12) have pointed out the importance of knowing quantitative values of these heats of formation in order to understand the ions resulting from nuclear decay of the radioactive alkyl halides. For example, in 69 percent of the radioactive decays of ^{131}I-labeled CH_3I the parent ion CH_3Xe^+ remains intact; by comparison, in the radioactive decay of ^{82}Br-labeled CH_3Br only 0.4 percent of the decays produce CH_3Kr^+ (*10*). This result is readily interpretable in terms of the carbon–rare gas bond energies estimated above (43 and 21 kcal/mole for xenon and krypton, respectively) and the average excitation energy deposited in the carbon–rare gas bond as a result of the β^--decay of the radioactive alkyl halide (5 and 56 kcal/mole for xenon and krypton, respectively) (*10*).

The findings presented here add to a growing body of evidence indicating the generality of gas-phase nucleophilic displacement reactions (*13, 14*). The results also indicate that the nucleophilic displacement process generalized in reaction 1 may be conveniently used in favorable cases for the gas-phase synthesis of rare gas–organic molecular ions of interest.

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References and Notes

1. G. A. Sinnott, *Univ. Colo. Joint Inst. Lab. Astrophys. Inform. Center Rep. No. 9* (1969), and references cited therein; F. H. Field and J. L. Franklin, *J. Amer. Chem. Soc.* **83**, 4509 (1961); in *Advances in Mass Spectrometry*, R. M. Elliott, Ed. (Pergamon, New York, 1963), vol. 2, pp. 484–502.
2. F. H. Field, H. H. Head, J. L. Franklin, *J. Amer. Chem. Soc.* **84**, 1118 (1962).
3. T. O. Tiernan and P. S. Gill, *J. Chem. Phys.* **50**, 5042 (1969); G. R. Hertel and W. S. Koski, *J. Amer. Chem. Soc.* **87**, 1686 (1965); S. Wexler, *ibid.* **85**, 272 (1963).
4. M. S. B. Munson and F. H. Field, *ibid.* **87**, 4242 (1965); F. S. Klein and L. Friedman, *J. Chem. Phys.* **41**, 1789 (1964); V. Aquilanti, A. Galli, A. Giardini-Guidoni, G. G. Volpi, *ibid.* **43**, 1969 (1965); W. A. Chupka and M. E. Russell, *ibid.* **49**, 5426 (1968).
5. L. P. Theard and W. H. Hamill, *J. Amer. Chem. Soc.* **84**, 1134 (1962).
6. P. S. Rudolph, S. C. Lind, C. E. Melton, *J. Chem. Phys.* **36**, 1031 (1962).
7. C. E. Melton and P. S. Rudolph, *ibid.* **33**, 1594 (1960).
8. M. S. B. Munson, J. L. Franklin, F. H. Field, *J. Phys. Chem.* **67**, 1541 (1963); J. S. Dahler, J. L. Franklin, M. S. B. Munson, F. H. Field, *J. Chem. Phys.* **36**, 3332 (1962).
9. M. S. B. Munson, F. H. Field, J. L. Franklin, *J. Chem. Phys.* **37**, 1790 (1962).
10. T. A. Carlson and R. M. White, *ibid.* **39**, 1748 (1963).
11. ———, *ibid.* **38**, 2075 (1963).
12. ———, *ibid.* **36**, 2883 (1962).
13. D. Holtz, J. L. Beauchamp, S. D. Woodgate, *J. Amer. Chem. Soc.* **92**, 7484 (1970). The methyl cation affinity of the species M is defined as the negative value of the enthalpy change for the process $CH_3^+ + M \rightarrow CH_3M^+$.
14. D. Holtz and J. L. Beauchamp, *Nature Phys. Sci.* **231**, 204 (1971).
15. Attempts to prepare stable neutral organoxenon compounds have thus far been unsuccessful [see T. C. Shieh, E. D. Feit, C. L. Chernick, N. C. Yang, *J. Org. Chem.* **35**, 4020 (1970)].
16. The instrumentation and techniques employed have been previously described in detail [see J. D. Baldeschwieler, *Science* **159**, 263 (1968); D. Holtz, J. L. Beauchamp, J. R. Eyler, *J. Amer. Chem. Soc.* **92**, 7045 (1970)].
17. S. L. Patt, J. L. Beauchamp, D. Holtz, unpublished results.
18. J. L. Beauchamp, D. Holtz, S. D. Woodgate, S. L. Patt, *J. Amer. Chem. Soc.*, in press.
19. This thermochemical result is based on the assumption that the $^2P_{3/2}$ state of Kr^+ undergoes reaction 5. If, instead, only the higher energy $^2P_{1/2}$ state of Kr^+ is reactive, then $\Delta H_f(CH_3Kr^+) = 265 \pm 22$ kcal/mole, equivalent to MCA(Kr) $= 14 \pm 22$ kcal/mole.
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7 June 1971 ■

Antiprismatic Coordination about Xenon: The Structure of Nitrosonium Octafluoroxenate(VI)

Abstract. *The structure of nitrosonium octafluoroxenate(VI), $2NOF \cdot XeF_6$, has been determined by means of single-crystal x-ray counter methods* (R*-index* = *0.046, weighted* R*-index* = *0.042). The space group is* Pnma, *with* a = *8.914(10) angstroms,* b = *5.945(10) angstroms, and* c = *12.83(2) angstroms (the numbers in parentheses are the standard deviations to the least significant digit or digits); the calculated density* (ρ) *is 3.354 grams per cubic centimeter, and there are four formula units per unit cell. The material consists of well-separated NO^+ and $(XeF_8)^{2-}$ ions; the structural formula is thus $(NO)_2(XeF_8)$. The anion configuration is that of a slightly distorted Archimedean antiprism. The observed distortion appears incompatible with a lone-pair repulsion model. Xenon-fluorine bond lengths of 1.971(7), 1.946(5), 1.958(7), 2.052(5), and 2.099(5) angstroms were found.*

Several addition compounds of XeF_6 with alkali fluorides (*1*) and with nitrosyl fluoride (*2*) have been prepared in the solid state. One of these compounds, $2NOF \cdot XeF_6$, has been prepared by Moody and Selig (*2*) who, on the basis of evidence from infrared and Raman measurements, suggested the formulation $(NO)_2(XeF_8)$ for the solid. The structural investigation reported here

Table 1. Positional and thermal parameters for $(NO)_2(XeF_8)$. The numbers in parentheses are the standard deviations to the least significant digit or digits.

Atom	Refined coordinates			Anisotropic temperature factor*					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Xe	0.21834(7)	¼	0.12717(5)	0.0054(1)	0.0071(2)	0.00234(5)	0	0.00039(5)	0
F(1)	.2650(8)	¼	−.0230(5)	.013(1)	.029(3)	.0033(4)	0	.0007(5)	0
F(2)	.0064(7)	¼	.1672(6)	.0058(8)	.021(2)	.0070(5)	0	.0021(5)	0
F(3)	.1302(5)	0.5224(9)	.0695(4)	.0105(7)	.019(2)	.0053(3)	0.0041(9)	.0006(4)	0.0035(6)
F(4)	.4048(5)	.4641(8)	.1152(3)	.0076(5)	.016(1)	.0046(3)	−.0036(7)	.0003(3)	.0002(6)
F(5)	.2131(5)	.4620(8)	.2533(3)	.0120(6)	.015(1)	.0030(2)	−.0010(8)	.0012(3)	−.0017(5)
N(1)	−.0016(13)	¼	.7319(8)	.010(2)	.008(3)	.0070(9)	0	.0032(9)	0
N(2)	.1143(15)	¼	.4667(11)	.015(2)	.023(4)	.0063(10)	0	−.0042(11)	0
O(1)	.0608(10)	¼	.7979(7)	.009(1)	.020(3)	.0057(6)	0	.0020(8)	0
O(2)	.2037(15)	¼	.4296(8)	.020(2)	.053(6)	.0028(6)	0	−.0010(9)	0

* The expression for the anisotropic temperature factor is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl]$.

provides definitive evidence for the suggested formulation with an eight-coordinate (XeF$_8$)$^{2-}$ anion and establishes the geometry of the ion to be essentially that of an Archimedean antiprism.

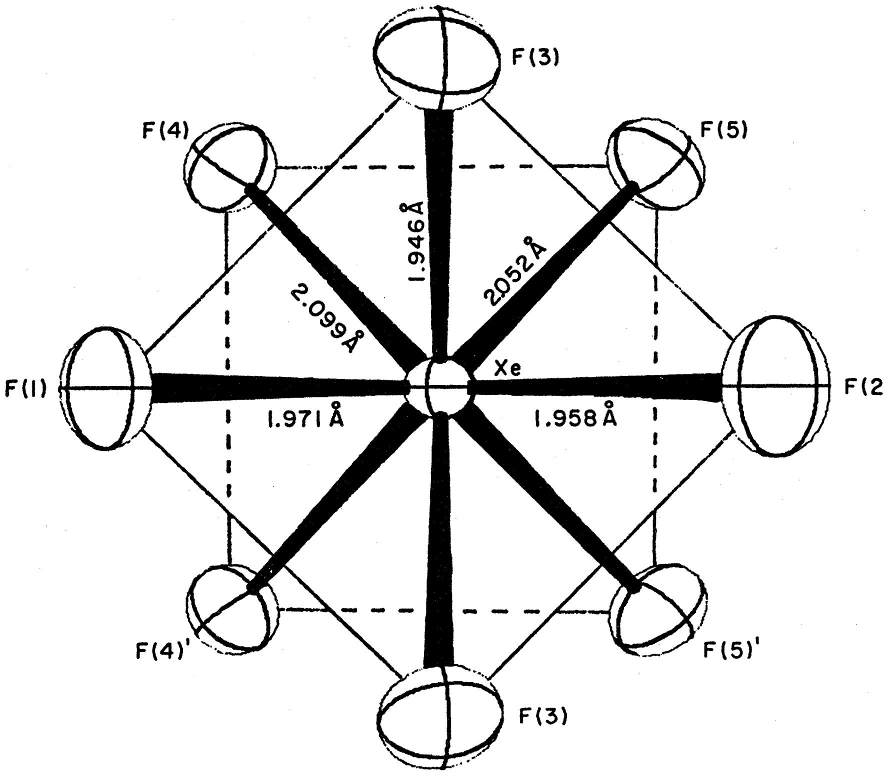

Fig. 1. Configuration of the (XeF$_8$)$^{2-}$ anion looking down the approximate $\bar{8}$ axis. Atoms F(1) and F(2) lie in the mirror plane which is the only symmetry element present. The magnitudes of the thermal motion of the individual atoms (indicated by the thermal ellipsoids in the diagram) are relatively small for such a volatile material.

We prepared the compound in a manner similar to that of Moody and Selig (*2*) and obtained single crystals by condensing the solid at -195°C (vapor pressure, ~ 8 mm at room temperature) into Kel-F capillaries that had earlier been treated with fluorine and allowing the condensate to stand at 28°C for 2 weeks. Preliminary infrared and Raman data were in agreement with those of Moody and Selig. Our infrared experiments showed strong peaks at about 540 and 2310 cm^{-1} whereas our Raman scans showed peaks at 543 and 2309 cm^{-1} [see also peaks at 540 and 2305 cm^{-1} (*2*)].

The crystal data are as follows: $a = 8.914(10)$ Å, $b = 5.945(10)$ Å, $c = 12.83(2)$ Å (the numbers in parentheses are standard deviations to the least significant digit or digits), cell volume $U = 679.9$ Å^3, calculated density $(\rho) = 3.354$, number of formula units per cell $(Z) = 4$, space group *Pnma* or *Pn*2$_1$*a*, with the former preferred on the basis of the structure refinement.

Diffraction data to $2\theta = 50°$ (MoKα radiation, wavelength $\lambda = 0.7107$ Å) were measured on a computer-controlled x-ray diffractometer (*3*) by the θ-2θ scan mode. All data were corrected for absorption (absorption coefficient $\mu = 53.6$ cm^{-1}), and the structure was solved by conventional Patterson and difference Fourier methods. The complete anisotropic structure factor refinement with 73 variables has led to residual values of an *R*-index of 0.046 and a weighted *R*-index of 0.042 for the 606 reflections above background out of some 673 reflections collected. Final structure and thermal parameters are listed in Table 1.

The structure consists of well-separated NO$^+$ and (XeF$_8$)$^{2-}$ ions, with all ions centered on the mirror planes $y = \pm 1/4$. The anion, which may be described as a slightly distorted antiprism, is depicted in Fig. 1. The four fluorine atoms which comprise one square face of this figure [F(1), F(3), F(2), and F(3)′] reside at the independent distances of 1.971(7), 1.946(5), and 1.958(7) Å, with a mean distance of 1.958(9) Å from the central xenon atom, whereas the four fluorine atoms comprising the other square face [F(4), F(5), F(4)′, F(5)′] are at the two independent distances of 2.099(5) and 2.052(5) Å. The shorter Xe–F distances found in this study compare favorably with those found for distances from the xenon atom to the terminal fluorine atoms in other xenon fluorides (*4*).

The distortion of the anion, which is constrained by the mirror plane, is slight and can be described as consisting largely of a stretch or elongation of the Xe–F(4) and Xe–F(5) bonds from the ideal antiprismatic configuration. This explanation is confirmed by the near equivalence of the angles F(1)–Xe–F(2), F(3)–Xe–F(3)′, and F(4)–Xe–F(5)′ which are, respectively, 117.4°, 112.6°, and 116.6°. Not surprisingly, the F(4) and F(5) atoms, which reside at greater distances from the xenon atom, are those fluorine atoms that have the closest contacts (2.424 to 2.560 Å) to the nitrogen atom of the cations. In addition, F(4), the fluorine atom farthest away from the xenon atom, has three nitrogen neighbors whereas F(5) has one nitrogen and two oxygen neighbors. We believe that the larger Xe–F separations are due to a weak interaction between fluorine atoms F(4) and F(5) and the neighboring (NO)$^+$ cations, thus causing a slight but significant distortion of the antiprism. However, the distortion might also be explained as a manifestation of some steric activity of the xenon lone pair. Since the eightfold xenon coordination observed here provides no clearly defined ninth coordination position for the lone pair, it appears to offer little support for electron repulsion models (*5*) which have been used with considerable success in rationalizing the structures of other noble gas compounds.

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References and Notes

1. R. D. Peacock, H. Selig, I. Sheft, *Proc. Chem. Soc.* **1964**, 285 (1964).
2. G. J. Moody and H. Selig, *Inorg. Nucl. Chem. Lett.* **2**, 319 (1966).
3. M. H. Mueller, L. Heaton, R. A. Aschenbrenner, L. Amiot, *Amer. Crystallogr. Ass. Progr. Abstr. E8, Minneapolis* (1967).
4. H. A. Levy and P. A. Agron, *J. Amer. Chem. Soc.* **85**, 241 (1963); J. H. Burns, P. A. Agron, H. A. Levy, *Science* **139**, 1208 (1963); R. D. Burbank and G. R. Jones, *ibid.* **168**, 248 (1970); N. Bartlett, F. Einstein, D. F. Stewart, J. Trotter, *J. Chem. Soc.* **1967A**, 1190 (1967); J. Martins and E. B. Wilson, Jr., *J. Chem. Phys.* **41**, 570 (1964); F. O. Sladky, P. A. Bulliner, N. Bartlett, J. B. DeBoer, A. Zalkin, *Chem. Commun.* **1968**, 1048 (1968).
5. R. J. Gillespie, *J. Chem. Soc.* **1963**, 4679 (1963).
6. We thank M. H. Mueller for use of the diffractometer for data collection. This report is based on work performed under the auspices of the U.S. Atomic Energy Commission.

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