$XeOF_5^-$ and $[(XeOF_4)_3F]^-$ Anions

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Summary The $XeOF_5^-$ and $[(XeOF_4)_3F]^-$ anions, which comprise a new class of xenon(VI) oxyfluoro-anion, have been synthesized as their caesium salts and their structures have been characterized for the first time using vibrational spectroscopy and X-ray powder diffraction; the $XeOF_5^-$ anion displays a stereochemically active lone pair, and the polyanion $[(XeOF_4)_3F]^-$ consists of three equivalent $XeOF_4$ groups bonded to an F^- ion.

ALTHOUGH the oxyfluoro- and fluoro-cations of xenon and krypton have been studied in considerable detail,[1] no detailed studies have been made of the structures of xenon fluoro- and oxyfluoro-anions, with the exceptions of XeF_8^{2-},[2] XeO_3F^-,[3] and $XeOF_3^-$.[4] Complexes of $XeOF_4$ with the alkali metal fluorides and NOF of unspecified structures were first reported by Selig[5a] and Moody and Selig[5b] who isolated complexes corresponding to the stoicheiometries $CsF{\cdot}XeOF_4$, $3RbF{\cdot}2XeOF_4$, $3KF{\cdot}XeOF_4$, and $NOF{\cdot}XeOF_4$. As there is a complete lack of structural information on these complexes, we have further investigated the complexes between CsF and $XeOF_4$ in order to establish their gross structures.

The reactions between thoroughly dried CsF and pure samples of natural abundance $XeOF_4$ and ^{18}O-enriched $XeOF_4$ (62 and 99%) have been carried out in FEP vessels at room temperature using an excess of liquid $XeOF_4$. Removal of excess of $XeOF_4$ at 0 °C after the mixtures had been left for 10 h at room temperature yielded a white powder which had a composition corresponding to $CsF{\cdot}3XeOF_4$ and was stable at room temperature. Static distillation at room temperature resulted in loss of two molecules of $XeOF_4$ from $CsF{\cdot}3XeOF_4$ and the formation of a stable white powder possessing the stoicheiometry $CsF{\cdot}XeOF_4$.†

On the basis of the Raman spectroscopic results, $CsF{\cdot}XeOF_4$ is best formulated as the salt $Cs^+XeOF_5^-$. The stereochemical activity of the lone pair on xenon should lead to an anion structure (**1**) which is distorted from C_{4v}-symmetry for a pseudo-octahedral species to C_s-symmetry.[6] Because of the greater stereochemical requirement of an Xe=O bond, the lone pair of the distorted $XeOF_5^-$ anion presumably occupies an octahedral face adjacent to the axial fluorine. Under C_{4v} symmetry, $XeOF_5^-$ exhibits 11 Raman-active bands ($4a_1 + 2b_1 + b_2 + 4e$) while the distorted C_s-structure (**1**) yields 15 Raman-active bands ($9a'$ and $6a''$). The vibrational data support the C_s-structure and have been assigned accordingly. The vibrational modes for IOF_5 and $TeOF_5^-$ (C_{4v}) have been correlated with those of $XeOF_5^-$ under C_s-symmetry for comparison (Table 1). A total of four $^{18}O/^{16}O$-dependent bands have been observed and these have accordingly been assigned to the various modes involving motions of the oxygen. The Xe=O and Xe–F stretching modes of $XeOF_5^-$ are lower in frequency than the corresponding modes in $XeOF_4$ (Table 1) and this is consistent with anion formation.

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† The X-ray powder pattern of $CsF{\cdot}XeOF_4$ could not be indexed (Table 2).

TABLE 1. Raman spectra and assignments for $XeOF_5^-$, $[(XeOF_4)_3F]^-$ and related species.

Raman frequency/cm^{-1} [a]			Assignment and approximate description, C_{4v}-symmetry [q]
$:XeOF_5^-$ [o]	IOF_5 [b]	$TeOF_5^-$ [c]	
883(66) [e]	927s	863s	a_1, $\nu(X{=}O)$
544 sh	710w	664sh	b_1, $\nu_{sym}(XF_4)$ out-of-phase
524(100)	680vs	650vs	a_1, $\nu_{sym}(XF_4)$
473(34), 468(29), 435(12) } [f]	647s	637vs [n]	e, $\nu_{asym}(XF_4)$
420(10)	640vs	581m	a_1, $\nu(XF')$
410(7), 396(24) } [f,g]	372m	347w	e, $\delta(F'XF_4)$, $F'{-}X{=}O$ bend
390(40)	363m [n]	—	b_2, $\delta_{sym}(XF_4)$ out-of-plane
361(17)	330w	327m	a_1, $\delta_{sym}(XF_4)$ in plane
384(18), 365(15) } [f,h]	341s	282w	e, $\delta(O{=}XF_4)$, OF_3 scissoring
293(13), 274(8) } [f,i]	307m	—	e, $\delta_{asym}(XF_4)$ in plane, OF_3 puckering
177(1)	205vw	—	b_1, $\delta_{asym}(XF_4)$ out-of-plane

Raman frequency/cm^{-1} [a]		Assignment and approximate description C_{4v}-symmetry
$Cs^+[(XeOF_4)_3F]^-$ [p]	$XeOF_4$ [d]	
905(41) [j]	919s	a_1, $\nu(Xe{=}O)$
556(110), 556(3), 551(3), 542(3), 534(1), 532(1), 521(4), 511(46) } [k]	609vs [n] 566vs 530w	e, $\nu_{asym}(XeF_4)$ a_1, $\nu_{sym}(XeF_4)$ b_1, $\nu_{sym}(XeF_4)$ out-of-plane
376(8), 368(2) } [l,m]	364mw	e, $\delta(F_4X{=}O)$
300(2), 292(1) } [m]	286vw	a_1, $\delta_{sym}(XeF_4)$ out-of-plane
238(2), 231(1) } [m]	231s	b_1, $\delta_{sym}(XeF_4)$ in plane
220(1)		
191(1·5), 187(0·5) } [m]	Not observed	b_2, $\delta_{asym}(XeF_4)$ out-of-plane
178(2), 173(2)		
163(2), 160(1) } [m]	161vw	e, $\delta_{asym}(XeF_4)$ in plane

Intensities: s, strong; m, medium; w, weak; vs, very strong; vw, very weak; sh, shoulder.

[a] Spectra were recorded using the 5145 Å exciting line of an argon ion laser; Raman shifts are accurate to ± 1 cm^{-1}. All data quoted are for the ^{16}O-compounds; $^{16}O/^{18}O$-isotopic shifts are given in subsequent footnotes to the Table. [b] J. H. Holloway, H. Selig, and H. H. Claassen, *J. Chem. Phys.*, 1971, **54**, 4305. [c] E. Mayer and F. Sladky, *Inorg. Chem.*, 1975, **14**, 589. [d] H. H. Claassen, C. L. Chernick, and J. G. Malm, in 'Noble-Gas Compounds,' ed. H. H. Hyman, University of Chicago Press, 1963, p. 287; D. F. Smith, *Science*, 1963, **140**, 899. [e] $^{16}O/^{18}O$-isotopic shift: 44 cm^{-1}. [f] The *e*-mode (C_{4v} symmetry) is split into its *a′*- and *a″*-components under C_s symmetry. [g] $^{16}O/^{18}O$-isotopic shifts: 3 and 6 cm^{-1} for the 410 and 396 cm^{-1} lines, respectively. [h] $^{16}O/^{18}O$-isotopic shifts: 6 and 13 cm^{-1} for the 384 and 365 cm^{-1} lines, respectively. [i] $^{16}O/^{18}O$-isotopic shifts: 3 and 7 cm^{-1} for the 293 and 274 cm^{-1} lines, respectively. [j] $^{16}O/^{18}O$-isotopic shift: 45 cm^{-1}. [k] Vibrationally coupled Xe–F stretching modes. [l] $^{16}O/^{18}O$-isotopic shift: 14 cm^{-1} (see Figure). [m] Represent the a_1 (high-frequency line), and *e* (low-frequency line), components owing to vibrational coupling under C_{3v} symmetry. [n] Not observed in the Raman spectrum; value obtained from the i.r. spectrum. [o] Lattice modes: 153(4), 116(6), 102(11), 89(13), and 76(6) cm^{-1}. [p] Lattice modes: 115(0·5), 101(1), 96(1), 87(1), 76(0·5), 66(2), 56(1), 48(0·5), and 38(2) cm^{-1}. [q] Correlations for the irreducible representations of $XeOF_5^-$ (C_s symmetry) and $[(XeOF_4)_3F]^-$ (C_{3v} symmetry) to those of XeO_6 and $XeOF_4$ (C_{4v} symmetries), respectively, may be found in W. G. Fateley, F. R. Dollish, N. T. McDevitt, and F. F. Bentley, 'Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: the Correlation Method,' Wiley, 1972.

The stoicheiometry $CsF{\cdot}3XeOF_4$ has not been reported previously. The presence of a single, sharp Xe=O stretching mode at 905 cm^{-1} (^{16}O-compound) and 860 cm^{-1} (^{18}O-compound indicates that all three co-ordinated $XeOF_4$ molecules are equivalently bonded to a central fluoride ion. The point symmetry of structure (**2**) is presumably C_{3v} as expected for an AX_3E_2 system (A = F, X = $XeOF_4$, and E = lone electron pair). A similar three-co-ordinate fluorine bridge is found in one of the crystalline forms of XeF_6 yielding trigonal-planar arrangements of xenon atoms about the central fluorine atoms.[7]

The *X*-ray powder diffraction data for $CsF{\cdot}3XeOF_4$ exhibit isomorphism with $CsF{\cdot}3IF_5$.[8–10] The principal lines at small Bragg angles can be indexed in a face-centred cubic cell with a = 6·932(7) Å for the xenon compound and a = 6·896(2) Å for the iodine compound. These reflections are listed in Table 2. From weak lines at small angles and the set of reflections at large angles, doubling of the cell is inferred (body-centred double cell). The small face-centred cubic cell gives only the arrangement of the heavy atoms without differentiating between them. However, a reasonable structural model leads to a xenon environment of caesium analogous to the iodine environment of caesium in $CsF{\cdot}3IF_5$, *i.e.* each Cs atom is surrounded by 12 Xe atoms and each Xe atom is surrounded by 4 Cs atoms. A trigonal planar arrangement of Xe or I atoms is then consistent with the proposed ionic formulations $Cs^+[(XeOF_4)_3F]^-$ and $Cs^+[(IF_5)_3F]^-$.

The proposed structure of the $(XeOF_4)_3F^-$ anion is supported by $^{16}O/^{18}O$-isotopic substitution experiments and the resulting vibrational coupling patterns. While the Xe=O stretching and $F_4Xe{=}O$ bending modes clearly exhibit the expected isotopic dependence in the ^{16}O (100%) and ^{18}O (99%) preparations, all vibrational modes, with the exception of the Xe=O stretches, are found to be strongly coupled (Figure and Table 1). For example, additional lines have been observed for the $F_4Xe{=}O$ bend and assigned to in-phase (a_1) and out-of-phase (*e*) components resulting from vibrational coupling under C_{3v}-symmetry.

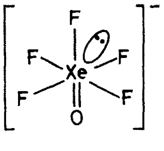
A detailed consideration of the strong vibrational coupling among the $F_4Xe{=}O$ bending modes confirms that three $XeOF_4$ molecules are equivalently bonded to a central fluorine atom. The a_1- and e-components which result from the easily resolved strong coupling of the $F_4Xe{=}O$ bends have identical relative intensities in both the ^{16}O- and ^{18}O-compounds and possess identical isotopic shifts of 14 cm^{-1} (Figure). Intermediate levels of enrichment (*i.e.* 62% ^{18}O) result in statistical mixtures of all possible isotopic isomers, *i.e.* the two C_{3v}-species $[(Xe^{16}OF_4)_3F]^-$ and $[(Xe^{18}OF_4)_3]^-$ discussed above and the two new C_{2v}-species $[(Xe^{16}OF_4)_2(Xe^{18}OF_4)F]^-$ and $[(Xe^{16}OF_4)(Xe^{18}OF_4)_2F]^-$. Reduction of C_{3v}-symmetry to C_{2v}-

TABLE 2. *X*-ray powder data for $CsF{\cdot}XeOF_4$, $CsF{\cdot}3XeOF_4$, and $CsF{\cdot}3IF._5$[a]

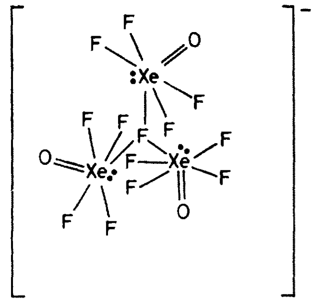
	$CsF{\cdot}XeOF_4$	
$d_{obs.}$	$d_{obs.}$	$d_{obs.}$
7·69 (mw)	2·752 (tr.)	1·890 (m)
5·98 (mw)	2·662 (w)	1·818 (vw)
4·67 (w)	2·493 (mw)	1·772 (w)
4·21 (s)	2·466 (m)	1·697 (w)
3·99 (tr.)	2·378 (tr.)	1·654 (vw)
3·82 (m)	3·336 (m)	1·606 (tr.)
3·70 (tr.)	2·279 (vw)	1·586 (w)
3·51 (tr.)	2·197 (mw)	1·538 (vw)
3·33 (ms)	2·097 (tr.)	1·485 (w)
3·23 (mw)	2·068 (vw)	1·451 (w)
2·957 (m)	2·013 (m)	1·426 (w)
2·837 (tr.)	1·954 (mw)	1·403 (w)

$CsF{\cdot}3XeOF_4$				$CsF{\cdot}3IF_5$			
hkl	$d_{obs.}$	$d_{calc.}$		*hkl*	$d_{obs.}$	$d_{calc.}$	
111	3·98	4·00	(s)	111	3·97	3·98	(s)
200	3·45	3·466	(m)	200	3·44	3·448	(m)
220	2·444	2·451	(m)	220	2·43	2·438	(m)
311	2·083	2·090	(ms)	311	2·069	2·079	(ms)
222	1·996	2·001	(mw)	222	1·983	1·990	(mw)
400	1·731	1·733	(w)	400	1·719	1·724	(w)
331	1·589	1·590	(m)	331	1·578	1·582	(m)
420	1·550	1·550	(m)	420	1·538	1·542	(m)
422	1·415	1·415	(mw)	422	1·406	1·407	(mw)
511/333	1·334	1·334	(mw)	511/333	1·326	1·327	(mw)
440	1·224	1·225	(w)	440	1·220	1·219	(w)

[a] Intensities: s, strong; m, medium; w, weak; vw, very weak; tr., trace.



(1)



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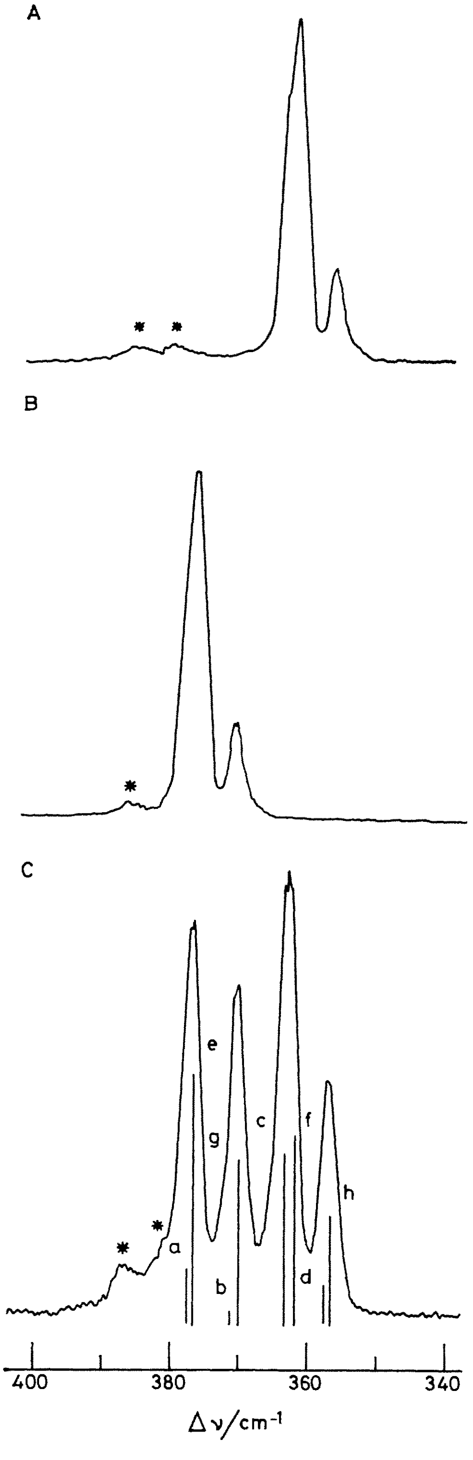

FIGURE. Vibrationally coupled $F_4Xe{=}O$ bends of the $[(XeOF_4)_3F]^-$ anion: (A) 99% ^{18}O-enriched. (B) 100% ^{16}O-enriched, (C) 62% ^{18}O-enriched, where a, b and c, d represent a_1– and e-modes of $[(Xe^{16}OF_4)_3F]^-$ and $[(Xe^{18}OF_4)_3F]^-$, respectively, under C_{3v} symmetry and e, f and g, h represent a'-modes of $[(Xe^{16}OF_4)_2(Xe^{18}OF_4)F]^-$ and $[(Xe^{16}OF_4)(Xe^{18}OF_4)_2F]^-$, respectively, under C_{2v} symmetry.

symmetry presumably results in splitting of the asymmetrically coupled $F_4Xe{=}O$ bends belonging to the *e*-symmetry species into their respective *a′* and *a″*-components for each C_{2v} species. The spectrum and overlap scheme for the a_1, *e*, and *a′* modes resulting from vibrational coupling of the $F_4Xe{=}O$ bends in statistical mixtures of four isotopic isomers are given in the Figure.‡

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‡ The two *a″* modes arising from $[(Xe^{16}OF_4)_2(Xe^{18}OF_4)F]^-$ and $[(Xe^{16}OF_4)(Xe^{18}OF_4)_2F]^-$ are not accounted for in the present scheme owing to their apparent low intensities. The observed splitting patterns arising from two isotopically pure and two mixed species nevertheless support the proposed structure (**2**).

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