

nificantly different from those recently observed<sup>11</sup> in these laboratories in the compound  $\text{U}(\text{OTeF}_5)_6$  where the U–O–Te angle is  $\sim 170^\circ$ . Although ligand crowding in the  $\text{U}(\text{OTeF}_5)_6$  compound alone could account for the approach to linearity, it is also possible that  $\pi$  bonding throughout the U–O–Te three-center system may be the inherent reason for the greater angle.  $\pi$ -Bonding influences are considered by us to be much less likely for the Xe-containing systems. As in  $\text{XeF}_2$ ,  $\text{FXeOSO}_2\text{F}$ , and related molecules we assume that the canonical forms  $(\text{F}_3\text{SeOXe})^+\text{OSeF}_5^-$  and  $\text{F}_5\text{SeO}^-(\text{XeOSeF}_5)^+$  are dominant.

Crystals of the corresponding tellurium compound,  $\text{Xe}(\text{OTeF}_5)_2$ , were found to be orthorhombic (space group *Cmca*),<sup>5</sup> 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  $\text{KrF}_2$  and  $\text{XeF}_2$ , which are both tetragonal, pack with two perpendicular orientations of the linear molecules in the krypton compound<sup>12</sup> and all parallel orientations in the xenon compound.<sup>13</sup> All of these molecules (to a first approximation at least) possess quadrupolar character but it is of interest that none adopts the *Pa3* space group utilized by  $\text{CO}_2$ .<sup>14</sup> It has been suggested that quadrupolar interactions determine the molecular orientations

of  $\text{CO}_2$  in this cubic structure.<sup>15</sup> Evidently the factors which determine the packing arrangement of such molecules are subtle indeed.

Registry No.  $\text{Xe}(\text{OSeF}_5)_2$ , 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

- (1) Work supported by the U.S. Energy Research and Development Administration and by a grant (to K.S.) from the Deutsche Forschungsgemeinschaft.
- (2) To whom correspondence should be addressed at the Department of Chemistry, University of California.
- (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).

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## Crystal and Molecular Structure of Uranium Hexakis(oxopentafluorotellurate), $\text{U}(\text{OTeF}_5)_6$ <sup>1</sup>

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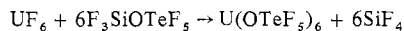
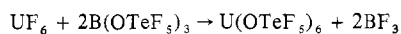
Crystals of  $\text{U}(\text{OTeF}_5)_6$  are monoclinic, space group *C2/m*, with cell dimensions at 23 °C:  $a = 10.30$  (1),  $b = 16.61$  (2),  $c = 9.98$  (1) Å,  $\beta = 114.14$  (6)°,  $Z = 2$ ,  $d_x = 3.562$  g cm<sup>-3</sup>,  $V = 1558.1$  Å<sup>3</sup>. X-ray diffraction data obtained with 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  $\text{OSeF}_5$  and  $\text{OTeF}_5$  are highly electronegative ligands, and the preparation of the transition metal derivatives  $\text{CrO}_2(\text{OSeF}_5)_2$ ,  $\text{VO}(\text{OSeF}_5)_3$ ,  $\text{Ti}(\text{OTeF}_5)_4$ , and  $\text{ClW}(\text{OTeF}_5)_5$ <sup>2</sup> gave us confidence that uranium derivatives could be made. The preparation of  $\text{U}(\text{OSeF}_5)_6$  has not yet been achieved, but good yields of  $\text{U}(\text{OTeF}_5)_6$  have been obtained by two different methods.<sup>3</sup> The present paper describes a study by x-ray diffraction of its crystal and molecular structure.

Uranium hexakis(oxopentafluorotellurate),  $\text{U}(\text{OTeF}_5)_6$ , 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  $\text{UF}_6$  by the reactions:



with yields of 96 or 97%. The reactions proceed stepwise, and all the compounds (including isomers)  $\text{F}_x\text{U}(\text{OTeF}_5)_{6-x}$  have been observed in liquid mixtures produced when excess  $\text{UF}_6$  is used.<sup>3</sup> Only  $\text{U}(\text{OTeF}_5)_6$  has been isolated in pure form.

### Experimental Section

The preparation of  $\text{U}(\text{OTeF}_5)_6$  is described elsewhere.<sup>3</sup> Crystals produced by sublimation or by recrystallization from  $\text{CFCl}_3$  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 ( $\lambda$  0.7107 Å for  $K\alpha$ ).

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Table I. Atomic Parameters and Estimated Standard Deviations (in Parentheses) for Uranium Hexakis(oxopentafluorotellurate),<sup>a</sup> U(OTeF<sub>5</sub>)<sub>6</sub>.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
U	0	0	0	5.95 (7)	6.41 (8)	5.07 (7)	0	1.24 (5)	0
Te(1)	0.2377 (2)	0	0.7869 (3)	8.7 (1)	11.9 (2)	9.3 (1)	0	4.5 (1)	0
Te(2)	0.2376 (2)	0.1614 (1)	0.2622 (2)	9.9 (1)	9.5 (1)	8.4 (1)	-2.63 (8)	2.73 (8)	-2.49 (7)
O(1)	0.111 (3)	0	0.871 (3)	11.4 (7) <sup>b</sup>					
O(2)	0.135 (2)	0.086 (1)	0.130 (2)	11.4 (5) <sup>b</sup>					
F(1)	0.340 (3)	0.234 (2)	0.394 (3)	25.0 (26)	21.0 (23)	18.1 (19)	-9.0 (21)	8.7 (19)	-8.8 (18)
F(2)	0.266 (6)	0.211 (2)	0.139 (4)	42.0 (57)	22.3 (25)	24.0 (28)	-15.3 (35)	21.4 (37)	-6.9 (26)
F(3)	0.095 (3)	0.214 (2)	0.241 (5)	15.2 (18)	22.3 (24)	29.6 (35)	2.8 (18)	5.6 (19)	-10.9 (27)
F(4)	0.225 (6)	0.112 (2)	0.398 (3)	47.8 (59)	25.7 (30)	12.6 (15)	-18.1 (38)	13.6 (26)	-4.6 (18)
F(5)	0.390 (3)	0.114 (3)	0.279 (5)	14.2 (17)	26.5 (31)	29.5 (36)	-1.1 (19)	4.0 (18)	-12.8 (30)
F(6)	0.339 (4)	0.075 (2)	0.910 (5)	21.2 (24)	27.7 (30)	32.9 (36)	-12.2 (24)	16.5 (28)	-14.9 (29)
F(7)	0.133 (3)	0.070 (2)	0.663 (4)	20.6 (25)	36.3 (43)	26.0 (27)	7.0 (26)	13.7 (23)	18.4 (31)
F(8)	0.349 (6)	0	0.710 (5)	42.6 (53)	53.3 (64)	29.1 (35)	0	23.2 (41)	0

<sup>a</sup> The form of the temperature factor is  $\exp[-0.25(h^2a^{*2}B_{11} + \dots + 2hka^*b^*B_{12} + \dots)]$  or  $\exp(-B\lambda^{-2} \sin^2 \theta)$ . <sup>b</sup> Isotropic *B*.

The best data set was collected on a yellow crystal of complex shape (ca. 0.19 × 0.044 × 0.22 mm). For the best set the  $\omega$  scan varied from sharp to fairly broad (0.1–0.4° half-width at half-peak-height) while on the first data set it was quite broad (0.35 to 0.75°). Unit cell dimensions were determined from the Bragg angles for seven reflections measured in the range 19° < 2 $\theta$  < 32°. Values based on all the setting angles of the same reflections were similar but were less precise because of the spread of orientation of the different mosaic blocks in the crystal.

Intensities were collected with the same instrument. The large angular mosaic spread of the crystals, the dimensions of the slit system, and limitations of the diffractometer program made it impossible to record valid integrated intensities by full scans of the peaks. Instead, we used a short scan of  $\theta-2\theta$  which yielded essentially a peak counting rate. This method had the advantage of improving the signal to background ratio for the high-angle reflections, which were weak enough even so. It had the risk of introducing systematic anisotropic errors into the thermal parameters, but such errors are not readily apparent in the final results. The scan was from 0.25° below the 2 $\theta$  angle for  $K\alpha_1$  to 0.25° above  $K\alpha_2$  at a rate of 1°/min. Background was counted for 10 s with an offset of 1.5° from each end of the scan. Three strong reflections (404, 004, 060) were checked at intervals of 200 measurements. One reflection (404) increased in intensity in an erratic manner while the other two showed no significant change; therefore no correction was made.

Absorption corrections calculated by an analytical integration<sup>4</sup> with the crystal shape described by seven faces ranged from 1.256 to 2.473. Their validity was justified by multiple measurements of several reflections at various azimuthal angles.

All the reflections within the sphere of reciprocal space up to 2 $\theta$  = 42° were measured, some more than once. Averaging of the 5346 reflections measured gave 884 that were unique and for 781 of them  $F^2 > \sigma(F^2)$ .

**Crystal Data.** The space group is *C2/m*; at 23 ± 1 °C, *a* = 10.30 (1), *b* = 16.61 (2), *c* = 9.98 (1) Å,  $\beta$  = 114.14 (6)°, *Z* = 2, *d<sub>x</sub>* = 3.562 g cm<sup>-3</sup>, mol wt = 1669.58, *V* = 1558.1 Å<sup>3</sup>.

**Determination of the Structure.** The coordinates of the uranium and tellurium atoms were obtained from the Patterson function. After four cycles of least-squares refinement of those three atoms ( $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.136$ ) a  $\Delta F$  Fourier map revealed the locations of the oxygen and fluorine atoms. Refinement of the 13 atoms in the asymmetric unit with anisotropic parameters for all atoms except for the two oxygens resulted in  $R = 0.067$  for 781 reflections with  $F^2 > \sigma(F^2)$  and using  $(0.12F^2)^2$  as the additional term in  $\sigma^2(F^2)$  to reduce the effect of strong reflections.  $R_2 = (\Sigma w(\Delta F)^2/\Sigma wF_o^2)^{1/2}$ , the quantity minimized, was 0.076 and  $R = 0.072$  for 884 reflections (includes zero-weighted data). The standard deviation of observation of unit weight was 1.044. The scattering factors used were those of Cromer and Waber<sup>5</sup> for the neutral tellurium atom, those of Doyle and Turner<sup>6</sup> for the neutral uranium, oxygen, and fluorine atoms, and the dispersion corrections from Cromer and Liberman<sup>7</sup> for all atoms. In the last cycle, no parameter changed more than 0.004 $\sigma$ . Final parameters are listed in Table I.

## Discussion

The molecular structure, Figure 1, consists of a uranium atom bonded octahedrally to six oxygen atoms and each of six tellurium atoms octahedrally bonded to an oxygen and five

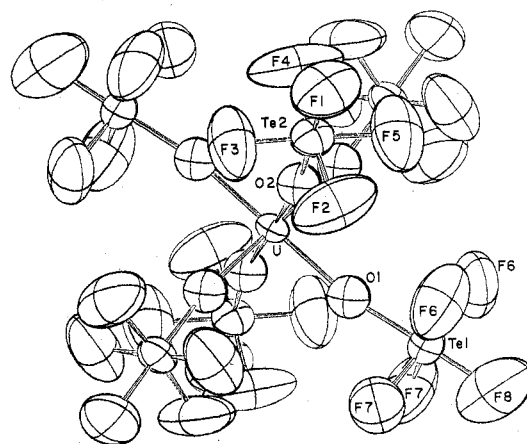


Figure 1. U(OTeF<sub>5</sub>)<sub>6</sub> molecule. The thermal ellipsoids are scaled to include 25% probability.

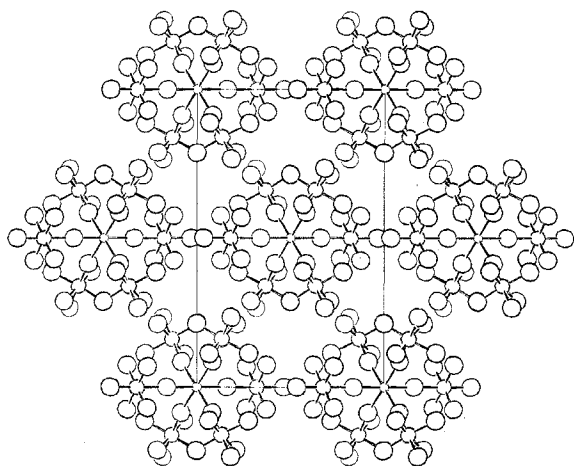
Table II. Bond Distances (Å)<sup>a</sup>

U–O(1)	2.04 (3)	
U–O(2)	2.05 (2)	
Te(1)–O(1)	1.82 (3)	
Te(1)–F(6)	1.76 (3)	[1.92]
Te(1)–F(7)	1.71 (3)	[1.88]
Te(1)–F(8)	1.62 (4)	[1.90]
Te(2)–O(2)	1.81 (2)	
Te(2)–F(1)	1.78 (2)	[1.89]
Te(2)–F(2)	1.61 (3)	[1.80]
Te(2)–F(3)	1.64 (3)	[1.80]
Te(2)–F(4)	1.64 (3)	[1.85]
Te(2)–F(5)	1.71 (3)	[1.86]
Te–F mean	1.69 (6) <sup>b</sup>	[1.86 (4)]

<sup>a</sup> Distances after correction for thermal motion by the riding model are given in brackets. <sup>b</sup> Standard deviation from the scatter.

Table III. Selected Bond Angles (deg)

O(1)–U–O(1)	180.0 (0)	O(2)–Te(2)–F(2)	92 (1)
O(2)–U–O(2)	180.0 (0)	O(2)–Te(2)–F(3)	93 (1)
O(1)–U–O(2)	89.6 (8)	O(2)–Te(2)–F(4)	92 (1)
O(1)–U–O(2)	90.4 (8)	O(2)–Te(2)–F(5)	90 (1)
O(2)–U–O(2)	91 (1)	F(1)–Te(2)–F(2)	89 (2)
O(2)–U–O(2)	89 (1)	F(1)–Te(2)–F(3)	88 (1)
O(1)–Te(1)–F(6)	91 (1)	F(1)–Te(2)–F(4)	87 (1)
O(1)–Te(1)–F(7)	88 (1)	F(1)–Te(2)–F(5)	90 (1)
O(1)–Te(1)–F(8)	179 (2)	F(2)–Te(2)–F(3)	94 (3)
F(6)–Te(1)–F(6)	90 (3)	F(1)–Te(2)–F(4)	174 (2)
F(6)–Te(1)–F(7)	92 (2)	F(2)–Te(2)–F(5)	82 (2)
F(6)–Te(1)–F(7)	177 (2)	F(3)–Te(2)–F(4)	90 (3)
F(6)–Te(1)–F(8)	90 (2)	F(3)–Te(2)–F(5)	176 (2)
F(7)–Te(1)–F(7)	85 (3)	F(4)–Te(2)–F(5)	94 (3)
F(7)–Te(1)–F(8)	91 (2)	U–O(1)–Te(1)	170 (2)
O(2)–Te(2)–F(1)	179 (1)	U–O(2)–Te(2)	171 (1)



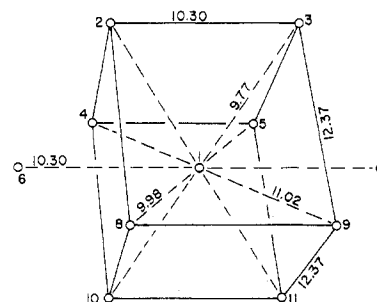
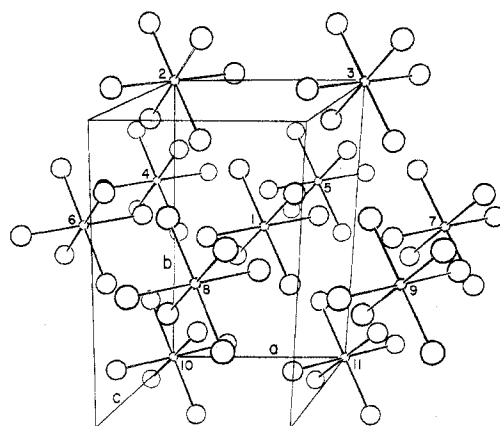
**Figure 2.** Molecular packing in the *ab* plane. The size of the atoms is arbitrary.

fluorines. O(1), Te(1), and F(8) are in the mirror plane and U is on a center of inversion. Bond lengths and angles are listed in Tables II and III. Average bond distances are U–O = 2.05, Te–O = 1.81, and Te–F = 1.69 Å with no correction for thermal motion. The bond angle at oxygen is 170 or 171° and the angles at the tellurium show octahedral coordination. The exceptionally large thermal parameters for fluorine, as well as evidence from Fourier maps, show that the fluoro-tellurate groups are undergoing angular motion of large amplitude. The Te–F distances are significantly affected by this thermal motion; after correction according to the riding model they average 1.86 Å, a more plausible value, and are more consistent with each other. Lacking anisotropic parameters for oxygen we do not report corrected values for its bond lengths, but we expect them to be less subject to this effect than the bonds to fluorine.

We have found no determination of the structure of any other uranium complex which is directly analogous to this one, but the average U–O distance, 2.05 (2) Å, is close to the value 2.08 Å assigned by Zachariasen<sup>8</sup> to U(VI)–O bonds of strength 1.0 according to results from oxide, uranate, and uranyl fluoride structures.

The bond distances in the  $\text{OTeF}_5^-$  ion in an alkali metal salt have not been determined and indeed the observed rhombohedral symmetry of the  $\text{NH}_4^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$  salts implies disordered structures.<sup>9</sup> The average Te–O distance, 1.81 (2) Å, may be compared with 1.909 (1) Å found for  $\text{Te}(\text{OH})_6$ .<sup>10</sup> Some of the difference is likely to be the result of thermal motion effects, and further work will be necessary to establish the magnitude of any remaining difference. The average Te–F distance, 1.86 (4) Å (corrected for thermal motion), is in harmony with 1.86 (1) Å found for  $\text{TeF}_6$  in the gas phase.<sup>11</sup>

The globular molecules pack in triangular fashion in layers, Figure 2, which stack to give each molecule ten nearest neighbors in a manner similar to the body-centered-tetragonal structure of protactinium metal.<sup>12</sup> Figure 3 shows the ten nearest neighbors of molecule 1. The top half shows the outline of the monoclinic cell and the bottom half shows the pseudotetragonal cell for the same 11 molecules. Uranium atoms labeled 2, 3, 10, and 11 are at 9.77; 5 and 8 at 9.98; 6 and 7 at 10.30; and 4 and 9 at 11.02 Å from atom 1. In the pseudotetragonal cell:  $a = b = 12.37$ ,  $c = 10.30$  Å,  $\alpha =$



**Figure 3.** Packing diagram. Only U and Te atoms are shown in the top half with an outline of the monoclinic cell. The lower half shows only U atoms and the pseudotetragonal cell. Numbering of the U atoms is the same in both halves.

$\beta = 95^\circ$ ,  $\gamma = 84^\circ$ . It is body centered and contains two molecules. The weak bonding between these molecules is reflected in the volatility of the compound which in spite of its high molecular weight can be sublimed at 60 °C. The same kind of molecular packing was observed in crystals of another globular and volatile complex of actinide ions, the hexa-fluoroacetylpyrazolide complex of uranium(IV) or thorium(IV).<sup>13</sup>

**Registry No.**  $\text{U}(\text{OTeF}_5)_6$ , 60282-51-1.

**Supplementary Material Available:** A listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

## References and Notes

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- (2) K. Seppelt, *Chem. Ber.*, **108**, 1823 (1975).
- (3) K. Seppelt, *Chem. Ber.*, **109**, 1046 (1976).
- (4) L. K. Templeton and D. H. Templeton, Abstracts, American Crystallographic Association Proceedings, Series 2, Vol. 1, 1973, p 143.
- (5) D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **18**, 104 (1965).
- (6) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
- (7) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (8) W. H. Zachariasen, *Acta Crystallogr.*, **7**, 795 (1954).
- (9) F. O. Sladky and N. Bartlett, unpublished observation.
- (10) O. Lindqvist and M. S. Lehman, *Acta Chem. Scand.*, **27**, 85 (1973).
- (11) K. Hedberg, private communication, and K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, *J. Chem. Phys.*, **44**, 1726 (1966).
- (12) W. H. Zachariasen, *Acta Crystallogr.*, **5**, 19 (1952).
- (13) K. Volz, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **15**, 1827 (1976).