clearly present in the phosphate tetrahedron, a Jahn–Teller type of electronic ordering takes place in the case of CrO_4^{3-} tetrahedron, nearly doubling the extent of distortion.

In VO_4^{3-} there is no electron in the d orbitals (ground state). Bond distances in VO_4^{3-} are similar to those in CrO_4^{3-}, but bond angles fall approximately between the values in the phosphate and chromate. The increased distortion in the vanadate tetrahedron as compared to PO_4^{3-} is tentatively attributed to the lowering of the interatomic force constants and vibration frequencies due to the increased mass. As the chromium(V) and vanadium(V) ions are not expected to differ appreciably in size the larger distortion in the CrO_4^{3-} tetrahedron appears to be electronic in nature. However, the excess distortion in VO_4^{3-} may also be due to the mixing of low-lying excited states in the d manifold. This should be investigated spectroscopically.

Similarly, in AsO_4^{3-}, there are no unpaired electrons (ground state); the crystal structure shows the distortion to be intermediate between the VO_4^{3-} and CrO_4^{3-}. On the basis of size considerations alone we might have expected the distortion of the arsenate to be smaller than that of the vanadate ion; although the differences between the distortions of the two tetrahedra are small, the arsenate is distorted to a significantly greater extent than the vanadate. The reasons are not clear.

Conclusion

Spodiosites with the general formula Ca_2XO_4Cl, with X = P, V, Cr, and As, have been prepared. Detailed crystal structure analyses of all four show that the XO_4^{3-} tetrahedra are considerably distorted from T_d symmetry. Interatomic distances are normal, and the distortions cannot be explained by considerations of crystal packing alone. The largest distortion is exhibited by the CrO_4^{3-} tetrahedron; this was attributed to electronic ordering of the lone electron in the d orbital. PO_4^{3-}, VO_4^{3-}, and AsO_4^{3-} do not contain unpaired electrons and the observed distortions are notably smaller than in CrO_4^{3-}.

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The Crystal Structure of the 1:1 Molecular Addition Compound Xenon Difluoride–Iodine Pentafluoride, $XeF_2 \cdot IF_5$

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The crystal structure of the 1:1 molecular addition compound xenon difluoride–iodine pentafluoride, $XeF_2 \cdot IF_5$, has been determined from three-dimensional X-ray data. The material crystallizes in the tetragonal system, with four molecules in a cell of dimensions $a = 7.65$ (1) and $c = 10.94$ (1) Å. A satisfactory refinement was obtained in the space group I4/m, with a final conventional R factor of 0.034 for 403 nonzero reflections. The structure has established the existence of discrete XeF_2 and IF_5 molecules, linear and square-based pyramidal, respectively. The alignment of the XeF_2 molecules, with each fluorine ligand directed toward the iodine atoms of neighboring IF_5 molecules, and the shortness of those interatomic distances (3.142 ($\sigma = 0.007$) Å) suggest that the ordered crystal lattice is largely a consequence of electrostatic attractions between the different components.

Introduction

Xenon difluoride is a fluoride ion donor[1-3] and forms salts with arsenic pentafluoride and strong fluoride ion acceptor metal pentafluorides. It also forms a 1:1 compound with iodine pentafluoride which Bartlett and Sladky[4] concluded was a molecular adduct on the basis of Raman spectroscopic evidence. The crystal structure of the compound confirms this representation, the geometry of each molecule being only slightly different from that of the "free" species.

The nature of the alignment of the molecules in the crystal lattice is consistent with coulombic attraction of negatively charged fluorine ligands of the XeF_2 molecules to the positively charged iodine atoms of nearest IF_5 molecules. This is similar to the 1:1 molecular adduct[5] $XeF_2 \cdot XeF_4$ and like the situations found[6,7] in crystalline XeF_2 and XeF_4.

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Experimental Section

The adduct $XeF_2 \cdot IF_5$ was prepared by the interaction of xenon difluoride and iodine pentafluoride.[4] Powdered material was transferred to thin-walled Pyrex capillaries in a Vacuum Atmospheres Corp. Drilab. Crystals were grown by sublimation at 60° under vacuum and suitable single crystals were sealed in small sections of capillary tube. The crystals were transparent multifaceted blocks.

Crystal Data

$XeF_2 \cdot IF_5$ (mol wt 391.2) is tetragonal with $a = 7.65 \pm 0.01$ Å, $c = 10.94 \pm 0.01$ Å, $V = 640$ Å^3, $Z = 4$, $d_m \approx 3.8$ g cm^{-3},[4] $d_c = 4.06 \pm 0.02$ g cm^{-3}, and $F(000) = 672$. The most probable space groups are I4/m, I4, and $I\bar{4}$ by systematic absence of *hkl* when $h + k + l \neq 2n$ on single-crystal precession photographs. The structure was successfully refined in the centrosymmetric space group I4/m.

X-Ray Measurements

The crystal used for intensity measurements was approximately equidimensional with a maximum diameter of ~0.1 mm at the start of the measurements. Data were recorded at laboratory temperatures of 24–25° with a manually operated single-crystal orienter on a GE diffractometer using Zr-filtered Mo Kα radiation, λ 0.7107 Å. The crystal was mounted with the [110] direction parallel to the φ axis of the orienter. Unit cell constants were derived from selected high-order $h00$ and $00l$ reflections. Intensities were measured with a scintillation counter by the stationary-crystal, stationary-counter technique using a takeoff angle of 5° and 20-sec counts. Backgrounds were measured at $2\theta \pm 1.2°$ for reflections up to 20° 2θ and at $2\theta \pm 2°$ beyond this point. Counting rates were kept below 10,000 counts/sec by using Zr filters of known attenuation when necessary. Measurements were made on 501 independent reflections occurring in the range $2\theta \leq 60°$, of which 415 were greater than 3 times their estimated standard deviation. Several standard reflections were used to monitor the experiment at approximately 4-hr intervals. The crystal sublimed at a rate that caused a 5–10% decrease in intensity during each monitoring interval. The data were treated as eight batches with a scale factor assigned to each batch. Corrections were made for the Lorentz and polarization effects. Absorption effects were ignored and are estimated to cause an error of 1% in the structure factors.

Structure Analysis

The Patterson function could be interpreted in terms of tetragonal-pyramidal IF_5 molecules with the apical F to I bond pointing along the *c* axis and linear XeF_2 molecules lying normal to the *c* axis. The position of I and the azimuthal orientation of IF_5 were known, but we did not know whether the molecules all had the apical F atoms pointing the same way or whether half were pointing $+c$ and half along $-c$ (call these options parallel or antiparallel). The position of Xe was known but there was an ambiguity of 90° in the azimuthal orientation of XeF_2 (call these options $\alpha°$ or $\alpha° + 90°$).

In I4 there are two independent IF_5 molecules in each of which the four basal F's are equivalent. The XeF_2 molecules may be bent. There are four models: (**1**) parallel, $\alpha°$; (**2**) parallel, $\alpha° + 90°$; (**3**) antiparallel, $\alpha°$; (**4**) antiparallel, $\alpha° + 90°$. In $I\bar{4}$ there are two nonequivalent pairs of basal F's in the IF_5 molecules; the XeF_2 molecules may be bent, and there are two models: (**5**) antiparallel, $\alpha°$; (**6**) antiparallel, $\alpha° + 90°$. In I4/m the four basal F's are equivalent. The XeF_2 molecules must be linear. There are two models: (**7**) antiparallel, $\alpha°$; (**8**) antiparallel, $\alpha° + 90°$. Therefore there were eight possible structures to investigate in space groups I4, $I\bar{4}$, and I4/m.

Each model was refined through three cycles of full-matrix least squares using eight factors, a single thermal parameter, and coordinates from the Patterson function with the following results in terms of the conventional factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$: (**1**) $R = 0.18$; (**2**) $R = 0.20$. [Programs employed during the analysis included FOUR (C. J. Fritchie, unpublished work, modified by L. Guggenberger and P. B. Jamieson), ORFLS (W. R. Busing, K. O. Martin, and H. A. Levy, ORNL Report TM-305, 1962, modified by B. B. Cetlin and W. C. Hamilton), ORFFE (W. R. Busing, K. O. Martin, and H. A. Levy, ORNL Report TM-306, 1964), and ORTEP (C. K. Johnson, ORNL Report 3794, 1965, modified by R. L. Kornegay).] There were serious discrepancies among the structure factors and both models were discarded: (**3**, **5**, **7**) $R = 0.11$; (**4**, **6**, **8**) $R = 0.15$. It was concluded that the azimuthal orientation of XeF_2 is $\alpha°$ rather than $\alpha° - 90°$ and models **4**, **6**, and **8** were discarded. Models **3**, **5**, and **7** were then refined through three least-squares cycles using individual isotropic thermal parameters. Model **3** was discarded because the thermal parameter of one of the apical F's began to increase without limit. Models **5** and **7** refined to $R = 0.075$. Five cycles of refinement with anisotropic thermal parameters led to $R = 0.052$ for model **5** while model **7** began to diverge with oscillation of the scale factors. (We wish to thank a reviewer for suggesting that this behavior was due to an uncorrected correlation.) The batch scale factors were examined and the maximum deviation of an individual from a mean value was $\lesssim 5\sigma$. It was concluded that the experimental scaling parameters were adequate and further anisotropic refinement was continued for models **5** and **7** utilizing a single scale factor. No significant deviations from the centrosymmetric model **7** were obtained by refinement of trial structure **5** in the space group $I\bar{4}$. It was assumed that I4/m is the correct space group. Model **7** was subjected to 15 more anisotropic cycles during which time four weak, high-order reflections apparently subject to gross experimental error were discarded, and eight strong, low-order reflections, all with $F_c > F_o$, which appeared to be subject to extinction were discarded. At the conclusion all parameter shifts were $<0.1\sigma$. The final agreement for 403 observed reflections was $R = 0.034$ and $R' = 0.034$ where $R' = \sqrt{\Sigma w(F_o - F_c)^2}/\sqrt{\Sigma w F_o^2}$ and w is the weighting parameter derived from counting statistics. The positional and thermal parameters are

TABLE I
FINAL POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Xe	0	$^1/_2$	0	0.0104 (2)	0.0148 (2)	0.0063 (1)	0.0015 (2)	0	0
I	0	0	0.2859 (1)[b]	0.0096 (1)	0.0096 (1)	0.0045 (1)	0	0	0
F_1	0	0	0.1198 (9)	0.0376 (26)	0.0376 (26)	0.0026 (8)	0	0	0
F_2	0.0596 (8)	0.2343 (7)	0.2589 (5)	0.0174 (10)	0.0111 (9)	0.0183 (5)	−0.0022 (8)	−0.0022 (8)	0.0034 (5)
F_3	0.2439 (12)	0.4035 (13)	0	0.0129 (15)	0.0217 (20)	0.0100 (7)	0.0038 (13)	0	0

[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] The number in parentheses is estimated standard deviation in the least significant digits.

listed in Table I. A comparison of F_o and F_c is presented in Table II.

TABLE II
COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	Fo	Fc
0	0	2	35.6	36.5
0	0	6	68.0	66.6
0	0	8	128.1	127.9
0	0	10	111.2	111.8
0	0	14	65.3	65.5
0	1	1	50.9	48.8
0	1	3	77.9	77.5
0	1	5	167.7	168.7
0	1	7	119.6	119.1
0	1	9	78.7	76.9
0	1	11	35.8	36.5
0	1	13	16.1	17.9
0	2	2	15.2	15.5
0	2	4	190.5	190.4
0	2	6	83.3	81.1
0	2	8	66.5	65.6
0	2	10	105.2	106.1
0	2	12	12.8	14.1
0	2	14	59.6	61.4
0	3	1	14.2	15.6
0	3	3	84.8	84.0
0	3	5	118.7	117.4
0	3	7	109.7	106.8
0	3	9	61.9	60.7
0	3	11	38.5	34.8
0	4	2	21.4	19.0
0	4	4	198.3	196.9
0	4	6	54.9	51.3
0	4	8	67.6	67.0
0	4	10	84.4	83.6
0	4	14	50.6	51.7
0	5	3	73.2	74.1
0	5	5	72.1	69.9
0	5	7	84.2	84.1
0	5	9	41.4	42.6
0	5	11	29.7	29.8
0	6	0	131.8	136.1
0	6	2	10.6	12.0
0	6	4	86.5	87.1
0	6	6	50.1	46.5
0	6	8	22.9	22.8
0	6	10	62.6	63.6
0	6	12	11.2	11.6
0	7	3	43.8	47.0
0	7	5	46.1	49.2
0	7	7	56.6	55.7
0	7	9	29.2	31.7
0	7	11	19.0	21.1
0	8	0	113.1	116.8
0	8	4	81.1	79.9
0	8	6	30.8	29.7
0	8	8	24.4	22.9
0	8	10	44.3	42.9
0	9	3	31.2	32.8
0	9	5	28.6	31.0
0	9	7	36.6	37.9
0	10	4	39.4	36.9
1	1	0	36.6	35.1
1	1	4	73.5	72.8
1	1	6	153.2	154.6
1	1	8	95.6	95.1
1	1	10	16.0	15.0
1	1	12	93.6	96.5
1	2	1	31.9	26.8
1	2	3	124.1	120.3
1	2	5	103.8	103.0
1	2	7	127.6	126.3
1	2	9	54.3	54.2
1	2	11	38.7	38.7
1	3	0	32.9	33.1
1	3	4	52.7	50.8
1	3	6	159.8	157.1
1	3	8	84.4	86.1
1	3	10	20.6	20.1
1	3	12	83.0	85.5
1	4	1	37.2	36.6
1	4	3	67.7	65.6
1	4	5	122.3	120.2
1	4	7	94.4	92.3
1	4	9	67.1	66.9
1	4	11	30.9	31.5
1	4	13	13.5	14.8
1	5	0	42.2	42.2
1	5	2	210.2	211.6
1	5	4	13.6	12.6
1	5	6	103.9	101.2
1	5	8	58.6	57.8
1	5	10	10.6	11.0
1	5	12	59.8	62.4
1	6	1	17.5	18.4
1	6	3	47.4	45.6
1	6	5	68.9	69.0
1	6	7	60.7	58.6
1	6	9	43.2	43.3
1	6	11	19.2	20.0
1	7	0	9.0	11.3
1	7	2	123.4	124.0
1	7	4	14.9	16.8
1	7	6	59.5	57.8
1	7	8	46.4	46.7
1	8	1	26.2	27.9
1	8	3	18.5	21.6
1	8	5	57.8	58.7
1	8	7	34.7	35.6
1	8	9	35.8	38.5
1	9	0	12.7	13.3
1	9	2	74.7	76.6
1	9	6	34.4	36.6
1	9	8	25.1	25.9
1	10	1	13.1	11.5
1	10	3	16.2	14.7
1	10	5	30.2	28.8
2	1	1	18.0	19.2
2	1	3	67.2	66.6
2	1	5	120.8	119.1
2	1	7	99.0	97.4
2	1	9	58.4	57.1
2	1	11	28.3	29.2
2	1	13	10.3	11.4
2	2	2	65.8	64.0
2	2	4	141.8	137.4
2	2	6	100.0	99.0
2	2	8	52.7	45.4
2	2	10	104.3	105.8
2	2	12	18.8	16.5
2	2	14	57.7	59.5
2	3	1	15.2	5.6
2	3	3	95.8	90.5
2	3	5	105.9	102.9
2	3	7	109.8	106.1
2	3	9	57.0	56.5
2	4	4	195.0	195.0
2	4	6	56.4	53.1
2	4	8	65.9	66.0
2	4	10	79.1	80.3
2	5	1	29.1	29.7
2	5	3	45.5	45.0
2	5	5	90.9	84.4
2	5	7	69.1	66.6
2	5	9	47.4	48.4
2	5	11	22.6	24.2
2	6	0	151.6	158.2
2	6	4	107.8	104.7
2	6	6	45.1	45.7
2	6	8	29.3	30.0
2	6	10	62.2	61.5
2	6	12	10.8	6.8
2	7	3	54.5	54.8
2	7	5	48.5	48.7
2	7	7	60.4	62.0
2	7	9	31.6	32.9
2	7	11	23.4	24.9
2	8	0	119.2	123.1
2	8	2	16.4	16.5
2	8	4	89.8	85.2
2	8	6	19.1	17.2
2	8	8	27.1	26.9
2	9	3	30.9	30.7
2	9	5	29.0	27.8
2	10	0	54.0	54.2
2	10	4	39.1	37.0
3	1	0	10.5	11.9
3	1	2	171.0	179.2
3	1	4	79.9	77.6
3	1	6	80.8	78.6
3	1	8	92.2	91.9
3	1	12	83.7	85.1
3	1	14	11.2	12.1
3	2	1	39.8	40.9
3	2	3	50.2	48.3
3	2	5	120.5	116.6
3	2	7	84.1	86.8
3	2	9	60.6	60.0
3	2	11	25.4	25.8
3	3	2	220.1	224.5
3	3	4	52.0	50.8
3	3	6	106.2	103.7
3	3	8	80.8	79.4
3	3	10	14.8	8.2
3	3	12	73.1	75.2
3	4	1	32.6	28.5
3	4	3	50.6	48.7
3	4	5	96.4	90.3
3	4	7	72.1	69.7
3	4	7	72.1	69.7
3	4	9	51.4	52.7
3	4	11	23.1	23.5
3	5	2	141.3	131.1
3	5	4	42.0	36.3
3	5	6	61.4	59.8
3	5	8	66.1	63.0
3	5	12	56.7	56.0
3	6	1	20.5	20.5
3	6	3	39.2	37.6
3	6	5	65.1	63.3
3	6	7	51.6	50.4
3	6	9	40.0	40.4
3	6	11	15.7	17.2
3	7	2	123.7	121.8
3	7	4	20.8	18.8
3	7	6	58.6	58.5
3	7	8	45.2	44.4
3	8	1	18.0	18.2
3	8	3	24.7	24.9
3	8	5	47.7	47.3
3	8	7	34.9	34.8
3	8	9	31.8	32.3
3	9	2	66.1	65.6
3	9	6	29.3	30.5
3	10	1	13.5	13.3
3	10	3	11.5	12.3
4	1	1	43.2	45.7
4	1	3	41.7	46.4
4	1	5	119.1	116.4
4	1	7	78.4	77.8
4	1	9	64.2	62.3
4	1	11	25.4	25.6
4	1	13	12.2	12.7
4	2	2	14.3	15.3
4	2	4	163.2	168.5
4	2	6	66.3	66.0
4	2	8	56.3	54.3
4	2	10	83.9	85.0
4	3	1	16.2	5.4
4	3	3	84.6	79.4
4	3	5	87.6	81.7
4	3	7	94.8	90.6
4	3	9	52.9	50.1
4	3	11	31.7	32.6
4	4	0	178.3	183.4
4	4	2	14.6	14.4
4	4	4	124.3	119.8
4	4	6	40.1	37.2
4	4	8	38.5	36.1
4	4	10	63.0	62.9
4	5	1	11.0	9.4
4	5	3	51.7	47.7
4	5	5	62.1	54.9
4	5	7	62.7	58.2
4	5	9	36.4	34.2
4	5	11	20.8	21.2
4	6	0	116.5	117.9
4	6	2	18.5	15.4
4	6	6	45.2	43.7
4	6	8	19.9	19.9
4	6	10	54.8	53.9
4	7	3	51.5	46.8
4	7	5	40.3	37.1
4	7	7	56.3	51.9
4	7	9	26.5	26.1
4	8	0	87.4	86.2
4	8	4	61.0	60.2
4	8	6	21.3	17.7
4	8	8	15.9	16.8
4	9	3	24.8	23.9
4	9	5	24.0	22.7
5	1	2	191.1	197.1
5	1	4	42.5	41.4
5	1	6	94.1	93.5
5	1	8	70.9	70.2
5	1	12	66.0	66.2
5	2	1	18.7	16.7
5	2	3	61.9	63.1
5	2	5	86.8	84.5
5	2	7	81.4	78.8
5	2	9	51.7	51.2
5	2	11	29.4	28.7
5	3	0	40.6	41.4
5	3	2	199.9	210.8
5	3	6	107.6	103.0
5	3	8	51.9	51.1
5	3	10	11.6	14.2
5	3	12	54.3	55.7
5	4	5	56.6	60.7
5	4	7	64.2	63.4
5	4	9	38.0	39.8
5	4	11	23.5	23.1
5	5	2	122.8	117.9
5	5	4	19.4	19.7
5	5	6	57.5	54.6
5	5	8	48.1	47.6
5	6	1	24.7	26.3
5	6	3	25.4	25.9
5	6	5	57.0	59.8
5	6	7	37.2	39.5
5	6	9	34.8	35.8
5	7	0	18.6	16.1
5	7	2	100.2	93.2
5	7	6	44.6	44.7
5	7	8	26.8	29.1
5	8	1	15.4	13.7
5	8	3	18.7	19.6
5	8	5	38.6	35.3
5	8	7	27.6	25.7
5	9	2	48.8	46.4
6	1	1	10.9	11.3
6	1	3	44.1	49.5
6	1	5	57.6	62.0
6	1	7	56.4	60.0
6	1	9	37.4	39.3
6	1	11	20.0	20.6
6	2	0	171.4	175.0
6	2	4	115.0	117.7
6	2	6	42.4	42.1
6	2	8	33.8	36.1
6	2	10	58.9	60.0
6	3	1	18.2	21.3
6	3	3	38.2	40.5
6	3	5	65.0	65.3
6	3	7	55.2	54.8
6	3	9	40.4	41.5
6	3	11	20.6	20.5
6	4	0	126.1	135.3
6	4	2	9.9	5.5
6	4	4	92.3	92.3
6	4	6	31.7	30.1
6	4	8	26.0	27.3
6	4	10	48.5	47.8
6	5	1	11.4	10.9
6	5	3	37.3	36.9
6	5	5	48.5	45.5
6	5	7	46.7	45.5
6	5	9	30.2	30.0
6	6	0	110.8	109.1
6	6	4	80.1	75.7
6	6	6	24.0	23.3
6	6	8	24.5	22.0
6	7	3	33.2	31.5
6	7	5	35.3	32.6
6	7	7	39.0	37.6
6	8	0	68.4	64.2
6	8	2	11.4	10.5
6	8	4	47.9	44.8
7	1	2	103.6	107.2
7	1	4	28.7	30.8
7	1	6	48.9	48.2
7	1	8	51.6	53.0
7	2	1	17.3	18.6
7	2	3	33.5	36.6
7	2	7	49.3	49.0
7	2	9	35.7	36.3
7	3	0	10.8	14.7
7	3	2	94.6	100.3
7	3	4	12.3	9.6
7	3	6	44.7	46.3
7	3	8	37.9	36.2
7	4	3	32.1	30.6
7	4	5	41.0	40.9
7	4	7	39.4	36.3
7	4	9	24.3	27.1
7	5	2	76.2	78.7
7	5	4	20.3	16.7
7	5	6	37.6	35.8
7	5	8	40.1	37.2
7	6	1	15.4	14.0
7	6	3	21.9	22.9
7	6	5	37.7	36.8
7	6	7	32.3	31.0
7	7	0	16.4	14.9
7	7	2	68.9	64.3
7	7	6	32.0	30.8
8	1	1	18.6	18.5
8	1	3	28.2	31.0
8	1	5	52.2	52.3
8	1	7	40.6	41.5
8	1	9	34.8	35.1
8	2	0	106.0	110.3
8	2	2	9.5	10.3
8	2	4	70.0	76.0
8	2	6	20.9	21.3
8	2	8	22.1	21.3
8	3	1	13.1	14.1
8	3	3	26.4	27.3
8	3	5	42.1	42.4
8	3	7	36.6	35.0
8	3	9	28.4	28.6
8	4	0	75.7	73.7
8	4	4	45.0	49.8
8	4	6	27.4	23.9
8	4	8	15.1	11.0
8	5	3	28.4	28.8
8	5	5	29.5	28.2
8	5	7	34.4	33.1
8	6	0	64.3	62.3
8	6	4	45.4	42.9
8	7	1	12.2	4.8
9	1	0	11.2	13.1
9	1	2	85.2	86.2
9	1	6	39.1	42.1
9	1	8	27.8	27.3
9	2	3	32.6	34.3
9	2	5	30.3	30.4
9	2	7	40.5	39.1
9	3	0	13.7	[illegible]
9	3	2	71.7	72.3
9	3	6	34.3	34.4
9	4	3	23.9	22.5
9	4	5	28.0	28.4
10	1	3	15.4	16.9
10	1	5	29.6	29.8
10	2	0	59.9	62.3

Description of Structure

Molecular dimensions are summarized in Table IIIa and b. The IF_5 molecule is required to have 4mm symmetry and has the expected shape of a tetragonal pyramid. The four basal I–F bonds are bent 9° from the basal plane toward the apical I–F bond. After correction for thermal riding motion there are no significant differences between the bond lengths, which have an average value of 1.877 (σ = 0.011) Å. The XeF_2 molecule has bond lengths of 2.018 (σ = 0.009) Å, corrected for riding motion, and is required to have the expected linear shape. The justification for making bond length corrections for thermal riding motion is presented in Table IV. The rms components of thermal displacements normal to the bonds are significantly larger than the components along the bonds.

Attractive interactions between XeF_2 and IF_5 are summarized in Table IIIc and illustrated in Figure 1. The 3.142 (σ = 0.007) Å distances between F(3) and I define a layer structure normal to the c axis. The IF_5 molecules form layers in which each molecule has close contacts with four neighbors of opposite apical orientation (Figure 2). The XeF_2 molecules form layers in which each molecule has close contacts with four neighbors (Figure 3).

TABLE III
INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

a. In IF_5 Molecule				
I–F(1)	1.817 (10)	1.862 (10)[a]		
I–F(2)	1.873 (5)	1.892 (5)[a]		
F(1)···F(2)	2.395 (9)		F(2)···F(2)^{I}	2.615 (8)
F(1)–I–F(2)	80.9 (0.2)			
b. In XeF_2 Molecule				
Xe–F(3)	2.007 (9)	2.018 (9)[a]		
c. Attractive Interactions between XeF_2 and IF_5				
F(3)···I	3.142 (7)		F(2)···Xe	3.516 (5)
F(2)···Xe^{II}	3.361 (6)[b]			
d. Intermolecular F···F Contacts				
F(1)···F(1)	2.621 (19)		F(2)–F(2)^{III}	2.929 (12)
F(2)···F(2)^{II}	2.953 (8)		F(2)–F(3)	3.418 (8)
F(2)···F(3)^{III}	3.124 (8)		F(2)–F(3)^{II}	2.901 (7)
F(3)···F(3)^{IV}	2.961 (14)			

[a] Corrected for thermal motion, assuming that the F atom rides on the heavy atom. All other distances were uncorrected. [b] Roman numbers refer to atoms at symmetry-equivalent positions, where I = $(y, -x, z)$, II = $(^1/_2 - y, ^1/_2 + x, ^1/_2 + z)$, III = $(^1/_2 - x, ^1/_2 - y, ^1/_2 - z)$, and IV = $(1 - y, x, z)$.

TABLE IV
RMS COMPONENTS OF THERMAL DISPLACEMENTS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	Component	Direction	Atom	Component	Direction
I	0.165 (1)	I–F(1)	F(1)	0.126 (18)	I–F(1)
	0.168 (1)	I–F(2)		0.334 (10)	F(2)–F(2′)
	0.168 (1)	I–F(2′)		0.334 (10)	F(2″)–F(2‴)
F(2)	0.163 (7)	I–F(2)	Xe	0.195 (2)	z axis
	0.268 (6)	I–F(1)		0.172 (2)	Xe–F(3)
	0.231 (6)	F(2)–F(2′)		0.213 (2)	n[b]
F(3)	0.185 (11)	Xe–F(3)			
	0.247 (9)	z axis			
	0.262 (11)	n[b]			

[a] Primed numerals refer to equivalent atoms within the same molecule. [b] n is normal to the preceding two directions.

The molecular coordination numbers and numbers of short intermolecular F–F contacts are remarkably high as indicated by the following cataloging. Each IF_5 has thirteen molecular neighbors, four IF_5 in the same plane, one IF_5 above or below, all with opposite apical orientation, four XeF_2 on the basal side, and four XeF_2 on the apical side. Each XeF_2 has twelve molecular neighbors, four XeF_2 in the same plane and four IF_5 above and below the plane. Each F(2) atom makes six contacts with F's from two IF_5 and three XeF_2. Each F(3) atom makes eight contacts with F's from two XeF_2 and four IF_5.

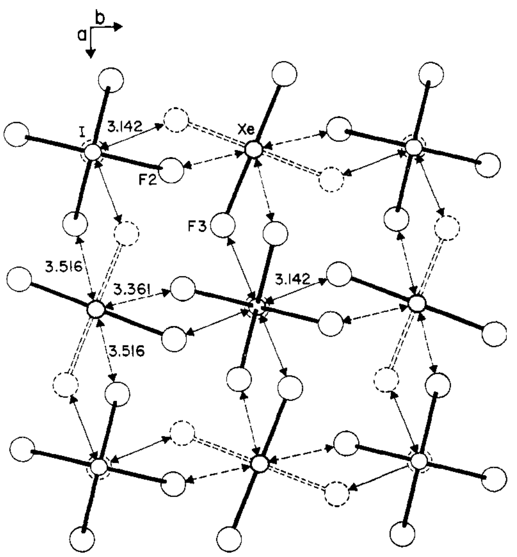

Figure 1.—Projection of structure on c axis. For clarity only IF_5 molecules with I at $c/4$ are included. Broken circles indicate apical F's situated below the basal plane. XeF_2 molecules at ~ 0 are indicated by solid circles; those at $\sim c/2$, by broken circles.

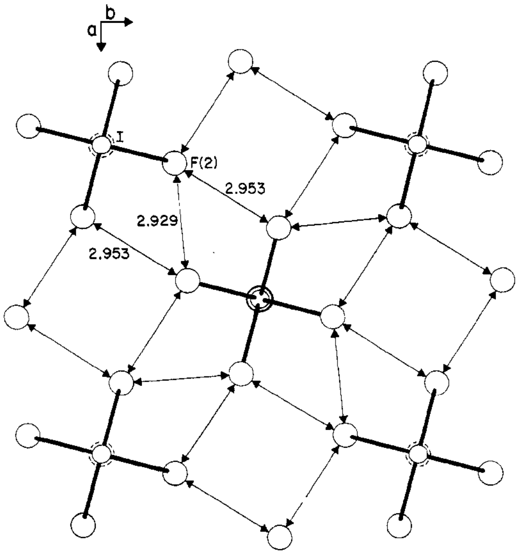

Figure 2.—Projection on c axis of a layer of IF_5 molecules. Broken circles indicate apical F's situated below the basal plane.

There is one notable exception to the high coordination. The apical F(1) atom makes only one contact of 2.621 (σ = 0.019) Å with a neighboring F(1) atom directly above or below. This contact undoubtedly represents the major intermolecular repulsion in the structure. The conventional ellipsoidal treatment of thermal motion may be inadequate for this atom. In Table IV the component of motion along the bond at F(1) is much smaller than the same type of motion at I, while the motion at F(1) normal to the bond is considerably larger than any other entries in the table. After the bond length has been corrected for riding motion, increasing it from 1.81 to 1.86 Å, it is probable that the apical F's bend off the c axis direction and the motions of neighboring apical F's are correlated. The structure, which is otherwise extremely compact, provides the necessary space for this correlated motion. The space can be seen clearly in Figure 4. The F(1) atom lies over a 5.09-Å square of F(3) atoms.

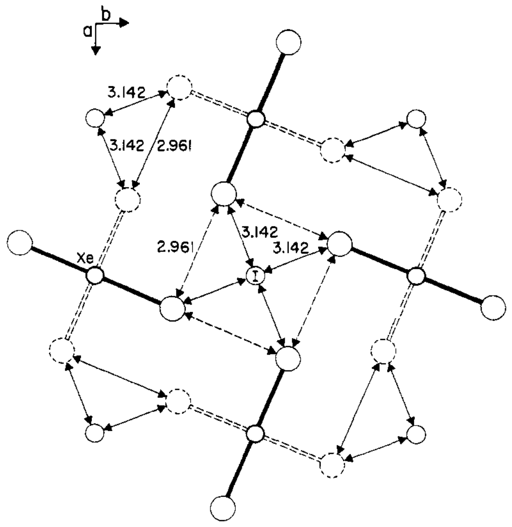

Figure 3.—Projection on c axis of two successive layers of XeF_2 molecules. Iodine atoms in intermediate layer indicated by small light circles.

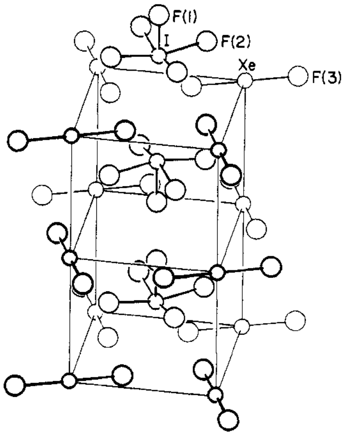

Figure 4.—A portion of the structure selected to indicate the basal to basal and apical to apical environment of IF_5 molecules. The "cells" which have been drawn through Xe atoms to assist in spatial perception should not be confused with the unit cell.

Each molecule is surrounded by an approximately cubic arrangement of molecules of the other kind. The detailed arrangement is consistent with close packing of the molecules and with electrostatic attraction of the negatively charged fluorine ligands of one molecular species for the positively charged central atom of the other, the attraction of the fluorine ligands of XeF_2 for the iodine atoms of the IF_5 molecules being particularly important. The disposition of the fluorine ligands in a layer of XeF_2 molecules is determined by the orientation of the nearest IF_5 molecules and is illustrated in Figure 4. Where superimposed IF_5 molecules, in adjacent layers, are base to base, the sandwiched XeF_2 molecules orient to make short I–F contacts. On the other hand, the XeF_2 molecules are oriented away from the IF_5 molecules where they abut apex to apex.

TABLE V

COMPARISON OF STRUCTURES IN ISOELECTRONIC SEQUENCE

	TeF_5^- [a]	IF_5	XeF_5^+ [b]
M–F(apical), Å	1.84	1.86[c]	1.81
M–F(basal), Å	1.94	1.89[c]	1.88
F(apical)–M–F(basal), deg	79	81	79

[a] A. J. Edwards and M. A. Mouty, *J. Chem. Soc. A*, 703 (1969). [b] N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, *ibid.*, *A*, 1190 (1967). [c] Corrected for thermal motion.

This arrangement suggests that the iodine atom bears an appreciable positive charge which is effectively shielded by fluorine ligands but not by the nonbonding valence electron pair. Presumably the nonbonding pair is concentrated significantly on the *c* axis rendering the IF_5 molecule pseudooctahedral. Consequently the centers of the faces of the pseudooctahedron on the "pair" end of the molecule would effectively possess positive charge (the "pair" screening being poor in this direction). The fluorine ligands of the XeF_2 molecules align approximately as this model dictates.

The Xe–F interatomic distance of 2.007 (σ = 0.009) Å in the XeF_2 molecules is not significantly different from that observed in crystalline XeF_2 (2.010 (σ = 0.006) Å).

The geometry of the IF_5 molecule is of particular interest since previous structural information concerning this molecule has been imprecise. No detailed crystallographic information is available although Burbank and Bensey[8] have reported the unit cell constants for solid IF_5. High-resolution nmr studies[9] have shown that liquid IF_5 contains molecules of C_{4v} symmetry. From vibrational spectroscopic studies Begun, *et al.*,[10] have concluded that IF_5 has C_{4v} symmetry, with an iodine to apical fluorine atom bond length of 1.75 Å, the equatorial bonds being somewhat longer at 1.86 Å. They assumed the apical to basal bond angle to be close to 90°. The 9° departure of the apical to basal bond angle in $XeF_2 \cdot IF_5$ is significant and, we believe, probably closely represents the angle in the free molecule. It is significant that similar apical to basal bond angles have been observed in the isoelectronic species TeF_5^- and XeF_5^+. The experimental findings are compared in Table V. Again, the supposition that the nonbonding valence electron pair is sterically active is in accord with the findings. Repulsive interaction of the "pair" with the basal I–F bond electrons outweighs all other repulsions.

Although iodine pentafluoride and bromine pentafluoride are known to be geometrically similar and must, qualitatively, represent similar bonding situations, it is of interest that BrF_5 does not form an adduct with XeF_2 even at −20°. The coordination in the BrF_5 molecule is probably tighter than in IF_5 and the positive charge on the bromine atom (which will be less than that of the iodine atom, because of the lower electronegativity of the latter) is therefore more effectively shielded by the equatorial fluorine ligands and the electron pair. The shielding of the central atom charge should also be more effective in $XeOF_4$ (which is isoelectronic with IF_5) since the xenon atom is in the same plane as the basal fluorine atoms,[11] whereas in IF_5 the iodine atom is below the basal plane. Recently, Bartlett and Wechsberg[12] have prepared the 1:1 adduct $XeF_2 \cdot XeOF_4$, which is an isomorph of the iodine analog, with *a* = 7.56 (1) and *c* = 11.36 (1) Å. It is presumably isostructural with $XeF_2 \cdot IF_5$. The Raman spectrum shows that the compound is essentially molecular. The ready dissociation of the compound and its low melting point of 29° indicate that the intermolecular forces are indeed weaker than those between IF_5 and XeF_2. The same authors have also isolated 1:1 and 1:2 compounds of XeF_2 with $[XeF_5]^+[AsF_6]^-$, the Raman spectra of which indicate the presence of molecular XeF_2, which is presumably interacting with the XeF_5^+ ions in much the same way as in $XeF_2 \cdot IF_5$.

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(8) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **27**, 928 (1957).

(9) H. S. Gutowsky and C. J. Hoffman, *ibid.*, **19**, 1259 (1951).

(10) G. M. Begun, W. H. Fletcher, and D. F. Smith, *ibid.*, **42**, 2236 (1965).

(11) J. Martins and E. B. Wilson, Jr., *ibid.*, **41**, 570 (1964).

(12) N. Bartlett and M. Wechsberg, to be submitted for publication.