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The Crystal and Molecular Structure of Potassium Monofluoroxenate(VI), $KXeO_3F$

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The crystal and molecular structure of potassium monofluoroxenate(VI), $KXeO_3F$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group C_{2v}^9-$Pn2_1a$ of the orthorhombic system with four molecules in a cell of dimensions $a = 7.374$ (5), $b = 6.811$ (5), $c = 8.185$ (6) Å. The calculated density is 3.835 g cm^{-3}. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.054 for the 830 independent reflections having $F^2 \geq 3\sigma(F^2)$. The crystal structure consists of infinite chains, parallel to the b axis, of XeO_3 units linked by bridging fluorine atoms, with the potassium cations at nonbonded distances from the oxygen and fluorine atoms. The geometry of the XeO_3 moiety is very similar to that of XeO_3 itself. The Xe–O distances are 1.75 (1), 1.76 (1), and 1.79 (1) Å, and the O–Xe–O bond angles are 97.8 (7), 100.5 (1.2), and 101.1 (9)°. The two independent Xe–F distances of 2.36 (1) and 2.48 (1) Å are considerably longer than the distances reported for nonbridging Xe–F bonds but are significantly shorter than the value of 3.5 Å predicted for nonbonded interactions between Xe and F. Thus, the description of this compound as a molecular addition complex of formula $K^+F^- \cdot XeO_3$ is incorrect, the correct formulation being $nK^+(XeO_3F^-)_n$.

Introduction

The preparation of a compound of formulation $CsFXeO_3$ was accomplished by Selig,[1] who exposed $CsF \cdot XeOF_4$ to the atmosphere. He also noted that the same compound is apparently obtained on slow hydrolysis of $CsXeF_7$. A more convenient method of preparation is by the action of CsF on XeO_3 solution.[2] This method can also be used to prepare the analogous rubidium and potassium compounds.

Selig originally proposed that these compounds are loosely bound molecular addition complexes of the type $MF \cdot XeO_3$,[1] since no absorptions occurred in the Xe–F bond stretching region. The $MFXeO_3$ compounds, however, are much more stable than XeO_3. XeO_3 detonates readily when subjected to physical shock and reacts explosively with methanol and other primary alcohols,[3] while $KFXeO_3$ is stable to shock and does not react with methanol. This enhanced stability favors the description of these compounds as ionic salts of the type $M^+XeO_3F^-$. The simple ionic salts of Xe(VI), however, are unstable: the reaction of NaOH on Xe(VI) solutions yields sodium perxenate, a salt of Xe(VIII), oxygen, and xenon.[4] Presumably, any Xe(VI) salt originally formed disproportionates to Xe(VIII) and Xe(IV), the Xe(IV) complex rapidly decomposing to give xenon and oxygen.

The molecular structures of several Xe(VI) molecular compounds of varying stability have been elucidated from diffraction and microwave data. XeO_3 has a pyramidal structure[5] very similar to those of IO_3^-[6] and NH_3.[7] All of these structures can be considered as distorted tetrahedra, with the lone pair of electrons on the central atom occupying the fourth coordination site. $XeOF_4$[8] and XeF_5^+[9] both have the square-pyramidal structure and may be considered as distorted octahedra with the lone pair on the Xe occupying the sixth coordination site. To this steric activity of the electron pair on the Xe atom may be ascribed the departure of XeF_6 from the octahedral geometry normally found in MF_6 complexes.[10] It has been suggested that the fluoride ion donor properties of XeF_6 result from the special stability of the octahedral configuration in Xe(VI) compounds; on donation of a fluoride ion XeF_6 becomes XeF_5^+ and can assume the distorted octahedral configuration mentioned above.[11]

A complete structural determination of $KFXeO_3$ was undertaken partly in the hope of resolving the problem of the two possible molecular descriptions discussed earlier and partly in order to increase our knowledge and understanding of the structures and bonding of Xe(VI) complexes in general.

Collection and Reduction of the X-Ray Data

Crystals of $KXeO_3F$ were generously supplied by Professors B. Jaselskis and T. M. Spittler and were loaded into quartz capillaries in a drybox. The capillaries had been evacuated for 2 days at 10^{-6} mm and 200° in order to ensure that they were free from

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(1) H. Selig, *Inorg. Chem.*, **5**, 183 (1966).

(2) T. M. Spittler, B. Jaselskis, and J. L. Huston, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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(5) D. H. Templeton, A. Zalkin, J. D. Forrester, and S. M. Williamson, *J. Am. Chem. Soc.*, **85**, 817 (1963).

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(10) B. Weinstock, E. E. Weaver, and C. P. Knop, *Inorg. Chem.*, **5**, 2189 (1966); L. S. Bartell, R. M. Gavin, Jr., H. B. Thompson, and C. L. Chernick, *J. Chem. Phys.*, **43**, 2547 (1965); K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, *ibid.*, **44**, 1726 (1966).

(11) N. Bartlett and F. O. Sladky, *J. Am. Chem. Soc.*, **90**, 5316 (1968).

moisture. On the basis of precession and Weissenberg photography using Mo Kα radiation we established that these crystals belong to the orthorhombic system. The observed extinctions are $0kl$ for $(k + l)$ odd and $hk0$ for h odd, which suggests that the space group is either D_{2h}^{16}-Pnma or C_{2v}^{9}-Pn2$_1$a. The former space group was initially chosen, but subsequent refinement of the data demonstrated that the acentric space group Pn2$_1$a is correct. The equivalent positions in Pn2$_1$a, an alternative setting of Pna2$_1$,[12] are: x, y, z; $\bar{x}, {}^1/_2 + y, \bar{z}$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 + z$; ${}^1/_2 + x, y, {}^1/_2 - z$.

The lattice constants, obtained by the least-squares procedure described below, are a = 7.374 (5), b = 6.811 (5), and c = 8.185 (6) Å. The observations were made at 23° with the wavelength of Mo Kα_1 radiation taken as 0.70930 Å. The density calculated for four molecules in the unit cell is 3.835 g cm^{-3}. Because of the high sensitivity of the compound to air, it was not possible to measure the density very accurately, but a pycnometric measurement with mercury as the liquid gave a value of 3.7 (3) g cm^{-3}, which is in agreement with the calculated value. Hence, if the correct space group assignment were Pnma, the K, Xe, and F atoms, plus at least one of the O atoms, would be constrained to lie on either the mirror plane or an inversion center. If, however, Pn2$_1$a were the correct space group, no crystallographic symmetry conditions would be imposed on the molecule.

Diffraction data were collected from a nearly spherical crystal of radius 0.025 cm enclosed in a quartz capillary. The intensity data were collected on a Picker four-circle automatic X-ray diffractometer, using Mo Kα radiation. The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique. The width at half-height for a typical strong reflection was found to be approximately 0.15°. This value is rather larger than we would normally consider acceptable, but in view of the instability of the compound and the difficulty of obtaining good crystals, we were forced to use this crystal. The general shape of the ω scans was symmetric and not split, which indicates that, while the mosaicity is rather high, this is a single crystal.[13] Twelve high-angle reflections from the crystal were accurately centered through a narrow vertical slit at a takeoff angle of 0.5°. These observations formed the basis for the least-squares refinement of cell parameters and crystal orientation; the refinement was effected in our program PICK as previously described.[14]

Intensity data were collected at a takeoff angle of 1.4°; at this angle the peak intensity of a typical strong reflection is about 75% of the maximum value as a function of the takeoff angle. The receiving aperture was 4.0 mm high by 4.0 mm wide and was placed 29 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 2.0°/min. The scan range for all reflections was 2.0° in 2θ, from -0.90 to $+1.10$° from the calculated value of 2θ. Stationary-counter, stationary-crystal background counts of 4 sec were taken at the end of each scan. The relatively large scan range was necessitated by the high mosaicity of the crystal. The relatively high scan rate and short background counting time were used in order to minimize exposure of the crystal to radiation, since preliminary indications were that slow decomposition occurs when the compound is subjected to X-rays. The diffracted Mo Kα beam was filtered through 4.5-mil Zr foil. Automatic attenuators were inserted when the intensity of the beam exceeded about 7000 counts/sec. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak.

A unique data set having $2\theta \leq 70°$ was gathered; a total of 956 independent intensities were recorded. No data were collected at values of $2\theta > 70°$, since very few reflections were above background in this range. The intensities of three standard reflections, measured after every 50 reflections, steadily diminished throughout the run. This diminution of intensity, presumably due to partial crystal decomposition in the X-ray beam, was plotted against cumulative X-ray exposure, and a least-squares fit was made. The observed intensities of all reflections were appropriately scaled upward to take into account this attenuation, which was such that the intensity of a typical standard reflection at the end of the run was only 75% of its original value.

All data processing was carried out as previously described.[14] The value of p in the expression

$$\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

was taken as 0.06. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization factors, and a spherical absorption correction was applied. The linear absorption coefficient, μ, for this compound for Mo Kα radiation is 94.7 cm^{-1}, and for the sample chosen the spherical absorption correction factor A^* at $\theta = 0°$ is 21.5.[15] Of the 956 independent reflections which were processed, 46 were less than their estimated standard deviations.

Solution and Refinement

The positions of the Xe and K atoms were determined from the three-dimensional Patterson function,[16] and these coordinates were refined by least-squares procedures. All least-squares refinements were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$.

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(12) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 119.

(13) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electic Co., Milwaukee, Wis., 1957.

(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(15) See ref 12, Vol. II, p 302.

(16) In addition to various local programs, programs for the CDC 6400 used in this analysis were local modifications of Zalkin's FORDAP Fourier program, Busing and Levy's ORFFE function and error and ORFLS least-squares programs, and Johnson's ORTEP thermal ellipsoid plotting program.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $KXeO_3F$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Xe	0.09468 (7)[b]	0.25[c]	0.15235 (7)	0.00782 (9)	0.0101 (1)	0.00981 (9)	−0.0006 (1)	−0.00001 (6)	0.0020 (1)
K	0.3802 (4)	0.7182 (5)	0.1465 (4)	0.0119 (4)	0.0147 (11)	0.0132 (4)	−0.0015 (4)	−0.0011 (3)	0.0024 (4)
F	0.045 (1)	0.597 (1)	0.073 (1)	0.017 (1)	0.016 (2)	0.013 (1)	−0.001 (1)	−0.003 (1)	0.001 (1)
O_1	0.290 (2)	0.254 (5)	0.032 (2)	0.021 (3)	0.031 (4)	0.034 (3)	−0.009 (5)	0.017 (3)	−0.008 (6)
O_2	0.170 (2)	0.382 (3)	0.329 (1)	0.030 (4)	0.025 (4)	0.010 (2)	−0.010 (3)	−0.010 (2)	0.005 (2)
O_3	0.109 (2)	0.011 (2)	0.235 (2)	0.015 (2)	0.015 (2)	0.019 (2)	−0.001 (2)	−0.002 (2)	0.007 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Figures in parentheses here and elsewhere in this paper are the estimated standard deviations of the least significant digits. [c] Polar space group $Pn2_1a$ requires one y parameter to be fixed.

In all calculations of F_c, the atomic scattering factor for Xe was taken from Cromer and Waber;[17] scattering factors for all other atoms were taken from the tabulation of Ibers.[18] The effects of anomalous dispersion were included in calculations of F_c,[19] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[20] Of the 956 independent reflections, 830 were greater than three times their estimated standard deviations. Only these reflections were used in the refinement of the structure.

Initially, the Xe and K atoms were assigned fixed isotropic thermal parameters. After two cycles of least-squares refinement in space group Pnma, with the atoms constrained to lie on the mirror plane, the agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (or weighted R factor) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ were 0.159 and 0.227, respectively. A difference Fourier synthesis at this stage showed the presence of light atoms in three apparently general positions and one apparently special position of space group Pnma. Examination of the difference map also suggested that the K atom was not located exactly on the mirror plane. From this combination of evidence, we deduced that the correct space group must be $Pn2_1a$, in which all fourfold positions are general. Two cycles of least-squares refinement of the Xe and K parameters, with anisotropic thermal parameters assigned to both atoms, yielded values of R_1 and R_2 of 0.107 and 0.165, respectively.

A difference Fourier synthesis run at this time was complicated by the presence of a false mirror plane which arises because the y coordinates of the Xe and K atoms differ by approximately 0.5. The positions of the light atoms were found to be at the four highest independent peaks in the map; these peaks were all found to be approximately 1 e Å^{-3} larger than their mirror-related peaks. Two cycles of least-squares calculation, with anisotropic thermal parameters assigned to all atoms, and with all four light atoms assumed to be oxygen atoms, led to values of R_1 and R_2 of 0.055 and 0.071, respectively. Three of these light atoms were found to lie between 1.72 and 1.82 Å from the Xe atom, while the fourth was more than 2.3 Å from the Xe. It was decided that this distant atom must be the F atom; one cycle of least-squares refinement with this atom as F instead of O gave values of R_1 and R_2 of 0.054 and 0.0693, respectively. This significant improvement in R_2 supports our choice of this atom as F. Attempts to distinguish between these two models by examination of the root-mean-square amplitudes of vibration of the atom under consideration[21,22] were inconclusive. It would appear that this method is only successful when the data are relatively free from systematic errors; in the present study there are errors due to the approximate nature of the absorption correction.

The Xe–O bond lengths obtained from this latest least-squares calculation were 1.73 (1), 1.75 (1), and 1.81 (1) Å, which is a surprisingly large range for three apparently equivalent bonds. The standard deviation of the Xe–O length calculated from the spread of these three distances is 0.044 Å, as compared with values of approximately 0.012 Å estimated from the least-squares refinement; these two estimates of the standard deviation of an Xe–O bond length would be expected to be approximately equal, and this large difference between the two values would normally be disturbing. At this stage, however, we did not know if the form which we had collected was $\{hkl\}$ or $\{\bar{h}\bar{k}\bar{l}\}$; these two forms are not equivalent in the acentric space group $Pn2_1a$. Two cycles of least-squares refinement were run with the substitution of $\bar{h}\bar{k}\bar{l}$ for hkl. The values of R_1 and R_2 obtained were 0.054 and 0.0691, respectively, a slight improvement in R_2. The range of Xe–O distances was greatly reduced, the values being 1.75 (1), 1.76 (1), and 1.79 (1) Å. The standard deviation calculated from the spread of these Xe–O distances is 0.019 Å, which is in fairly good agreement with the value of 0.012 Å estimated from the least-squares refinement. The changes in the individual Xe–O bond lengths were in excellent agreement with those calculated from the polar dispersion error model of Ueki, Zalkin, and Templeton.[23] This reversed-polarity model was accepted as being the correct description of this particular crystal because of the more reasonable chemical model which it provides. The slight im-

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(17) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(18) See ref 12, Vol. III, Table 3.3.1.

(19) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(20) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(21) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967).

(22) D. J. Hodgson and J. A. Ibers, *ibid.*, **7**, 2345 (1968).

(23) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **20**, 836 (1966); D. W. J. Cruickshank and W. S. McDonald, *ibid.*, **23**, 9 (1967).

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) IN ELECTRONS FOR $KXeO_3F$

H	L	FO	FC
**** K = -10 *****			
-4	-2	65	53
-4	-1	153	149
-4	0	196	182
-3	-4	102	152
-3	-3	71	61
-3	-2	245	230
-2	-5	229	234
-2	-4	62	70
-2	-3	86	79
-2	-1	235	231
-2	0	94	93
-1	-5	57	38
-1	-4	93	91
-1	-3	240	241
-1	-2	130	150
-1	-1	149	146
0	-4	197	193
0	-2	112	99
0	0	257	278
**** K = -9 *****			
-6	-3	54	63
-6	-2	55	47
-6	-1	232	216
-6	0	130	133
-5	-4	175	165
-5	-2	298	276
-4	-6	127	123
-4	-5	187	191
-4	-4	146	143
-4	-3	57	56
-4	-2	67	68
-4	-1	223	218
-4	0	260	246
-3	-4	64	57
-3	-3	346	332
-3	-2	106	92
-3	-1	240	227
-2	-6	185	197
-2	-5	91	105
-2	-4	217	220
-2	-2	133	133
-2	-1	138	127
-2	0	413	383
-1	-7	116	123
-1	-6	105	117
-1	-4	166	170
-1	-3	187	199
-1	-2	311	308
-1	-1	150	147
0	-7	93	105
0	-5	268	299
0	-3	114	112
0	-1	369	376
**** K = -8 *****			
-8	-1	225	218
-7	-4	145	155
-7	-3	159	148
-7	-2	243	238
-7	-1	105	93
-6	-6	187	172
-6	-5	110	100
-6	-4	194	193
-6	-3	57	33
-6	-2	113	106
-6	-1	143	132
-6	0	347	310
-5	-7	197	197
-5	-4	58	57
-5	-3	149	353
-5	-2	72	77
-5	-1	250	240
-4	-7	73	66
-4	-6	193	199
-4	-5	211	216
-4	-4	217	213
-4	-3	94	92
-4	-2	138	129
-4	-1	267	256
-4	0	370	345
-3	-8	207	207
-3	-6	148	158
-3	-4	268	262
-3	-3	86	85
-3	-2	446	440
-3	-1	55	57
-2	-7	100	105
-2	-6	87	92
-2	-5	316	346
-2	-4	119	120
-2	-3	108	109
-2	-2	84	70
-2	-1	441	424
-2	0	207	181
-1	-9	101	104
-1	-8	124	133
-1	-7	183	210
-1	-6	86	105
-1	-4	147	155
-1	-3	363	387
-1	-2	273	285
-1	-1	276	250
0	-6	380	402
0	-4	321	350
0	-2	200	202
0	0	624	611
**** K = -7 *****			
-9	-2	177	164
-9	-1	141	136
-8	-4	206	210
-8	-2	95	96
-8	0	319	307
-7	-6	71	70
-7	-4	106	109
-7	-3	272	277
-7	-2	160	166
-7	-1	196	192
-6	-7	90	91
-6	-6	120	119
-6	-5	306	299
-6	-4	168	161
-6	-3	115	103
-6	-2	60	42
-6	-1	325	312
-6	0	258	242
-5	-8	242	230
-5	-7	67	71
-5	-6	171	178
-5	-4	244	265
-5	-3	113	110
-5	-2	474	472
-5	-1	58	46
-4	-9	84	95
-4	-7	90	91
-4	-6	212	216
-4	-5	288	292
-4	-4	233	233
-4	-3	111	121
-4	-2	124	117
-4	-1	333	321
-4	0	375	342
-3	-9	144	141
-3	-7	262	290
-3	-6	61	72
-3	-5	68	59
-3	-4	62	61
-3	-3	503	513
-3	-2	160	159
-3	-1	392	300
-2	-9	65	72
-2	-8	82	90
-2	-7	59	54
-2	-6	359	337
-2	-5	184	194
-2	-4	413	440
-2	-3	57	29
-2	-2	231	219
-2	-1	172	170
-1	-9	91	79
-1	-8	247	256
-1	-7	159	173
-1	-6	188	218
-1	-4	316	331
-1	-3	270	291
-1	-2	465	481
-1	-1	212	210
0	-9	168	175
0	-7	167	168
0	-5	451	513
0	-3	149	154
0	-1	523	529
**** K = -6 *****			
-9	-4	118	126
-9	-3	150	155
-9	-2	216	214
-9	-1	90	87
-8	-5	280	291
-8	-4	59	68
-8	-3	99	91
-8	-1	292	291
-8	0	97	91
-7	-7	138	130
-7	-6	152	158
-7	-4	214	228
-7	-3	241	241
-7	-2	369	364
-7	-1	166	154
-6	-8	70	70
-6	-6	272	268
-6	-5	153	158
-6	-4	309	307
-6	-3	66	45
-6	-2	134	135
-6	-1	132	130
-6	0	492	465
-5	-9	161	150
-5	-7	295	284
-5	-3	439	452
-5	-2	117	122
-5	-1	341	332
-4	-10	172	162
-4	-9	115	117
-4	-8	91	86
-4	-7	112	120
-4	-6	316	322
-4	-5	308	316
-4	-4	383	391
-4	-3	171	193
-4	-2	197	178
-4	-1	404	392
-4	0	593	554
-3	-10	62	76
-3	-8	433	431
-3	-7	64	79
-3	-6	262	273
-3	-4	353	365
-3	-3	121	130
-3	-2	712	711
-3	-1	66	43
-2	-10	109	79
-2	-9	168	166
-2	-8	53	47
-2	-7	147	160
-2	-6	125	136
-2	-5	460	508
-2	-4	207	207
-2	-3	222	223
-2	-2	97	83
-2	-1	537	527
-2	0	344	314
-1	-11	61	61
-1	-10	58	56
-1	-9	174	168
-1	-8	211	222
-1	-7	253	248
-1	-6	159	181
-1	-5	57	34
-1	-4	218	229
-1	-3	406	531
-1	-2	484	486
-1	-1	419	415
0	-10	257	255
0	-8	98	120
0	-6	424	493
0	-4	590	629
0	-2	239	215
0	0	1027	1021
**** K = -5 *****			
10	-3	70	66
10	-1	224	229
10	0	104	90
-9	-6	83	93
-9	-4	139	134
-9	-3	271	277
-9	-2	246	235
-9	-1	197	189
-8	-6	227	240
-8	-4	278	289
-8	-3	52	41
-8	-2	138	157
-8	0	446	449
-7	-8	108	102
-7	-7	199	204
-7	-6	74	83
-7	-5	55	25
-7	-4	148	140
-7	-3	335	342
-7	-2	216	212
-7	-1	224	229
-6	-9	163	150
-6	-8	59	66
-6	-7	140	131
-6	-6	200	189
-6	-5	407	412
-6	-4	297	210
-6	-3	134	118
-6	-2	139	128
-6	-1	472	473
-6	0	417	403
-5	-9	54	40
-5	-8	335	332
-5	-7	90	90
-5	-6	260	258
-5	-5	69	40
-5	-4	372	375
-5	-3	160	156
-5	-2	710	713
-5	-1	134	133
-4	-10	157	153
-4	-9	129	124
-4	-8	58	60
-4	-7	106	100
-4	-6	307	310
-4	-5	334	343
-4	-4	346	346
-4	-3	123	116
-4	-2	195	190
-4	-1	447	422
-4	0	697	644
-3	-11	96	76
-3	-9	202	192
-3	-8	128	114
-3	-7	306	326
-3	-6	106	103
-3	-5	65	44
-3	-4	177	181
-3	-3	697	700
-3	-2	267	254
-3	-1	433	417
-2	-11	66	55
-2	-10	277	273
-2	-9	74	77
-2	-8	120	136
-2	-7	73	81
-2	-6	472	506
-2	-5	262	275
-2	-4	616	641
-2	-3	95	85
-2	-1	337	316
-2	0	1176	1111
-1	-9	110	125
-1	-8	450	371
-1	-7	221	228
-1	-6	271	305
-1	-5	63	66
-1	-4	476	494
-1	-3	408	417
-1	-2	486	476
-1	-1	366	340
0	-11	179	167
0	-9	210	231
0	-7	162	170
0	-5	345	398
0	-3	212	210
0	-1	746	741
**** K = -4 *****			
11	-1	156	165
10	-5	116	114
10	-4	205	207
10	-2	104	102
10	-1	117	119
10	0	344	353
-9	7	108	8
-9	6	104	9
-9	4	147	147
-9	-3	180	181
-9	-2	266	282
-9	-1	126	114
-8	-7	111	107
-8	-5	334	357
-8	-4	87	84
-8	-3	116	118
-8	-1	405	430
-8	0	159	156
-7	-9	91	84
-7	-8	255	236
-7	-7	175	179
-7	-6	207	204
-7	-4	287	291
-7	-3	422	436
-7	-2	546	557
-7	-1	192	184
-6	-10	206	184
-6	-8	86	80
-6	-6	367	370
-6	-5	116	101
-6	-4	407	416
-6	-2	244	248
-6	-1	222	220
-6	0	741	722
-5	-9	185	168
-5	-7	331	329
-5	-5	80	56
-5	-4	56	44
-5	-3	658	600
-5	-2	98	103
-5	-1	489	455
-4	-11	137	118
-4	-10	231	209
-4	-9	169	161
-4	-8	110	94
-4	-7	169	165
-4	-6	380	382
-4	-5	457	469
-4	-4	540	538
-4	-3	121	96
-4	-2	351	334
-4	-1	631	586
-4	0	1024	955
-3	-10	74	63
-3	-9	62	46
-3	-8	451	454
-3	-7	80	63
-3	-6	373	400
-3	-4	650	656
-3	-3	206	199
-3	-2	1085	1032
-3	-1	113	102
-2	-11	161	150
-2	-10	113	104
-2	-9	207	214
-2	-8	57	56
-2	-7	138	142
-2	-6	245	260
-2	-5	560	567
-2	-4	274	271
-2	-3	65	63
-2	-2	314	292
-2	-1	767	730
-2	0	403	359
-1	-12	111	97
-1	-11	81	74
-1	-9	183	193
-1	-8	289	325
-1	-7	363	405
-1	-6	283	232
-1	-5	136	129
-1	-4	464	478
-1	-3	801	810
-1	-2	492	463
-1	-1	449	429
0	-12	88	81
0	-10	311	344
0	-8	181	205
0	-6	647	691
0	-4	721	789
0	-2	528	515
0	0	1461	1522
**** K = -3 *****			
11	-2	218	229
10	-6	62	54
10	-5	242	251
10	-3	92	78
10	-1	253	267
10	0	76	75
-9	-7	177	198
-9	-6	124	133
-9	-4	163	179
-9	-3	342	349
-9	-2	293	301
-9	-1	234	233
-8	-8	60	61
-8	-6	318	324
-8	-5	60	32
-8	-4	390	392
-8	-2	205	210
-8	-1	88	82
-8	0	444	558
-7	-9	129	114
-7	-8	119	112
-7	-7	255	252
-7	-6	88	88
-7	-5	85	66
-7	-4	155	144
-7	-3	405	412
-7	-2	254	253
-7	-1	241	232
-6	-10	138	119
-6	-9	186	171
-6	-8	80	56
-6	-7	182	179
-6	-6	277	281
-6	-5	515	529
-6	-4	299	309
-6	-3	172	165
-6	-2	156	145
-6	0	510	483
-5	-10	54	42
-5	-9	56	48
-5	-8	465	449
-5	-7	99	95
-5	-6	357	354
-5	-4	512	504
-5	-3	191	176
-5	-2	1038	997
-5	-1	241	229
-4	-11	137	101
-4	-10	202	195
-4	-9	141	126
-4	-7	146	135
-4	-6	375	382
-4	-5	425	411
-4	-4	505	493
-4	-3	117	99
-4	-2	176	158
-4	-1	463	426
-4	0	1067	1002
-3	-12	64	44
-3	-9	261	249
-3	-8	187	186
-3	-7	405	413
-3	-6	156	167
-3	-5	62	44
-3	-4	343	348
-3	-3	406	492
-3	-2	409	402
-3	-1	635	607
-2	-12	79	81
-2	-11	101	92
-2	-10	363	332
-2	-9	74	74
-2	-8	148	147
-2	-7	112	102
-2	-6	672	676
-2	-5	306	321
-2	-4	952	978
-2	-3	187	182
-2	-2	442	414
-2	-1	521	484
-1	-12	182	165
-1	-10	76	75
-1	-9	150	161
-1	-8	477	494
-1	-7	254	251
-1	-6	400	410
-1	-5	105	87
-1	-4	577	619
-1	-2	1494	1476
-1	-1	818	564
0	-11	181	194
0	-9	196	217
0	-7	230	235
0	-5	564	611
0	-3	455	479
0	-1	1056	987
**** K = -2 *****			
11	-4	57	52
11	-3	272	279
11	-2	110	119
11	-1	173	190
10	-6	195	216
10	-5	141	149
10	-4	259	263
10	-3	55	46
10	-2	101	106
10	-1	160	166
10	0	387	398
-9	-8	159	158
-9	-7	122	103
-9	-6	102	103
-9	-4	150	168
-9	-3	181	193
-9	-2	321	325
-9	-1	110	115
-8	-9	139	138
-8	-7	141	135
-8	-6	97	84
-8	-5	412	439
-8	-4	112	110
-8	-3	140	148
-8	-1	436	459
-8	0	134	133
-7	-9	119	102
-7	-8	332	311
-7	-7	218	216
-7	-6	286	277
-7	-4	354	371
-7	-3	412	427
-7	-2	683	679
-7	-1	232	237
-6	-10	229	211
-6	-9	61	40
-6	-8	90	74
-6	-7	85	79
-6	-6	458	459
-6	-5	114	118
-6	-4	517	537
-6	-3	144	133
-6	-2	245	236
-6	-1	127	125
-6	0	859	831
-5	-11	73	64
-5	-9	224	220
-5	-7	382	343
-5	-6	62	38
-5	-5	99	67
-5	-4	126	125
-5	-3	693	677
-5	-2	48	28
-5	-1	475	537
-4	-12	71	62
-4	-11	157	135
-4	-10	292	297
-4	-9	184	180
-4	-8	114	105
-4	-7	182	192
-4	-6	434	542
-4	-5	543	554
-4	-4	821	802
-4	-3	253	240
-4	-2	332	307
-4	-1	638	638
-4	0	1138	1058
-3	-12	210	181
-3	-9	53	45
-3	-8	583	576
-3	-7	68	57
-3	-6	526	511
-3	-5	95	88
-3	-4	789	790
-3	-3	113	106
-3	-2	1505	1430
-3	-1	98	93
-2	-11	177	173
-2	-10	134	125
-2	-9	199	203
-2	-8	62	55
-2	-7	238	250
-2	-6	289	285
-2	-5	765	793
-2	-4	419	420
-2	-3	254	246
-2	-2	335	309
-2	-1	642	605
-2	0	570	495
-1	-12	134	120
-1	-11	79	67
-1	-9	217	235
-1	-8	368	420
-1	-7	406	476
-1	-6	337	346
-1	-5	101	98
-1	-4	467	493
-1	-3	817	871
-1	-2	1227	1210
-1	-1	547	498
0	-12	106	95
0	-10	372	436
0	-8	175	173
0	-6	889	947
0	-4	1132	1270
0	-2	378	342
0	0	2219	2228
**** K = -1 *****			
11	-4	154	148
11	-2	251	264
10	-7	85	97
10	-5	248	253
10	-3	84	94
10	-1	286	308
10	0	66	72
-9	-8	169	162
-9	-7	222	220
-9	-6	142	142
-9	-4	144	192
-9	-3	371	390
-9	-2	359	379
-9	-1	259	242
-8	-8	70	61
-8	-6	332	324
-8	-5	70	73
-8	-4	425	442
-8	-2	224	224
-8	-1	86	89
-8	0	648	682
-7	-9	157	146
-7	-8	146	133
-7	-7	261	240
-7	-6	137	123
-7	-5	62	61
-7	-4	173	134
-7	-3	442	456
-7	-2	258	269
-7	-1	297	314
-6	-11	163	144
-6	-10	174	152
-6	-9	189	173
-6	-8	80	64
-6	-7	167	159
-6	-6	267	270
-6	-5	502	558
-6	-4	386	393
-6	-3	154	158
-6	-2	116	114
-6	-1	668	642
-6	0	733	741
-5	-8	475	435
-5	-7	197	196
-5	-6	392	383
-5	-5	61	60
-5	-4	610	611
-5	-3	244	237
-5	-2	1335	1236
-5	-1	233	211
-4	-11	141	135
-4	-10	216	217
-4	-9	128	131
-4	-8	114	110
-4	-7	134	149
-4	-6	454	450
-4	-5	444	440
-4	-4	542	514
-4	-3	162	151
-4	-2	303	282
-4	-1	570	541
-4	0	1015	923
-3	-12	69	62
-3	-11	83	79
-3	-9	238	235
-3	-8	142	147
-3	-7	483	435
-3	-6	199	194
-3	-5	119	113
-3	-4	205	206
-3	-3	1115	1053
-3	-2	547	524
-3	-1	485	446
-2	-12	90	98
-2	-11	78	82
-2	-10	375	395
-2	-9	137	135
-2	-8	184	191
-2	-7	85	78
-2	-6	877	916
-2	-5	417	435
-2	-4	1176	1203
-2	-3	179	174
-2	-2	894	850
-2	-1	300	341
-2	0	2321	2153
-1	-13	78	69
-1	-12	207	175
-1	-9	123	131
-1	-8	499	575
-1	-7	270	275
-1	-6	505	541
-1	-5	97	107
-1	-4	850	945
-1	-3	320	335
-1	-2	1450	1521
-1	-1	438	432
0	-11	230	213
0	-9	232	274
0	-7	304	343
0	-5	751	878
0	-1	1187	1250
**** K = 0 *****			
11	-3	278	295
11	-2	119	135
11	-1	191	190
10	-7	56	50
10	-6	204	223
10	-5	144	160
10	-4	259	256
10	-2	129	145
10	-1	153	165
10	0	408	430
-9	-8	168	177
-9	-7	142	138
-9	-6	134	136
-9	-4	176	183
-9	-3	212	224
-9	-2	317	330
-9	-1	95	98
-8	-9	171	155
-8	-8	61	53
-8	-7	138	124
-8	-6	92	80
-8	-5	415	437
-8	-4	100	94
-8	-3	96	87
-8	-2	85	76
-8	-1	490	503
-8	0	148	151
-7	-9	131	129
-7	-8	358	334
-7	-7	242	238
-7	-6	291	276
-7	-5	54	5
-7	-4	450	484
-7	-3	425	458
-7	-2	705	722
-7	-1	290	285
-6	-10	261	227
-6	-9	74	76
-6	-8	130	106
-6	-7	68	61
-6	-6	441	434
-6	-5	129	121
-6	-4	529	506
-6	-3	51	43
-6	-2	293	281
-6	-1	175	164
-6	0	984	943
-5	-11	91	55
-5	-10	58	35
-5	-9	211	224
-5	-8	52	34
-5	-7	378	343
-5	-5	158	153
-5	-3	797	759
-5	-2	138	119
-5	-1	533	541
-4	-12	79	57
-4	-11	131	150
-4	-10	304	303
-4	-9	176	191
-4	-8	140	138
-4	-7	143	147
-4	-6	592	591
-4	-5	431	426
-4	-4	811	787
-4	-3	353	332
-4	-2	642	614
-4	-1	846	776
-4	0	1506	1415
-3	-12	200	191
-3	-8	517	564
-3	-6	467	473
-3	-5	55	40
-3	-4	940	907
-3	-2	1888	1734
-3	-1	358	306
-2	-11	230	215
-2	-10	153	162
-2	-9	214	214
-2	-8	77	45
-2	-7	246	252
-2	-6	155	153
-2	-5	641	687
-2	-4	437	456
-2	-3	91	91
-2	-2	233	217
-2	-1	1397	1322
-2	0	755	674
-1	-13	134	116
-1	-12	156	140
-1	-11	89	76
-1	-9	227	231
-1	-8	359	384
-1	-7	325	345
-1	-6	316	328
-1	-4	340	403
-1	-3	726	846
-1	-2	1210	1332
-1	-1	880	811
0	-12	120	125
0	-10	451	463
0	-8	123	130
0	-6	917	947
0	-4	1080	1316

provement in R_2 is not taken as support, since there remain systematic errors in the data. It should be stressed, however, that the possible ambiguity is of no significance to the chemical interpretation of the structure. It was not possible to check the polarity directly at this stage by collection of Friedel-related reflections because the crystal used had decomposed, and a cursory examination of a different crystal would not provide us with any useful information about the polarity of the original crystal.

The value of R_2 obtained from this final least-squares refinement shows no dependence on $|F_o|$ or on $\sin \theta$, which indicates that our choice of $p = 0.06$ is essentially correct. Comparison of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is necessary. A final difference Fourier map shows peaks in the range -4.0 to $+4.4$ e Å^{-3}; the estimated standard deviation, $\sigma(\Delta\rho)$, is 0.4 e Å^{-3}. An observed Fourier calculation shows the Xe atom to have an electron density of 230 e Å^{-3}, and the average oxygen atom to have electron density of 11.3 e Å^{-3}. The final difference Fourier map shows two peaks greater than 1.4 e Å^{-3} (*i.e.*, greater than about 0.1 of an O atom); these are of 4.4 and 4.1 e Å^{-3} and are located on either side of the Xe atom in the *z* direction at a distance of approximately 0.5 Å. This residual electron density in the difference map is not chemically significant.

The positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Table I, along with the associated standard deviations in these parameters as estimated from the inverse matrix. The final values of $|F_o|$ and $|F_c|$ (in electrons) are presented in Table II; only the 830 reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement, and so only these reflections are listed in Table II. Those reflections for which $F_o^2 \leq 3\sigma(F_o^2)$ all have $|F_o|/|F_c| < 3.0$. The estimated error in an observation of unit weight is 1.88. In the final cycle of least-squares calculations the largest shift of any parameter was exhibited by the *y* coordinate of the F atom; this parameter shifted by 0.65σ.

Description of the Structure

The structure consists of infinite chains of XeO_3 units linked by bridging fluorine atoms; these chains are deposed about the twofold screw axes parallel to the *b* axis. The potassium cations are at nonbonding distances from the other atoms, as expected. The inner coordination geometry is shown in Figure 1, and a view of the polymeric linking is shown in Figure 2. The Xe is five-coordinated, the coordination being best described as a distorted tetragonal pyramid with *cis* F and *cis* O atoms in the base and the other O atom at the apex.

A selection of intramolecular and intermolecular distances and angles is given in Table III. The root-mean-square amplitudes of vibration of the atoms are given in Table IV. The values shown in Table IV are consistent with what one would expect for a compound of this type, which suggests that any errors due to the approximate nature of the absorption correction are small. The bond distances shown in Table III can be "corrected" for thermal motion using the "riding" and "independent" models of Busing and Levy.[24] The differences between the various bond lengths remain essentially the same when either of these "corrections" is applied.

Table III

Selected Intramolecular and Intermolecular Distances and Angles

Distance, Å			
Xe–O$_1$	1.75 (1)	O$_3$–F$_1$	4.23 (2)
Xe–O$_2$	1.79 (1)	O$_3$–F$_2$	2.82 (2)
Xe–O$_3$	1.76 (1)	F$_1$–F$_2$	3.669 (7)
Xe–F$_1$	2.48 (1)	Xe–Xe′[b]	4.446 (2)
Xe–F$_2$[a]	2.36 (1)	Xe–O	1.767[h]
O$_1$–O$_2$	2.73 (2)	K–O$_1$′[c]	2.84 (1)
O$_1$–O$_3$	2.70 (3)	K–F$_1$	2.67 (1)
O$_1$–F$_1$	2.98 (3)	K–F′[d]	2.73 (1)
O$_1$–F$_2$	2.83 (2)	K–O$_3$′[e]	2.92 (1)
O$_2$–O$_3$	2.68 (2)	K–O$_3$″[f]	2.79 (1)
O$_2$–F$_1$	2.72 (2)	K–O$_2$′[g]	2.85 (1)
O$_2$–F$_2$	4.13 (2)		

Angle, deg			
O$_1$–Xe–O$_2$	101.1 (8)	O$_2$–Xe–F$_2$	171.8 (7)
O$_1$–Xe–O$_3$	100.5 (1.2)	O$_2$–Xe–F$_1$	171.2 (5)
O$_2$–Xe–O$_3$	97.8 (7)	O$_3$–Xe–F$_2$	85.3 (5)
O$_1$–Xe–F$_1$	87.6 (1.1)	F$_1$–Xe–F$_2$	98.7 (2)
O$_1$–Xe–F$_2$	85.8 (7)	Xe–F–Xe′[b]	133.7 (4)
O$_2$–Xe–F$_1$	77.2 (6)	O–Xe–O	99.8[h]

[a] F$_2$ is related to F$_1$ by the twofold screw axis. [b] Xe′ is related to Xe by the twofold screw axis. [c] O$_1$′ is related to O$_1$ by the twofold screw axis. [d] F′ is related to F$_1$ by the *a* glide plane. [e] O$_3$′ is related to O$_3$ by a translation along the *b* axis. [f] O$_3$″ is related to O$_3$ by the *a* glide plane. [g] O$_2$′ is related to O$_2$ by the *n* glide plane. [h] Average of three.

Table IV

Root-Mean-Square Amplitudes[a] of Vibration (Å)

Atom	Min	Intermed	Max
Xe	0.141 (1)	0.150 (1)	0.190 (1)
K	0.171 (5)	0.182 (3)	0.222 (4)
F	0.186 (11)	0.195 (11)	0.235 (11)
O$_1$	0.161 (15)	0.251 (21)	0.398 (28)
O$_2$	0.142 (14)	0.205 (17)	0.337 (20)
O$_3$	0.161 (14)	0.201 (13)	0.273 (16)

[a] Measured along the principal axes of the thermal ellipsoids.

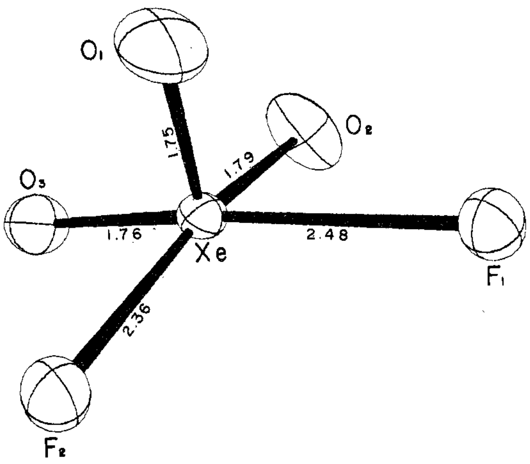

Figure 1.—The inner coordination geometry around Xe in KXeO$_3$F.

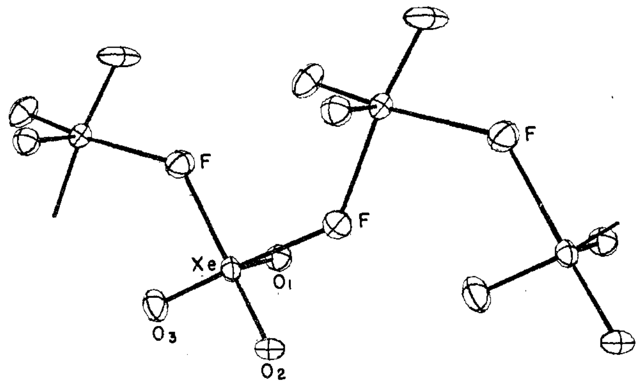

Figure 2.—A view of the XeO$_3$F$^-$ anion showing the bridged Xe–F–Xe bonds and the polymeric nature of the ion. The infinite chains are parallel to the *b* axis, which is horizontal in the figure. Atom O$_1$ has been given an artificial spherical thermal parameter of 3.0 Å^2 for clarity.

It is clear from the data given in Table III that the molecular addition complex description, K$^+$F$^-$·XeO$_3$, is inappropriate. If this were an addition complex, with no bonding between Xe and F atoms, we would expect the closest Xe–F contact to be approximately equal to the sum of the van der Waals radius of Xe and the ionic radius of F$^-$. The van der Waals radius of Xe is approximately 2.18 Å,[25] and the ionic radius of F$^-$ is approximately 1.36 Å.[26] Thus, for a nonbonded Xe–F contact we would expect a minimum separation of approximately 3.5 Å; the Xe–F distances of 2.36 (1) and 2.48 (1) Å are significantly shorter than this calculated value. They are also significantly shorter than the values of about 3.2 Å found for nonbonded Xe–F distances in XeF$_4$.[27] Evidently, the correct description of this substance is as an ionic polymer of formula nK$^+$[XeO$_3$F$^-$]$_n$. The Xe–F bond lengths are longer than the values of 1.953 (2) and 2.00 (1) Å found for XeF$_4$[27] and XeF$_2$,[28] respectively, which is to be expected since the fluorine atoms are terminal in the binary fluorides and bridging here. They are, however, shorter than the values reported for bridging fluorines in xenon compounds which are

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known to contain fluorine bridges; in $[XeF_5^+][PtF_6^-]$, which contains Xe–F–Pt bridges, the bridging Xe–F distances are 2.52, 2.65, and 2.95 Å,[9] and in $(XeF_6)_4$, which contains Xe–F–Xe bridges, the bridging Xe–F distances are approximately 2.5 Å.[29] The Xe–F distances found in $KXeO_3F$, therefore, are certainly indicative of covalent bonding between Xe and F. Moreover, if this were an addition complex involving XeO_3, one would expect the K^+ ions to interact with the lone pairs on the Xe atoms. The K^+ ions, however, are located on the same side of the Xe atoms as the oxygen atoms—it is the fluorine atoms which are in the appropriate location to interact with the lone pairs on Xe. Evidently, therefore, it is very unlikely that the Xe lone pair is in the same location as in XeO_3.

The geometry of the XeO_3 moiety is very similar to that found for XeO_3 itself. In XeO_3 the Xe–O bond lengths and O–Xe–O bond angles are 1.74 (3), 1.76 (3), and 1.77 (3) Å and 100 (2), 101 (2), and 108 (2)°,[5] the average values being 1.76 Å and 103°; these compare with the values of 1.75 (1), 1.76 (1), and 1.79 (1) Å and 97.8 (7), 100.5 (1.2), and 101 (9)° found in $KXeO_3F$, the average values being 1.767 Å and 100°. In each case the geometry is similar to that of the IO_3^- ion, which has an average I–O bond length of 1.823 (6) Å and an average O–I–O bond angle of 97.1 (3)°.[6]

The K^+ ions have nonbonded contacts of 2.67 (1) and 2.73 (1) Å with the F atoms and of 2.79 (1), 2.84 (1), 2.85 (1), and 2.92 (1) Å with the O atoms. The geometry around the K^+ ions is best described as a distorted trigonal antiprism. The nonbonded distances found are in good agreement with the values of 2.68 and 2.73 Å calculated from the sums of the ionic radius of K^+ (1.33 Å)[26] and the van der Waals radii of F (1.35 Å) and O (1.40 Å),[30] respectively.

The Xe–F–Xe moiety has a bond angle of 133.7 (4)°, which is considerably less than the value of approximately 151° found in $Xe_2F_3^+$.[31] In $Xe_2F_3^+$, however, the bridging Xe–F distances are only 2.14 Å;[31] this gives rise to an Xe–Xe separation of 4.13 Å, slightly smaller than the value of 4.36 Å calculated for a nonbonded contact. If the F–Xe–F angle in $Xe_2F_3^+$ were 134°, the Xe–Xe separation would be only 3.94 Å, and, obviously, nonbonded contacts cause a larger angle. In $KXeO_3F$, the Xe–Xe separation is 4.446 (2) Å, slightly larger than the calculated value.

This structure analysis explains both the unusual stability of $KXeO_3F$ and the apparent absence of Xe–F stretching modes in the infrared spectrum. The coordination around the Xe is analogous to that found in XeF_5^+[9] and $XeOF_4$[8] and may be considered to be a distorted octahedron with the Xe lone pair occupying the sixth coordination site. This would put the electron pair in the right region to interact with the neighboring K^+ ions in the crystal. It would appear, therefore, that this is further evidence for the special stability of octahedral coordination in Xe(VI) compounds. The XeO_3 moiety is stabilized by entering into bonding with the fluorine atoms. The Xe–F bonds, however, are considerably longer than those found in the binary fluorides, and, consequently, the Xe–F stretching modes would be expected to occur at much lower frequencies. The Xe–F stretching frequency decreases rapidly with increased bond length. Thus, it is at 576 cm^{-1} in $XeOF_4$[32] (Xe–F = 1.95 (5) Å[8]), at 543 cm^{-1} in XeF_4[33] (Xe–F = 1.953 (2) Å[27]), and at 497 cm^{-1} in XeF_2[34] (Xe–F = 2.00 (1) Å[28]). For an Xe–F separation of 2.36 Å, as found in $KXeO_3F$, therefore, we would expect the Xe–F stretch to be at or below 400 cm^{-1}.

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