Trifluoroxenon(IV) μ-fluoro-bispentafluoroantimonate(V): the XeF_3^+ Cation

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Summary The Raman spectrum of the complex XF_4,$2SbF_5$ is consistent with the ionic formulation XeF_3^+,$Sb_2F_{11}^-$, and the ^{19}F n.m.r. spectrum of the complex in solution in antimony pentafluoride has an AB_2 spectrum in the F-on-Xe region which may be unambiguously assigned to the XeF_3^+ ion.

ALTHOUGH a large number of complexes of XeF_2 and some of XeF_6 with other fluorides has been prepared,[1] no complexes of xenon tetrafluoride have been well characterized although some evidence exists for an unstable xenon tetrafluoride–antimony pentafluoride complex.[2] The complex was believed to have the composition XeF_4,$2SbF_5$ but no analytical or other conclusive evidence in support of this formulation has been published. Recently Bartlett *et al.*[3] reported that attempts to prepare $XeF_3^+RuF_6^-$ failed. A recent photoionization mass-spectrometric study has provided evidence for the XeF_3^+ ion in the gas phase.[4]

Cohen and Peacock[2] reported that xenon tetrafluoride or mixtures of xenon tetrafluoride and xenon difluoride dissolve in antimony pentafluoride with gas evolution to give green solutions. On removing the solvent by pumping at 25° they obtained an easily decomposed white solid in addition to the yellow XeF_2,$2SbF_5$ complex, but they were unable to isolate the white compound. They found that the n.m.r. spectra of the green solutions contained other peaks due to fluorine on xenon in addition to the peak that arises from XeF_2 and which has subsequently been shown to be due to XeF^+.[5]

In attempting to repeat this work we have found that XeF_4 is soluble in redistilled antimony pentafluoride at 50° to give a yellow–green solution which crystallizes at lower temperatures. The ^{19}F n.m.r. spectrum of the solution at 50° showed several poorly resolved peaks to low-field of an intense broad peak in the F-on-Sb region. In addition there was a very weak peak due to XeF^+ (*ca.* 2% of the intensity of the low-field peaks). We have found however that a mixture of XeF_2 and XeF_4 is quite soluble in SbF_5 at room temperature. The enhanced solubility of XeF_4 in solutions containing XeF_2 is apparently due to the increased ionizing power of the solvent resulting from the presence of the XeF^+ and $Sb_nF_{5n+1}^-$ ions. The room-temperature ^{19}F n.m.r. spectrum of the solution was similar to that described above, except that the resolution of the low-field peaks was considerably enhanced (Figure). The low-field F-on-Xe region of the spectra consists of an AB_2 spectrum with ^{129}Xe satellites. The ^{19}F n.m.r. parameters are listed in the Table. The spectrum is consistent with the expected C_{2v} geometry for XeF_3^+ in which two lone pairs occupy equatorial positions as in ClF_3 and BrF_3. The relative chemical shifts of the A and B parts of the spectrum are consistent with the suggested geometry, *i.e.*, the B (axial) fluorines occur at lower field than the A (equatorial) fluorine.[6]

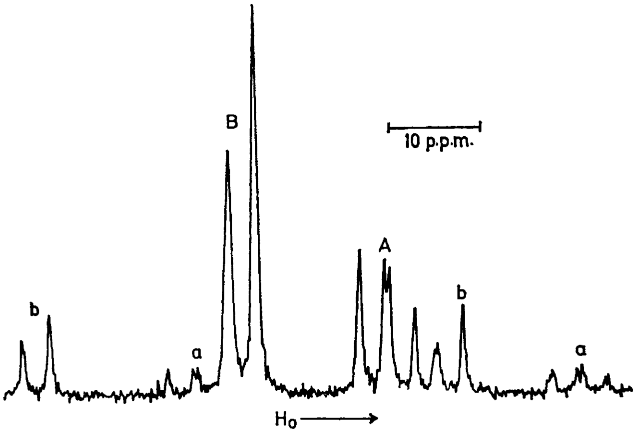


FIGURE. ^{19}F *n.m.r. spectrum* (26°, 56·4 *MHz*) *of the* XeF_3^+ *cation in a solution having the composition* $XeF_4 : XeF_2 : SbF_5 = 1{\cdot}00 : 2{\cdot}55 : 23{\cdot}3$. (A) *axial fluorines and* (a) ^{129}Xe *satellites*; (B) *equatorial fluorine and* (b) ^{129}Xe *satellites.*

TABLE

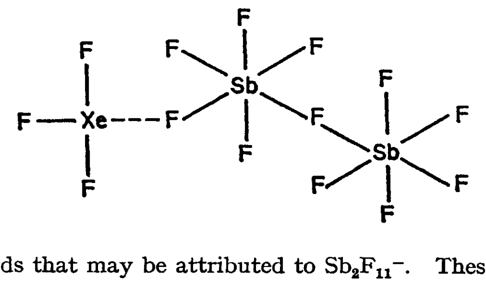
^{19}F *n.m.r. parameters for the* XeF_4–XeF_2–SbF_5 *system*

		Chemical shift (p.p.m.)[a]	J_{FF}(Hz)	J (^{129}Xe–F)
XeF_3^+	A	−23·0	174	2440
	B	−38·7		2620
XeF^+		+291·5		7260
SbF_5/$Sb_2F_{11}^-$		+112·5		

[a] With respect to external $CFCl_3$.

When a solution of XeF_4 in SbF_5 was pumped under vacuum until constant weight was obtained in approximately 36 h the final weight of the yellow crystalline material corresponded to a quantitative yield of XeF_3,Sb_2F_{11}. Elemental analysis of this material was in excellent agreement with this composition.

The Raman spectrum of a solution of XeF_4 in SbF_5 has, in addition to the bands due to SbF_5, two strong polarized bands at 584 and 643 cm^{-1}. The same two bands are observed in the spectrum of the solid compound, in addition



to bands that may be attributed to $Sb_2F_{11}^-$. These bands are not due to XeF_4 which has Raman bands at 543, 502 and 235 cm^{-1},[1] nor are they due to XeF^+ which in SbF_5 has a single strong Raman band[5] at 619 cm^{-1} or to $Xe_2F_3^+$ which has strong Raman bands[5] at 582 and 592 cm^{-1} and in any case is not expected to be present in an excess of

SbF_5. We conclude that these two bands are due to the XeF_3^+ ion. The ClF_3 molecule has two strong polarized Raman lines at 753 and 529 cm^{-1} which have been assigned as ν_1 (a_1) and ν_2 (a_1) which may be approximately described as the Cl–F equatorial stretch and the Cl–F symmetrical axial stretch. The analogous frequencies for BrF_3 have been calculated to be 662 and 528 cm^{-1}.[7] It seems reasonable therefore to assign the two strong polarized lines observed in a solution of XeF_4 in SbF_5 to the same vibrations of the T-shaped XeF_3^+ molecule. It is very probable that this ion is strongly fluorine bridged to the $Sb_2F_{11}^-$ (or $Sb_nF_{5n+1}^-$) anion and that this reduces the difference between the frequencies of the axial and equatorial bonds. The frequencies are higher than in XeF_4 because of the positive charge just as the frequency of XeF^+ is higher than those of XeF_2.

(*Received, September 13th,* 1971; *Com.* 1592.)

[1] J. H. Holloway, "Noble-Gas Chemistry," Methuen, London, 1968.

[2] B. Cohen and R. D. Peacock, *J. Inorg. Nuclear Chem.*, 1966, **28**, 3056.

[3] D. Gibler, B. Morrell, N. Bartlett, and A. Zalkin, *Abstracts* 162nd A.C.S. National Meeting, Washington, D.C., 1971.

[4] J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Spohr, *J. Chem. Phys.*, 1971, **75**, 1461.

[5] R. J. Gillespie, B. Landa, and A. Netzer, unpublished work.

[6] A. Engelbrecht and P. Peterby, *Angew. Chem. Internat. Edn.*, 1969, **8**, 768.

[7] H. H. Claassen, B. Weinstock, and J. G. Malm, *J. Chem. Phys.*, 1958, **28**, 285.