The Preparation and Characterisation of $XeF_2.WOF_4$ and $XeF_2.2WOF_4$ by ^{19}F Nuclear Magnetic Resonance and Raman Spectroscopy. Examples of Non-labile Xenon–Fluorine–Metal Bridges.

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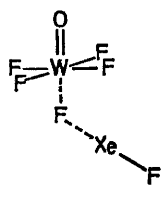
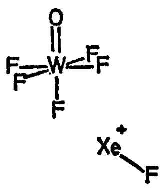
Summary Raman and ^{19}F n.m.r. spectroscopy show that the adducts $XeF_2{\cdot}WOF_4$ and $XeF_2{\cdot}2WOF_4$, both in the solid state and in solution, are best formulated as covalent structures containing Xe---F---W bridges. ^{19}F n.m.r. spectra of $XeF_2{\cdot}2WOF_4$ dissolved in SO_2ClF also show that complex equilibria involving Xe-O-W and Xe---F---W bridged species occur.

The only previously reported adducts of XeF_2 involve the interaction of XeF_2 with a pentafluoride to form adducts $2XeF_2{\cdot}MF_5$, $XeF_2{\cdot}MF_5$, and $XeF_2{\cdot}2MF_5$ (M = As, Sb, Nb, Ta, Pt, Ir, *etc.*).[1] The structures of these compounds have been interpreted in terms of ionic formulations involving the $Xe_2F_3^+$ and XeF^+ cations and the MF_6^- and $M_2F_{11}^-$ anions.



(I)



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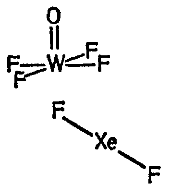
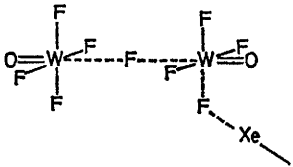


(III)

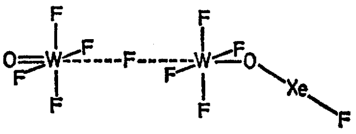
The XeF^+ compounds contain a weak covalent interaction, through a fluorine bridge, between the anion and the cation.[2] Low temperature ^{19}F n.m.r. studies reveal, however, that the Xe---F---M fluorine bridge interaction is labile in solution.[3] Tungsten oxide tetrafluoride behaves as a fluoride acceptor and both the mononuclear WOF_5^- anion[4,5] and the fluorine-bridged dinuclear $W_2O_2F_9^-$ anion[5,6] have been previously characterised by ^{19}F n.m.r. spectroscopy. Since it was anticipated that these anions would be stronger fluoride-ion bases than MF_6^- or $M_2F_{11}^-$, we have investigated the reaction of WOF_4 with XeF_2 in the hope that adducts containing non-labile fluorine bridges in solution would result.

Stoicheiometric amounts of XeF_2 and WOF_4 react in HF at room temperature and in the melts at 30—75 °C to give stable, white, crystalline solids at room temperature which have the compositions $XeF_2{\cdot}WOF_4$ and $XeF_2{\cdot}2WOF_4$. No evidence for $2XeF{\cdot}WOF_4$ was obtained in the present work.

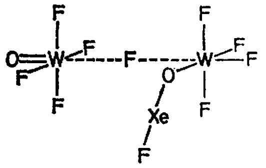
The low-temperature ^{19}F n.m.r. spectra of solutions of $XeF_2{\cdot}WOF_4$ in BrF_5 and SO_2ClF have been studied. In addition to the solvent line(s) both solutions showed a doublet of quintets and a doublet in the F-on-Xe^{II} region and a doublet in the F-on-W region of the spectrum. The three environments had relative intensities of 1:1:4, respectively, and constituted an AMX_4 spin system with accompanying ^{129}Xe and ^{183}W satellites. $XeF_2{\cdot}WOF_4$ is, therefore, best represented as a covalent species (I) in solution rather than as the ionic formulation (II) and is of particular interest since it contains a bridging fluorine atom. As in the case of $Xe_2F_3^+$, (ref. 3) the low-field F-on-Xe^{II} environment is assigned to the bridging fluorine while the high-field environment is assigned to the terminal fluorine. The assignments are confirmed by the observation of coupling between the bridging fluorine (two 1:4:6:4:1 quintets) and the equatorial fluorines on tungsten (doublet) and are, therefore, unambiguous.



(IV)



(V)



(VI)

Details of the *X*-ray crystallographic investigation of $XeF_2{\cdot}WOF_4$ will be published elsewhere.[7] The $XeF_2{\cdot}WOF_4$ structural unit has approximately C_s symmetry. The terminal Xe–F bond length (1·89 Å), which is less than that of XeF_2 (2·00 Å), is similar to the terminal Xe–F bond length (1·90 Å) observed in $Xe_2F_3^+AsF_6^-$ (ref. 8) while the Xe---F bridge bond length (2·04 Å) is shorter than the Xe---F bridge bonds in $Xe_2F_3^+$ (2·14 Å) and somewhat longer than the Xe–F bonds of XeF_2. The W---F---Xe bridge angle (147°) is also similar to that of the Xe---F---Xe bridge angle in the $Xe_2F_3^+$ cation (151°).

The covalent nature of the fluorine bridge bonds in $XeF_2{\cdot}WOF_4$ is further substantiated by the observation of vibrational modes in the Raman spectrum which can be associated with the fluorine bridge. The Raman spectrum of the linear F–Xe---F portion of the molecule (C_s site symmetry) is characterised by a strong factor-group split band at 573(100), 577(83) cm^{-1} assigned to the terminal, totally symmetric Xe-F stretching mode, a weak band at 458(8) cm^{-1} assigned to the bridging Xe---F stretching mode and a broad weak band at 153(14) cm^{-1} which is assigned to the two F–Xe---F bending modes expected for a molecule with a bent fluorine bridge. The equivalent frequencies for $Xe_2F_3^+$ (ref. 2) occur at 585 (sym. str.), 418 and 162 cm^{-1} and are in substantial agreement with the corresponding modes in $XeF_2{\cdot}WOF_4$. It is of interest to note that the terminal Xe–F stretching frequency of $XeF_2{\cdot}WOF_4$ is intermediate between that of XeF^+ compounds and XeF_2, that the bridging Xe---F stretching frequency occurs at a somewhat lower frequency than XeF_2 and that the W---F bridging stretching frequency, 439(11) cm^{-1}, is considerably less than $\nu_1(a_{1g})$ of WF_6, 771 cm^{-1}. The factor-group split band at 1044(14), 1033(56)cm^{-1} is assigned to the W=O stretching mode. These observations are in accord with the *X*-ray crystal investigation[7] which show the terminal Xe–F bond to have a length between that of XeF_2 and XeF^+, the bridging Xe---F bond being slightly longer than those of XeF_2 and the axial W–F bond being abnormally long in comparison to the equatorial W–F bonds.

From the distribution of bond lengths and the spectroscopic data, it is clear that structure (II) is not a major contributing valence-bond structure and a description in terms of the major valence-bond structures (I) and (III) is more appropriate.

The Raman spectrum of solid $XeF_2{\cdot}2WOF_4$ is consistent with the fluorine-bridged structure (IV). The F–Xe---F modes of $XeF_2{\cdot}2WOF_4$ are ν(Xe–F) 585(100), ν(Xe---F) 409(5) and δ(F-Xe---F) 144(5), 154(9) cm^{-1}. The two W=O stretching modes expected for structure (IV) were observed at 1044(24) and 1052(49)cm^{-1}. A line at 541(1) cm^{-1} can be assigned to ν (W---F). The W---F bridge bond *cis* to the oxygen in structure (IV) therefore is expected to be substantially shorter than the W---F bond in $XeF_2{\cdot}WOF_4$ (2·18 Å, 439 cm^{-1}).

Dissolution of $XeF_2{\cdot}2WOF_4$ in SO_2ClF resulted in a complex ^{19}F n.m.r. spectrum at −107°. In addition to lines associated with the fluorine-bridged structures (I) and (IV) and free WOF_4, lines attributable to the oxygen-bridged structures (V) and (VI) were also present. The spectrum is the result of a complex series of equilibria among structures (I), [(IV)—(VI)] and WOF_4. Although it has not yet been possible to assign the F-on-W region of the spectrum unambiguously, the ^{19}F n.m.r. parameters for the F-on-Xe region and their assignments are given in the Table. In addition to $XeF_2{\cdot}WOF_4$ and the fluorine-bridged $XeF_2{\cdot}2WOF_4$ isomer, the $Kr_2F_3^+$ (ref. 9) and $Xe_2F_3^+$ (ref. 3) cations, which have recently been characterised by ^{19}F n.m.r. spectroscopy in BrF_5 solution, are the only other noble-gas species which have thus far been shown to possess non-labile fluorine bridges in solution.

TABLE

^{19}F N.m.r. parameters for $XeF_2{\cdot}WOF_4$ and $XeF_2{\cdot}2WOF_4$

Solute conc/*m* temp./°C	Structure		Chemical shift /p.p.m.[a]	J_{FF}/Hz	$J_{^{129}Xe-^{19}F}$/Hz
$XeF_2{\cdot}WOF_4$ BrF_5(0·99) −62°	(I)	A	228·7	275	6128
		M	168·9		5016
		X_4	−65·3[b]	50·4	
$XeF_2{\cdot}2WOF_4$ SO_2ClF(0·64) −107°	(I)	A	226·2	279	6150
		M	168·1[c]		5000[c]
		X_4	−66·3	49	
	(IV[d])	A	237·0	279	6260
		M	168·1[c]		5000[c]
	(V)[d,e]		244·4		6330
	(VI)[d,e]		240·8		6315
	WOF_4		−73·4		

[a] Spectra recorded at 94·1 MHz and referenced with respect to external $CFCl_3$. [b] $J_{^{183}W-^{19}F}$ is 69 Hz. [c] The environments are near-coincident; additional fine structure due to spin–spin coupling with fluorine on tungsten was visible on each branch of the overlapping doublets arising from the Xe---F---W bridges. [d] Assignments for the fluorine-on-tungsten environments of structures [(IV)—(VI)] are not given in the present work. [e] Assignments are tentative.

Attempts to prepare the KrF_2 analogues were unsuccessful. The reaction of KrF_2 with WOF_4 in HF at −78° is vigorous resulting in the formation of Kr, WF_6 and oxygen according to the equation

$$KrF_2 + WOF_4 \rightarrow Kr + WF_6 + \tfrac{1}{2}O_2$$

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