Xenon Derivatives of the Highly Electronegative $O{=}IF_4O$ Group†

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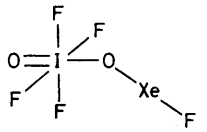
Stable oxygen-bonded xenon(II) and xenon(IV) derivatives of the highly electronegative $O{=}IF_4O$ group have been shown to exist in solution by ^{19}F and ^{129}Xe n.m.r. spectroscopy; the solid derivative, *cis,cis*-$Xe(OIF_4O)_2$, has also been isolated and characterized, and ^{129}Xe n.m.r. chemical shifts have been used to established the $O{=}IF_4O$ group as the most electronegative group known next to fluorine.

In addition to the simple binary fluorides, oxides, and fluoride oxides of xenon,[1] a number of ligands are known which are bonded to xenon through either oxygen[2] or nitrogen.[3] Each of these groups exists in the form of its monoprotic acid and possesses an effective group electronegativity which is very high. In the case of the $OTeF_5$ group, the effective electronegativity approaches that of fluorine itself, *i.e.* 3.87 on the Pauling scale.[4]

In the present work we have investigated the formation of xenon derivatives of the highly electronegative $O{=}IF_4O$ group. The latter group has been little studied with respect to derivative formation although $FOIOF_4$, $ClOFOF_4$, and $IO_2F_4^-$ salts are presently known.[5] It is generally convenient to synthesize xenon(II) derivatives by direct interaction of the xenon fluoride with the corresponding acid. In the case of $HOIOF_4$ we have discovered that this route was unsafe, leading to the formation of $FOIOF_4$ and its subsequent detonation. Attempts to prepare the $O{=}IF_4O$ analogue of $B(OTeF_5)_3$, the most widely used ligand-transfer reagent for the $OTeF_5$ group,[2] by the interaction of BCl_3 and $HOIOF_4$ also lead to the formation of explosive side products (believed to be chlorine oxides). Rather, insertion reactions of the type given in equations (1) and (2) utilizing the IO_2F_3 dimer[6] and an acid displacement reaction [equation (3)] were employed.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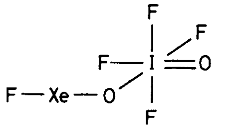
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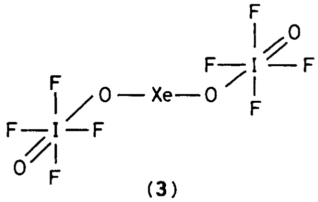
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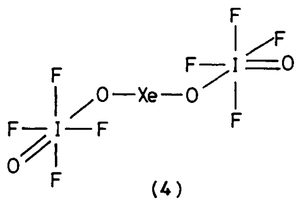
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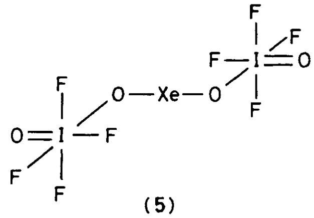
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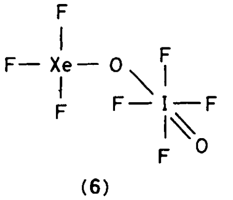
(6)

$$XeF_2 + (IO_2F_3)_2 \xrightarrow[SO_2ClF]{CFCl_3 \text{ or}} FXeOIF_4O + IOF_3 + \tfrac{1}{2}O_2 \quad (1)$$

$$FXeOIF_4O + (IO_2F_3)_2 \xrightarrow[SO_2ClF]{CFCl_3 \text{ or}} Xe(OIF_4O)_2 + IOF_3 + \tfrac{1}{2}O_2 \quad (2)$$

$$Xe(OTeF_5)_2 + 2HOIOF_4 \xrightarrow{CFCl_3} Xe(OIF_4O)_2 + 2HOTeF_5 \quad (3)$$

The compounds were characterized in $CFCl_3$ or SO_2ClF solution by ^{129}Xe n.m.r. spectroscopy (Figures 1a,b and 2) and

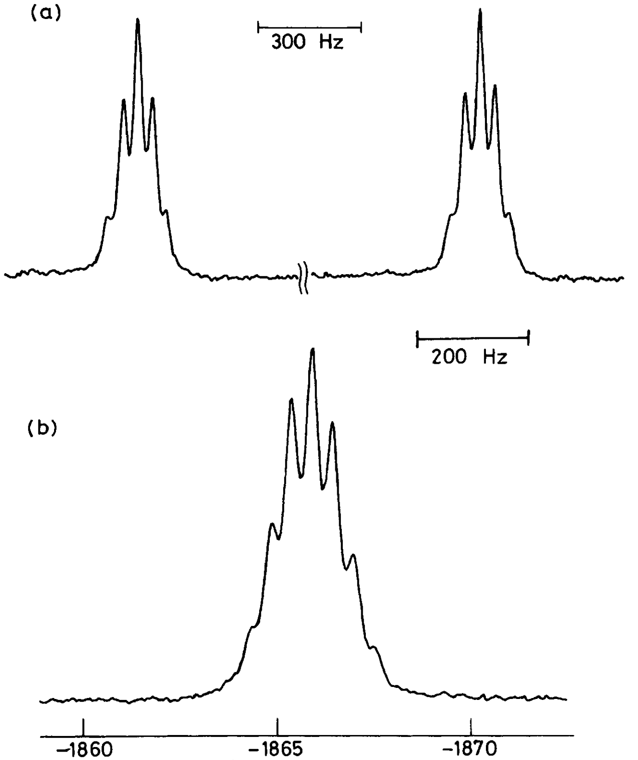

Figure 1. ^{129}Xe N.m.r. spectrum (69.38 MHz) of a 1 : 3.53 XeF_2–IO_2F_3 mixture recorded in SO_2ClF at −5 °C showing (a) the doublet of quintets [δ (^{129}Xe) = −1741.8 p.p.m.] arising from *trans*-$FXeOIOF_4$ (**1**); (b) the nonet [δ (^{129}Xe) = −1859.0 p.p.m.] arising from *trans,trans*-$Xe(OIOF_4)_2$ (**3**).

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† *Added in proof:* The work described in this communication was reported in part at the 8th European Symposium on Fluorine Chemistry, Jerusalem, Israel, August 21—26, 1983. Complementary work was also presented at the same conference by J. H. Holloway and D. Laycock. Abstracts: J. H. Holloway and D. Laycock, *J. Fluorine Chem.*, 1983, **23**, 443; G. A. Schumacher, T. R. G. Syvret and G. J. Schrobilgen, *ibid.*, 1983, **23**, 444.

Table 1. N.m.r. parameters for (δ values in p.p.m. and J in Hz) for the XeF_2–IO_2F_3 and XeF_4–IO_2F_3 systems

Species[a]	Solvent	Temp.°C	$\delta\,(^{129}Xe)^{b,c}$	$\delta\,(^{19}F)^{c,d}$	$^1J\,(^{129}Xe–^{19}F)$	$^3J\,(^{129}Xe–^{19}F)$
(1)	SO_2ClF	−5	−1741.8	−168.0	5909	41.8
	$CFCl_3$	24	−1856.7	–	5876	43.0
(2)	SO_2ClF	−5	−1868.5	−158.2	5866	
	$CFCl_3$	24	−1966.1	–	5848	e
(3)	SO_2ClF	−5	−1859.0			
	$CFCl_3$	24	−1990.6			38.3
(4)	SO_2ClF	−5	−1985.3			
	$CFCl_3$	24	−2116.3			e
(5)	SO_2ClF	−5	−2102.0			
	$CFCl_3$	24	−2231.0			e
(6)[c]	$CFCl_3$	24	24.4	8.98(t)	3417(d)	49[f]
				−8.65(d)	3658(t)	

[a] Xenon fluoride: IO_2F_3 ratio = 1:2. [b] Recorded at 69.38 MHz and referenced with respect to external neat $XeOF_4$ at 24 °C. [c] Positive chemical shifts signify a high frequency shift with respect to the reference. [d] Recorded at 235.31 MHz and referenced with respect to external neat $CFCl_3$ at 24 °C. ^{19}F Chemical shifts reported are for fluorine on xenon. [e] Multiplet fine structure was only partially resolved. [f] Value obtained from the ^{129}Xe satellite spacings in the ^{19}F n.m.r. spectrum.

Table 2. Some key Raman frequencies for *cis,cis*-$Xe(OIOF_4)_2$ (**5**).

Wavenumber/cm$^{-1\,a}$	Tentative assignment
889(32)	$\nu(I=O)$
745(8)	$\nu_{asym}(IF_2)_{eq.}$
688(56)	$\nu_{sym}(IF_2)_{eq.}$
668(38)	$\nu_{asym}(IF_2)_{ax.}$
614(54)	$\nu_{sym}(IF_2)_{ax.}$
464(100)	$\nu_{sym}(Xe–O–I)$, $\nu_{sym}(XeO_2)^b$
443(3)	$\nu_{asym}(Xe–O–I)$, $\nu_{asym}(XeO_2)^b$
148(78)	$\delta(O–Xe–O)$

[a] Raman spectrum recorded at −196 °C in an FEP sample tube. [b] These modes are presumed to be strongly coupled.

their characterization was corroborated, along with other fluorinated products, by ^{19}F n.m.r. spectroscopy. For the sake of brevity the ^{19}F n.m.r. results are not included in the present communication. Table 1 provides a summary of relevant ^{19}F and ^{129}Xe parameters associated with the xenon derivatives of the $O=IF_4O$ group [structures (**1**)—(**6**)]. On the basis of a comparison of the ^{129}Xe chemical shifts of $FXeOTeF_5$ [δ (^{129}Xe) −2051 p.p.m in SO_2ClF solvent at 24 °C] and $Xe(OTeF_5)_2$ (−2447 p.p.m. in $CFCl_3$ solvent at 24 °C) with those of the corresponding $O=IF_4O$ derivatives it is apparent that the latter group is more electronegative than $OTeF_5$, making it the most highly electronegative ligand known next to fluorine itself. This is also confirmed by the preparation of $F_3XeOIOF_4$ in solution and comparison of its ^{129}Xe chemical shift with that of the corresponding $OTeF_5$ derivative [δ (^{129}Xe) −25.5 p.p.m for $F_3XeOTeF_5$ in $CFCl_3$ solvent at 24 °C]. The ^{129}Xe chemical shifts of the xenon(II) derivatives are also noted to be additive, progressing to lower frequency with increased substitution of the *cis*-$O=IF_4O$ group. Additivity in chemical shifts is well established and, in the present instance, serves to confirm our structural assignments.

In addition $Xe(OIOF_4)_2$ has been prepared and isolated according to equation (3) as a pale yellow solid at 0 °C. The Raman, and ^{19}F and ^{129}Xe n.m.r. spectra are consistent with proposed *cis,cis*-structure (**5**); thus, only a single I=O stretch is observed and only the *cis,cis*-isomer is confirmed to be present in solutions when the solid sample is redissolved in $CFCl_3$.

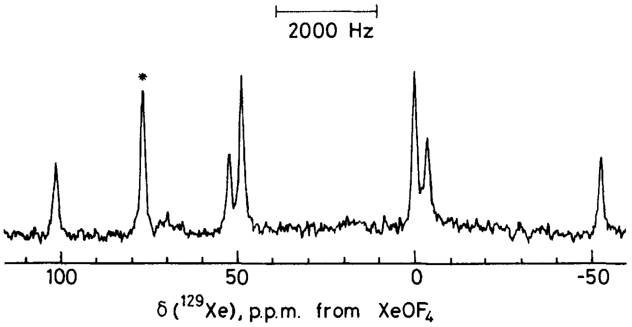

Figure 2. ^{129}Xe N.m.r. spectrum (69.38 MHz) of a 1 : 1.98 XeF_4–IO_2F_3 mixture recorded in $CFCl_3$ at 24 °C showing the doublet of triplets [δ (^{129}Xe) 24.4 p.p.m.] arising from F_3XOIOF_4 (**6**). The asterisk (*) denotes an XeF_4 multiplet peak.

Some key Raman frequencies are given in Table 2. The compound is unstable at room temperature, rapidly undergoing decomposition according to equation (4).

$$\begin{array}{l} cis,cis\text{-}Xe(OIOF_4)_2 \longrightarrow IF_5 + \underset{\displaystyle \tfrac{1}{2}IF_5 + \tfrac{1}{2}IO_2F}{\underset{\downarrow}{IOF_3}} + Xe + {}^3/_2O_2 \end{array} \qquad (4)$$

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References

1 N. Barlett and F. O. Sladky, in 'Comprehensive Inorganic Chemistry,' A. F. Trotman-Dickenson, Pergamon, Oxford, 1973, vol. 1, p. 213.
2 K. Seppelt, *Acc. Chem. Res.*, 1979, **12**, 211.
3 J. F. Sawyer, G. J. Schrobilgen, and S. J. Sutherland, *Inorg. Chem.*, 1982, **21**, 4064.
4 T. Birchall, R. D. Myers, H. De Waard, and G. J. Schrobilgen, *Inorg. Chem.*, 1982, **21**, 1068.
5 K. O. Christe, R. D. Wilson, and C. J. Schack, *Inorg. Chem.*, 1981, **20**, 2104.
6 L. E. Smart, *J. Chem. Soc., Chem. Commun.*, 1977, 519.