in the three positions with one-third and two-thirds probability, respectively. The peak shapes are irregular and suggest that they are almost resolved into separate peaks for the alternate orientations.

Space group $R32$ offers no alternative for the positions of Xe and Se; $R3m$ permits two different Xe–Se distances, but such a difference is chemically unrealistic. Neither of these noncentric groups permits any escape from the orientational disorder, and in the face of the large amplitudes of thermal motion, together with the disorder, it is implausible that the lower symmetry could be maintained. For these reasons the centric group $R\bar{3}m$ was used in the analysis.

A model was tested which assigned a single atom to each peak (four distinct atoms in the asymmetric unit), with scattering power of one-third oxygen and two-thirds fluorine for the peak which bridged between Xe and Se. Least-squares refinement, with individual anisotropic thermal parameters (18 independent parameters in all), reduced $R_1 = \sum|\Delta F|/\sum|F_0|$ to 0.061 and $R_2 = [\sum w(\Delta F)^2/\sum w F_0^2]^{1/2}$ to 0.085 for 122 reflections. This model gives reasonably good agreement with the diffraction data but fails to give molecular dimensions which differentiate the role of oxygen and fluorine in the structure.

Several attempts were made to determine independent parameters for oxygen and fluorine, which of necessity were assigned to the three molecular orientations with one-third probability. Refinement reduced R_2 as low as 0.059, but the resulting bond distances and thermal parameters were unrealistic. We conclude that the data are insufficient to permit valid refinement of so many independent variables which are highly correlated with each other.

The model finally adopted, Figure 1, used this approach, but several chemically plausible constraints beyond those required by the space group were imposed. It consists of the superposition of three molecules with identical Xe and Se positions. One of these molecules is shown in Figure 2. The three crystallographically independent Se–F bond lengths are constrained to be equal, the F(1)–Se–F(3) bond angle is required to be 180°, and F(1) and F(3) are given equal thermal parameters, as are F(2) and O. These constraints on the thermal parameters are in harmony with the fact that selenium has the smallest thermal parameters of any atom in the structure, including xenon, and with the concept of a relatively rigid OSeF$_5$ group. The molecule has 2/m symmetry, and F(2) and O are constrained to lie in the mirror plane. With this model of six atoms in the asymmetric unit and anisotropic thermal parameters (22 independent parameters in all) the full-matrix least-squares refinement reduced R_2, the quantity

Table I. Atomic Parameters and Esd's[a]

Atom	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Xe	0	0	0	14.8 (2)	14.8	7.7 (2)	7.4	0	0
Se	0	0	0.2723 (2)	8.5 (2)	8.5	7.5 (2)	4.2	0	0
F(1)	−0.201 (2)	−0.074 (16)	0.207 (2)	9.7 (10)	23.5 (77)	11.0 (10)	8.7 (32)	−2.8 (9)	−1.2 (19)
F(2)	−0.077 (2)	0.077	0.378	13.7 (21)	13.7	12.4 (20)	10.8 (21)	−1.4 (6)	1.4
F(3)	0.201	0.074	0.337	9.7	23.5	11.0	8.7	−2.8	−1.2
O	0.055 (2)	−0.055	0.164 (5)	13.7	13.7	12.4	10.8	−1.4	1.4

[a] Estimated standard deviation of last digit is enclosed in parentheses; if none is given, the parameter is subject to a constraint. [b] The form of the temperature factor is $\exp[-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots)]$.

Table II. Bond Angles (deg) with Esd's

O–Xe–O	180[a]	F(2)–Se–F(3)	92 (3)
F(1)–Se–F(1')	88 (8)	F(2)–Se–O	170 (2)
F(1)–Se–F(2)	88 (3)	Xe–O–Se	125 (2)
F(1)–Se–F(3)	180[b]	F(3)–Se–F(3')	88 (8)
F(1)–Se–F(3')	92 (8)	F(3)–Se–O	95 (2)
F(1)–Se–O	85 (2)		

[a] By symmetry. The diffraction data, with the disorder, would permit alternative values of 141°, but these are rejected on chemical grounds. [b] Assumed value.
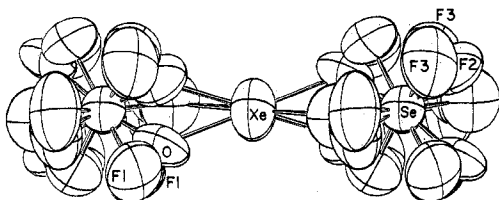
Figure 1. Xe(OSeF$_5$)$_2$ molecule. Disorder model.
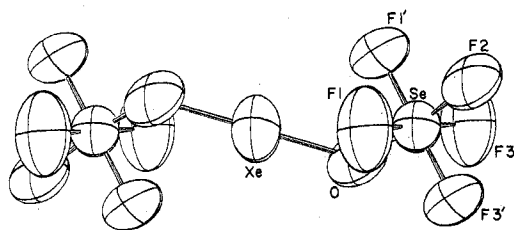
Figure 2. Xe(OSeF$_5$)$_2$ molecule as refined by least squares; three of these molecules are superimposed to give the disorder model shown in Figure 1.

minimized, to 0.080 and R_1 to 0.064 for 122 reflections with $F^2 > \sigma(F^2)$. We used $\sigma^2(F^2) = s^2(F^2) + (0.10F^2)^2$; $s^2(F^2)$ is the variance of F^2 based on counting statistics or alternatively that based on the scatter of measurements of equivalent reflections when the latter exceeds 16 times the former. The factor 0.10 which reduced the effect of strong reflections was chosen by trial and error to give a flat distribution of $\langle w(\Delta F)^2 \rangle$ as a function of magnitude of F; $w = (\sigma(F))^{-2}$, or zero for reflections weaker than $\sigma(F^2)$. The standard deviation of observation of unit weight was 1.345. In the last cycle, no parameter changed more that 0.0045σ. Final parameters are listed in Table I.

Discussion

The bond angles are listed in Table II. The F–Se–F angles in each OSeF$_5$ group, other than the two constrained to be 180°, are 90° within the experimental accuracy and thus correspond to a regular octahedral configuration. The O–Se–F(2) angle deviates by 10° from linearity, a deviation which, although outside the accuracy limits estimated by least squares, nevertheless has rather doubtful significance in view of the constrained nature of the model. For the same reason the Xe–O–Se angle, 125 (2)°, may not be as accurate as indicated.

The bond distances are Xe–O = 2.12 (5), Se–O = 1.53 (5), and Se–F = 1.70 (2) Å, uncorrected for thermal motion. It is clear that thermal motion effects are significant, and a
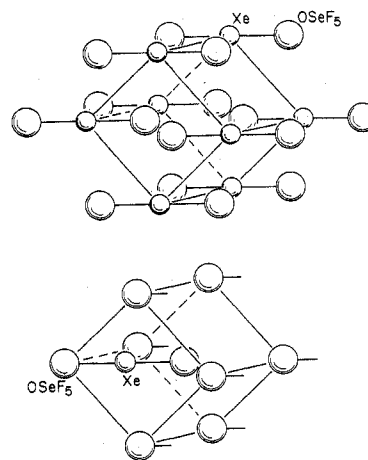

Figure 3. Molecular packing of Xe(OSeF$_5$)$_2$. The upper diagram shows the arrangement with respect to the primitive rhombohedral unit cell with $a = 6.354$ A and $\alpha = 85.04°$. The 3-fold axis is horizontal. In the lower diagram the origin is shifted to a fluoroselenate ion to show the nearly body-centered packing in the nearly cubic cell.

correction based on the riding model gives a weighted average of 1.77 Å for the Se–F bonds. Thermal corrections for bonds to oxygen are not reported because the thermal parameters of this atom were not determined independently and because the propriety of the riding model is doubtful. We estimate that the thermal effects for oxygen are less than for fluorine. Judging from data for other sulfur, selenium, and tellurium compounds the Se–O distance of 1.53 (5) Å appears to be too short. Probably it is unrealistically small because of the constraints imposed with our model.

Figure 3 shows how the dumbbell shaped molecules, one per primitive cell, pack in the pseudo-cubic rhombohedral unit cell. The packing is dominated by the interactions of the nearly spherical fluoroselenate groups; from this point of view the structure is nearly body-centered cubic. It is evident from a comparison of the vibrational spectra[7] of Xe(OSeF$_5$)$_2$ and OSeF$_5^-$ salts that the OSeF$_5$ group in the xenon compound is not simply ionic. In particular the ν(Se–O) in KOSeF$_5$ is ~920 cm^{-1} whereas in the xenon compound the highest frequency fundamentals lie at 791 and 731 cm^{-1}. Unfortunately the alkali oxopentafluoroselenates(VI) are all cubic[7] and the anions are evidently disordered. The OSeF$_5^-$ ion has therefore not been defined. We can be sure, however, that the O–Se distance in Xe(OSeF$_5$)$_2$ is longer than that which occurs in the discrete anion. Moreover, the Xe–O distance of 2.12 (5) Å is less than one would anticipate for a Xe^{2+} cation–OSeF$_5^-$ anion contact. The Xe–O distance is indeed not significantly different from the Xe–O distance of 2.155 (8) Å observed[6] in the FXe–OSO$_2$F compound. The Xe–O–Se angle of 125 (2)° is also similar to the Xe–O–S angle (123.7 (5)°) found[6] in FXeOSO$_2$F. Evidently the Xe–O bonding is essentially the same in both Xe(OSeF$_5$)$_2$ and FXeOSO$_2$F with the orbital hybridization of the oxygen atom approximately sp^2. It is of interest that the Xe–O–Se(S) angles are sig-

nificantly different from those recently observed[11] in these laboratories in the compound U(OTeF5)6 where the U–O–Te angle is ~170°. Although ligand crowding in the U(OTeF5)6 compound alone could account for the approach to linearity, it is also possible that π bonding throughout the U–O–Te three-center system may be the inherent reason for the greater angle. π-Bonding influences are considered by us to be much less likely for the Xe-containing systems. As in XeF2, FXeOSO2F, and related molecules we assume that the canonical forms (F5SeOXe)+OSeF5- and F5SeO-(XeOSeF5)+ are dominant.

Crystals of the corresponding tellurium compound, Xe(OTeF5)2, were found to be orthorhombic (space group *Cmca*),[5] but a detailed structure has not been determined. The unit cell and symmetry require the molecular axes to have two orientations rather than the single one found in the selenium compound. It is intriguing that the molecules of these two substances, which one supposes will be similar in size and shape (apart from the relatively subtle changes anticipated to accompany substitution of Se by Te), pack somewhat differently. It is of interest also that KrF2 and XeF2, which are both tetragonal, pack with two perpendicular orientations of the linear molecules in the krypton compound[12] and all parallel orientations in the xenon compound.[13] All of these molecules (to a first approximation at least) possess quadrupolar character but it is of interest that none adopts the *Pa*3 space group utilized by CO2.[14] It has been suggested that quadrupolar interactions determine the molecular orientations

of CO2 in this cubic structure.[15] Evidently the factors which determine the packing arrangement of such molecules are subtle indeed.

Registry No. Xe(OSeF5)2, 38344-58-0.

Supplementary Material Available: Listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

References and Notes

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(3) (a) K. Seppelt, *Angew. Chem.*, **84**, 715 (1972): *Angew. Chem., Int. Ed. Engl.*, **11**, 723 (1972). (b) K. Seppelt and D. Nothe, *Inorg. Chem.*, **12**, 2727 (1973).
(4) N. Bartlett and F. Sladky, "Comprehensive Inorganic Chemistry", Pergamon Press, Oxford and New York, 1973, p 213.
(5) F. Sladky, *Monatsh. Chem.*, **101**, 1559 (1970).
(6) N. Bartlett, M. Wechsberg, G. R. Jones, and R. D. Burbank, *Inorg. Chem.*, **11**, 1124 (1972).
(7) K. Seppelt, *Z. Anorg. Allg. Chem.*, **339**, 87 (1973).
(8) L. K. Templeton and D. H. Templeton, Abstracts, American Crystallographic Association Proceedings, Series 2, Vol. 1, 1973, p 143.
(9) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
(10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(11) L. K. Templeton, D. H. Templeton, N. Bartlett, and K. Seppelt, *Inorg. Chem.*, following paper in this issue.
(12) R. D. Burbank, W. E. Falconer, and W. A. Sunder, *Science*, **178**, 1285 (1972).
(13) S. Siegel and E. Gebert, *J. Am. Chem. Soc.*, **85**, 240 (1963).
(14) J. de Smedt, *Proc. K. Ned. Akad. Wet.*, **27**, 839 (1924).
(15) A. D. Buckingham, *Q. Rev., Chem. Soc.*, **13**, 183 (1959).

Crystal and Molecular Structure of Uranium Hexakis(oxopentafluorotellurate), U(OTeF5)6[1]

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Crystals of U(OTeF5)6 are monoclinic, space group *C2/m*, with cell dimensions at 23 °C: $a = 10.30$ (1), $b = 16.61$ (2), $c = 9.98$ (1) Å, $\beta = 114.14$ (6)°, $Z = 2$, $d_x = 3.562$ g cm^{-3}, $V = 1558.1$ Å^3. X-ray diffraction data obtained with an automatic diffractometer were refined to $R = 0.067$ for 781 independent reflections with $F^2 > \sigma(F^2)$, using anisotropic thermal parameters for all atoms except oxygen. The uranium atom is octahedrally bonded to six oxygen atoms and each tellurium atom has a pseudooctahedral coordination of one oxygen and five fluorine atoms. Average bond distances, uncorrected, are U–O = 2.05 (2), Te–O = 1.81 (2), and corrected for thermal motion, Te–F = 1.86 (4) Å. The bond angles at the two crystallographically different oxygen atoms are 170 and 171°. The globular molecules pack in triangular fashion in layers which stack to give each molecule ten nearest neighbors as in the body-centered-tetragonal structure of protactinium metal.

Introduction

Because of their potential technical value in isotope separation processes, and to extend our basic knowledge of the chemistry of uranium, we are interested in volatile compounds of this element with bulky and electronegative ligands. It is known that OSeF5 and OTeF5 are highly electronegative ligands, and the preparation of the transition metal derivatives CrO2(OSeF5)2, VO(OSeF5)3, Ti(OTeF5)4, and ClW(OTeF5)5[2] gave us confidence that uranium derivatives could be made. The preparation of U(OSeF5)6 has not yet been achieved, but good yields of U(OTeF5)6 have been obtained by two different methods.[3] The present paper describes a study by x-ray diffraction of its crystal and molecular structure.

Uranium hexakis(oxopentafluorotellurate), U(OTeF5)6, is a yellow crystalline solid, melting at 160 °C with slow decomposition. It can be sublimed at 60 °C under 10^{-2} mm of pressure to yield large crystals. It is very sensitive to water

and hydrolyzes rapidly. It was produced from UF6 by the reactions:

$$UF_6 + 2B(OTeF_5)_3 \rightarrow U(OTeF_5)_6 + 2BF_3$$

$$UF_6 + 6F_3SiOTeF_5 \rightarrow U(OTeF_5)_6 + 6SiF_4$$
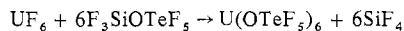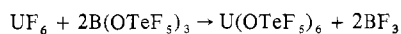
with yields of 96 or 97%. The reactions procede stepwise, and all the compounds (including isomers) F$_x$U(OTeF5)$_{6-x}$ have been observed in liquid mixtures produced when excess UF6 is used.[3] Only U(OTeF5)6 has been isolated in pure form.

Experimental Section

The preparation of U(OTeF5)6 is described elsewhere.[3] Crystals produced by sublimation or by recrystallization from CFCl3 were sealed in glass capillaries and examined by x-ray diffraction. Because none of the diffraction patterns were of high quality, a large number of crystals were examined by photographic (precession) and by counter methods.

Data sets were collected on two crystals, from two different crystallizations, with a Picker FACS-I diffractometer equipped with a graphite monochromator and Mo radiation (λ 0.7107 Å for Kα).

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