1564 *Inorg. Chem.* **1989**, *28*, 1564-1573

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario L8S 4M1, Canada

$FXeOIOF_4$ and $Xe(OIOF_4)_2$: Preparation and Study by ^{129}Xe and ^{19}F NMR Spectroscopy and Raman Spectroscopy and NMR Characterization of $LXeOIOF_4$ (L = $-OTeF_5$, $-OSO_2F$)

Robert G. Syvret[1] and Gary J. Schrobilgen*

Received September 29, 1988

The novel xenon(II) derivatives $FXeOIOF_4$ and $Xe(OIOF_4)_2$ have been shown by their solution ^{19}F and ^{129}Xe NMR spectra to result from the reaction between IO_2F_3 and XeF_2 in SO_2ClF, $CFCl_3$, and BrF_5 solvents. The covalently bonded $-OIF_4O$ groups are shown to be equilibrium mixtures of their cis and trans isomers and are oxygen-bonded to xenon. The solid derivative *cis,cis*-$Xe(OIOF_4)_2$ has been isolated from the acid displacement reaction between $Xe(OTeF_5)_2$ and the strong protonic acid *cis*/*trans*-$HOIOF_4$. In addition, a mixture of *cis*- and *trans*-$FXeOIOF_4$ was prepared by the reaction of stoichiometric amounts of IO_2F_3 and XeF_2 in HF solvent. Both *cis*- and *trans*-$FXeOIOF_4$ and *cis,cis*-$Xe(OIOF_4)_2$ were characterized by ^{19}F and ^{129}Xe NMR spectroscopy and low-temperature Raman spectroscopy. A comparison of ^{129}Xe NMR chemical shifts among Xe(II) compounds, including the mixed derivatives $F_4OIOXeOSO_2F$ and $F_4OIOXeOTeF_5$, indicates the effective group electronegativity order is $-F > -OSO_2F >$ *trans*-$OIF_4O >$ *cis*-$OIF_4O > -OTeF_5$.

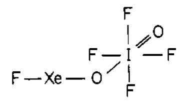
Introduction

In addition to the simple binary fluoride XeF_2,[2-6] a number of ligands are known to form covalent derivatives with Xe(II). Included in this list of ligands are $-OSO_2F$,[7] $-OTeF_5$,[8,9] $-OPOF_2$,[10] $-OSeF_5$,[11] $-OClO_3$,[7,12] $-OCOCF_3$,[13] $-ONO_2$,[14] $-N(SO_2F)_2$,[15,16] and $-N(SO_2CF_3)_2$[17] and, most recently, the novel nitrogen-bonded nitrile cations ($RC{\equiv}N{-}XeF^+$ (R = H, CH_3, CH_2F, C_2H_5, CF_3, C_2F_5, C_3F_7, C_6F_5),[18,20] the perfluoropyridine cations $C_5F_5N{-}XeF^+$ and $4\text{-}CF_3C_5F_5N{-}XeF^+$,[19] and the *s*-trifluorotriazine cation *s*-$C_3F_3N_2N{-}XeF^+$.[20] With the exception of the latter cations, nearly all of these ligand groups satisfy the same set of criteria;[21] namely, they form moderate to strong monoprotic acids, positive chlorine derivatives, and stable alkali-metal salts. All have high group electronegativities and are resistant to oxidation by Xe(II).

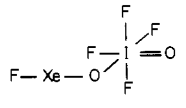
Although the $-OIF_4O$ group has been little studied with respect to derivative formation, the aforementioned criteria for stable xenon(II) derivatives have been met from among the limited list of previously known $-OIF_4O$ group derivatives, namely, $HOIOF_4$,[22-24] $K^+[IO_2F_4]^-$,[25] $Cs^+[IO_2F_4]^-$,[24,26] $FOIOF_4$,[24,27] and $ClOIOF_4$.[24] Preliminary solution NMR and solid-state Raman studies relating to the formation of the xenon(II) and xenon(IV) derivatives $FXeOIOF_4$, $Xe(OIOF_4)_2$, and $F_3XeOIOF_4$ and the isolation of *cis,cis*-$Xe(OIOF_4)_2$ have been reported in our earlier communication.[28] The details of preliminary investigations relating to the Xe(II) derivatives as well as the previously unreported isolation of $FXeOIOF_4$ are discussed in the present paper.

Results and Discussion

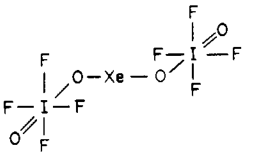
Identification of Xenon(II) Derivatives of $-OIF_4O$ in Solution by ^{129}Xe NMR Spectroscopy: The XeF_2/IO_2F_3 System. Varying proportions of XeF_2 and IO_2F_3 were initially investigated in SO_2ClF, $CFCl_3$, and BrF_5 solvents by ^{129}Xe and ^{19}F NMR spectroscopy. Iodine dioxide trifluoride inserts into the Xe–F bond of XeF_2 to give pseudooctahedral *cis*- and *trans*-OIF_4O oxygen-bonded derivatives of xenon(II) (structures I–V) according to eq 1 and 2.



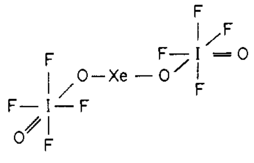
I



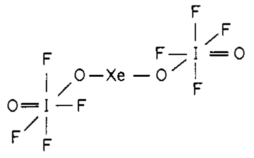
II



III



IV



V

$$IO_2F_3 + XeF_2 \underset{BrF_5\text{ or }CFCl_3}{\overset{SO_2ClF}{\rightleftharpoons}} FXeOIOF_4 \qquad (1)$$

$$IO_2F_3 + FXeOIOF_4 \underset{CFCl_3}{\overset{SO_2ClF\text{ or}}{\rightleftharpoons}} Xe(OIOF_4)_2 \qquad (2)$$

Established trends in ^{129}Xe chemical shifts[29] and $^{129}Xe{-}^{19}F$ spin–spin coupling constants form the basis for our structural assignments.

---

(1) Present address: Corporate Science and Technology Center, Air Products and Chemicals, Inc., Allentown, PA 18195.

(2) Chernick, C. L.; et al. *Science* **1962**, *138*, 136.

(3) Smith, D. F. *J. Chem. Phys.* **1963**, *38*, 270.

(4) Claassen, H. H.; Selig, H.; Malm, J. G. *J. Am. Chem. Soc.* **1963**, *85*, 1927.

(5) Smith, D. F. *Science* **1963**, *140*, 899.

(6) Weeks, J. L.; Chernick, C. L.; Matheson, M. S. *J. Am. Chem. Soc.* **1962**, *84*, 4612.

(7) Bartlett, N.; Wechsberg, M.; Sladky, F. O.; Bulliner, P. A. *J. Chem. Soc., Chem. Commun.* **1969**, 703.

(8) Sladky, F. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 373.

(9) Sladky, F. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 523.

(10) Eisenberg, M.; DesMarteau, D. D. *Inorg. Chem.* **1972**, *11*, 1901.

(11) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 723.

(12) Wechsberg, M.; Bulliner, P. A.; Sladky, F. O.; News, R.; Bartlett, N. *Inorg. Chem.* **1972**, *11*, 3063.

(13) Sladky, F. *Monatsh. Chem.* **1970**, *101*, 1571.

(14) Eisenberg, M.; DesMarteau, D. D. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 29.

(15) Sawyer, J. F.; Schrobilgen, G. J.; Sutherland, S. J. *J. Chem. Soc., Chem. Commun.* **1982**, 210.

(16) Sawyer, J. F.; Schrobilgen, G. J.; Sutherland, S. J. *Inorg. Chem.* **1982**, *21*, 4064.

(17) Foropoulos, J.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 4260.

(18) Schrobilgen, G. J.; Emara, A. A. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1644.

(19) Schrobilgen, G. J.; Emara, A. A. A. *J. Chem. Soc., Chem. Commun.* **1988**, 257.

(20) Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1506.

(21) DesMarteau, D. D.; LeBlond, R. D.; Hossain, S. F.; Nothe, D. *J. Am. Chem. Soc.* **1981**, *103*, 7734.

(22) Engelbrecht, A.; Peterfy, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 768.

(23) Engelbrecht, A.; Peterfy, P.; Schandara, E. *Z. Anorg. Allg. Chem.* **1971**, *384*, 202.

(24) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1981**, *20*, 2104.

(25) Gillespie, R. J.; Krasznai, J. P. *Inorg. Chem.* **1977**, *16*, 1384.

(26) Carter, H. A.; Ruddick, J. M.; Sams, J. R.; Aubke, F. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 29.

(27) Christe, K. O.; Wilson, R. D. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 375.

(28) Syvret, R. G.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1529.

(29) Schrobilgen, G. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 14.

0020-1669/89/1328-1564$01.50/0

Table I. ^{129}Xe and ^{19}F NMR Parameters for the IO_2F_3/XeF_2 System

species	chem shift, ppm[a] $\delta(^{129}Xe)$	$\delta(^{19}F)$[b]	$\delta(^{19}F)$[c]	coupling const, Hz $^1J(^{129}Xe–^{19}F)$	$^3J(^{129}Xe–^{19}F)$	solvent[d]	temp, °C
trans-$FXeOIOF_4$	−1741.2	−168.4	71.8	5913	42	SO_2ClF	−5
	−1853.6	−164.8	79.9	5880	43	$CFCl_3$	24
	−1720.5	*h*	*h*	5910	*f*	BrF_5	0
cis-$FXeOIOF_4$	−1865.0	−158.7	*e*	5870	*f*	SO_2ClF	−5
	−1962.0	−156.3	*e*	5849	*f*	$CFCl_3$	24
	−1823.5	*h*	*h*	5803	*f*	BrF_5	0
$FXeOSO_2F$	−1725	−170.9		5837	*f*	SO_2ClF	−5
trans,trans-$Xe(OIOF_4)_2$	−1860.7		76.9		38	SO_2ClF	−5
	−1994.6		*e*		38	$CFCl_3$	24
cis,trans-$Xe(OIOF_4)_2$	−1987.0		76.3[g]		19	SO_2ClF	−5
	−2120.0		79.2[g]		*f*	$CFCl_3$	24
cis,cis-$Xe(OIOF_4)_2$	−2105.8		*e*		*f*	SO_2ClF	−5
	−2235.7		*e*		*f*	$CFCl_3$	24
$LXeOSO_2F$							
trans-OIF_4O	−1834.2	*h*	*h*		*f*	SO_2ClF	−5
cis-OIF_4O	−1956.4	*h*	*h*		*f*		

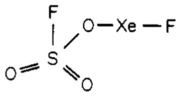
[a] IUPAC conventions have been used in reporting chemical shift data (*Pure Appl. Chem.* **1972**, *29*, 627; **1976**, *45*, 217); i.e., a positive chemical shift denotes a positive frequency and vice versa. ^{129}Xe and ^{19}F spectra have been referenced relative to liquid $XeOF_4$ and $CFCl_3$ at 24 °C, respectively. [b] F-on-Xe resonance. [c] F-on-I(VII) resonance. [d] NMR parameters are reported as average values determined for $XeF_2:IO_2F_3$ ratios between 1:0.88 and 1:3.53 for SO_2ClF solvent, between 1:1.65 and 1:3.70 for $CFCl_3$ solvent, and at 1:1.97 for BrF_5 solvent. [e] Overlapping or the nonresolved resonances preclude a definitive assignment for this species. [f] Spin–spin coupling was not resolved. [g] Refers to the singlet fluorine resonance arising from the *trans*-OIF_4O group. [h] Not determined.

For a given $XeF_2:IO_2F_3$ ratio, the ratios $FXeOIOF_4:Xe(OIOF_4)_2$ and *cis*-OIF_4O:*trans*-OIF_4O were found to be dependent on both temperature and solvent polarity. At low $XeF_2:IO_2F_3$ ratios (1:0.877), the ^{129}Xe NMR spectrum recorded in SO_2ClF solvent at −5 °C showed evidence for three doublet resonances at high frequency as well as four multiplet resonances at low frequency (Table I). The three high-frequency doublets arise from $^1J(^{129}Xe–^{19}F)$ and are assigned to the terminal fluorines on Xe(II) of the trans and cis isomers of $FXeOIOF_4$ (structures I and II) and of $FXeOSO_2F$ (structure VI) and are discussed in detail below. The fluorosulfate and the mixed bis isomers *cis*-$F_4OIOXeOSO_2F$ (structure VII) and *trans*-$F_4OIOXeOSO_2F$ (structure VIII) result from the reaction of $FXeOIOF_4$ with SO_2ClF solvent and are presumed to arise according to eq 3 and 4. The resonances assigned to *cis*- and *trans*-$FXeOIOF_4$ and

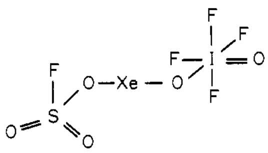
$$SO_2ClF + FXeOIOF_4 \rightarrow FXeOSO_2F + IOF_3 + [ClF]^{30} \quad (3)$$

$$FXeOSO_2F + IO_2F_3 \rightleftharpoons F_4OIOXeOSO_2F \quad (4)$$

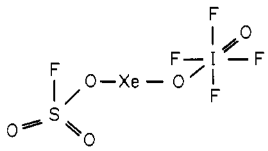
$FXeOSO_2F$ were found to predominate at this low $XeF_2:IO_2F_3$ ratio. The four multiplet resonances occurring to low frequency of the doublets were much less intense and could not be assigned with any certainty at this ratio. In the absence of any apparent spin–spin coupling, they were tentatively assigned to *trans,-trans*-$Xe(OIOF_4)_2$ (structure III), *cis,trans*-$Xe(OIOF_4)_2$ (structure IV), *cis,cis*-$Xe(OIOF_4)_2$ (structure V), and *cis*-$F_4OIOXeOSO_2F$ (structure VII) pending verification at lower $XeF_2:IO_2F_3$ ratios where the bis structures would be expected to dominate.



VI



VII



VIII

At high $IO_2F_3:XeF_2$ ratios in SO_2ClF solvent, ^{129}Xe and ^{19}F NMR spectra for all Xe(II) derivatives of the $-OIF_4O$ group could be observed in a single sample. At a $XeF_2:IO_2F_3$ ratio of 1:3.53 the $Xe(OIOF_4)_2:FXeOIOF_4$ ratio was increased, giving the cis,cis-, cis,trans, and trans,trans isomers of $Xe(OIOF_4)_2$ in the relative ratios 1.00:7.62:9.46, respectively, and the *trans*- and *cis*-$FXeOIOF_4$ isomers in the ratio 1.66:1. In addition, resonances arising from cis and trans isomers of $F_4OIOXeOSO_2F$ were also evident. The ^{129}Xe NMR spectrum of a 1:3.53 XeF_2/IO_2F_3 mixture recorded in SO_2ClF solvent at −5 °C is depicted in Figure 1a. The ^{129}Xe NMR chemical shifts as well as the $^1J(^{129}Xe–^{19}F)$ and $^3J(^{129}Xe–^{19}F)$ coupling constants are summarized in Table I.

The assignments for the doublet resonances are straightforward, being based on spin-multiplicity considerations and established ^{129}Xe chemical shift trends.[29,31] The assignment of the high-frequency doublet A to $FXeOSO_2F$ is based upon ^{129}Xe chemical shifts and $^1J(^{129}Xe–^{19}F)$ coupling constants previously reported[31] for this species. Resonance B on expansion (Figure 1b) consists of a doublet splitting (5923 Hz) arising from the one-bond Xe–F coupling $^1J(^{129}Xe–^{19}F)$. The doublet is further split into a quintet (42 Hz) resulting from the three-bond spin–spin coupling $^3J(^{129}Xe–^{19}F)$ arising from the four equivalent equatorial fluorines of the *trans*-OIF_4O group. The one-bond Xe–F coupling (5923 Hz) is similar in magnitude to other one-bond Xe–F couplings reported previously, i.e., $FXeOTeF_5$ (SO_2ClF, 26 °C, 5743 Hz),[32] $FXeOSO_2F$ (HSO_3F, −84 °C, 5975 Hz),[29,31] $FXeOSeF_5$ ($CFCl_3$, −40 °C, 5790 Hz),[11] and $FXeN(SO_2F)_2$ (BrF_5, −58 °C, 5586 Hz).[15] The three-bond Xe–F coupling (42 Hz) is consistent with the analogous couplings reported for other pseudooctahedral species, i.e., $FXeOTeF_5$ (34 Hz)[32] and $FXeOSeF_5$ (37 Hz).[29] The remaining doublet with unresolved fine structure, C (expanded in Figure 1c), is assigned to *cis*-$FXeOIOF_4$ by virtue of its one-bond Xe–F coupling (5879 Hz) and unresolved multiplet fine structure arising from the three-bond spin–spin coupling of four fluorines in three magnetically nonequivalent environments to the central ^{129}Xe nucleus (X) to give a first-order A_2GMX pattern.

The multiplet resonances in Figure 1a arise from the bis isomers and are assigned as follows: Resonance E on expansion (Figure 1d) shows an odd-line multiplet with seven lines resolved (^3J-

---

(30) Chlorine monofluoride is presumed to be formed during this reaction, though no supporting evidence has been obtained.

(31) Seppelt, K.; Rupp, H. H. *Z. Anorg. Allg. Chem.* **1974**, *409*, 331.

(32) Birchall, T.; Myers, R. D.; DeWaard, H.; Schrobilgen, G. J. *Inorg. Chem.* **1982**, *21*, 1068 and references therein.

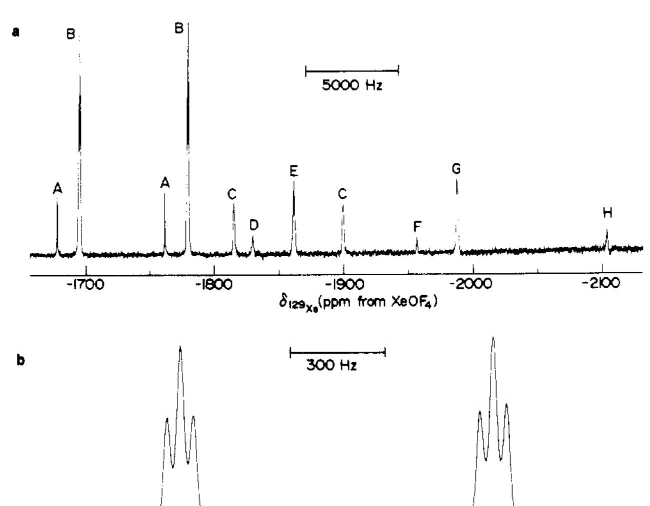


Figure 1. Xenon-129 NMR spectrum obtained at 69.56 MHz of a 1:3.530 molar mixture of XeF_2 and IO_2F_3 recorded in SO_2ClF solvent at -5 °C: (a) (A) $FXeOSO_2F$, (B) *trans*-$FXeOIOF_4$, (C) *cis*-$FXeOIOF_4$, (D) *trans*-$F_4OIOXeOSO_2F$, (E) *trans,trans*-$Xe(OIOF_4)_2$, (F) *cis*-$F_4OIOXeOSO_2F$, (G) *cis,trans*-$Xe(OIOF_4)_2$, and (H) *cis,cis*-$Xe(OIOF_4)_2$; (b) expansion of the doublet of quintets representing *trans*-$FXeOIOF_4$; (c) expansion of the doublet of unresolved multiplets representing *cis*-$FXeOIOF_4$; (d) expansion of the nonet representing *trans,trans*-$Xe(OIOF_4)_2$.

(^{129}Xe–^{19}F) = 38 Hz). The bis isomer *trans,trans*-$Xe(OIOF_4)_2$ (structure III) is expected to display a binomial 1:8:28:56:70:56:28:8:1 nonet in its ^{129}Xe NMR spectrum resulting from the spin–spin coupling of eight equivalent fluorines on two $-OIF_4O$ groups bonded to the central xenon atom. The fact that only seven lines are resolved is a consequence of the low relative intensities of the two outermost lines of the nonet. The resonances G and H show partially resolved fine structure and are assigned to the bis isomers *cis,trans*-$Xe(OIOF_4)_2$ and *cis,cis*-$Xe(OIOF_4)_2$, respectively. These assignments stem from the fact that a *cis*-OIF_4O group, having three nonequivalent fluorine environments, does not show a well-resolved long-range spin–spin coupling by analogy with *cis*-$FXeOIOF_4$. In addition, by comparison of the position of *cis*-$FXeOIOF_4$ to low frequency of *trans*-$FXeOIOF_4$, the bis isomers containing one (G) or two (H) *cis*-OIF_4O groups are expected to resonate to low frequency of *trans,trans*-$Xe(OIOF_4)_2$. Similar criteria were applied for the assignments of the multiplet resonances to *trans*-$F_4OIOXeOSO_2F$ (D) and *cis*-$F_4OIOXeOSO_2F$ (F). Further evidence in support of the assignment of resonance D to *trans*-$F_4OIOXeOSO_2F$ comes from the resolved fine structure resulting from the three-bond spin–spin coupling of four equivalent fluorines on the *trans*-OIF_4O group to the central ^{129}Xe nucleus ($^3J(^{129}Xe-^{19}F)$ = 37 Hz). These assignments have been corroborated through ^{129}Xe NMR studies on the pure derivatives and are discussed later in this paper.

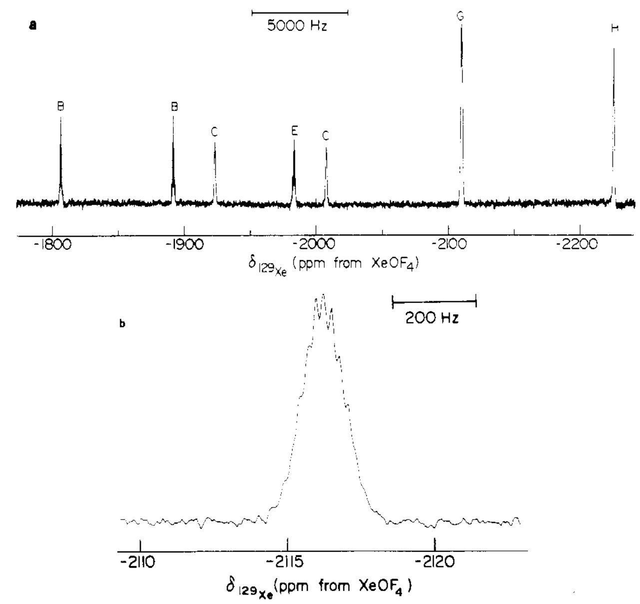


Figure 2. ^{129}Xe NMR spectrum of a 1:1.653 XeF_2/IO_2F_3 mixture recorded in $CFCl_3$ solvent at 24 °C: (a) (B) *trans*-$FXeOIOF_4$, (C) *cis*-$FXeOIOF_4$, (E) *trans,trans*-$Xe(OIOF_4)_2$, (G) *cis,trans*-$Xe(OIOF_4)_2$, and (H) *cis,cis*-$Xe(OIOF_4)_2$; (b) expansion of the odd-line multiplet representing *cis,trans*-$Xe(OIOF_4)_2$.

In order to determine the effect of solvent polarity on the XeF_2/IO_2F_3 system and, at the same time, circumvent the problem of solvent reactivity, a series of XeF_2/IO_2F_3 mixtures were prepared in $CFCl_3$ solvent. The ^{129}Xe chemical shifts and ^{129}Xe–^{19}F coupling constants are summarized in Table I. The ^{129}Xe NMR spectrum recorded in $CFCl_3$ solvent at 24 °C is depicted in Figure 2a. In this spectrum there was no evidence for the fluorosulfate derivatives (structures VI–VIII), precluding the possibility that the IO_2F_3 used for the reactions carried out in SO_2ClF solvent was contaminated with HSO_3F in the course of its preparation (see Experimental Section), which then would have reacted with XeF_2[7,12] according to eq 5. The previous assignments for the cis

$$XeF_2 + HSO_3F \rightarrow FXeOSO_2F + HF \qquad (5)$$

and trans isomers of $FXeOIOF_4$ and $Xe(OIOF_4)_2$, made in the SO_2ClF solvent system, are confirmed in this solvent and have been assigned. In addition, resonance G shows resolved fine structure under expansion (Figure 2b) in $CFCl_3$ solvent that was not resolved in SO_2ClF solvent. The relative ratio $Xe(OIOF_4)_2$:$FXeOIOF_4$ in $CFCl_3$ was significantly enhanced (1:1.6 at 24 °C) compared to the same ratio measured in SO_2ClF solvent (1:76 at -5 °C). In addition, the cis isomer of the $-OIF_4O$ group is favored over that of the trans isomer. This is reflected through the integrated ratios of the Xe(II) derivatives giving a trans,trans:cis,trans:cis,cis ratio of 1:3.2:2.7 for $Xe(OIOF_4)_2$ and a trans:cis ratio of 1:1.3 for $FXeOIOF_4$. At lower XeF_2:IO_2F_3 ratios, the intensities of cis isomers over trans isomers as well as the ratio $Xe(OIOF_4)_2$:$FXeOIOF_4$ were further enhanced in $CFCl_3$.

To further test the effect of increasing the solvent polarity, a ^{129}Xe NMR spectrum of a 1:1.996 XeF_2/IO_2F_3 mixture was recorded in BrF_5 solvent. This spectrum showed only cis and trans isomers of $FXeOIOF_4$ (Table I) in the ratio 1:3.7, respectively, as well as XeF_2. Furthermore, the ratio of XeF_2 to $FXeOIOF_4$ was 2.5:1, suggesting that equilibrium 1 lies even further to the left in BrF_5 solvent than in SO_2ClF solvent.

The ^{129}Xe NMR results for the XeF_2/IO_2F_3 system have demonstrated that the ratio of mono species to bis species and the ratio of cis to trans isomers of these species exhibit a marked dependence on the polarity of the solvent medium as well as the ratio XeF_2:IO_2F_3. In general, as the XeF_2:IO_2F_3 ratio decreases, the formation of bis isomers is favored over the formation of mono isomers as expected. As the polarity of the solvent increases, i.e., from $CFCl_3$ to BrF_5, the formation of mono species is favored over the formation of bis species. In fact, in BrF_5 solvent the more polar cis and trans isomers of $FXeOIOF_4$ exist exclusively in equilibrium with XeF_2 with no evidence for the formation of bis isomers. This result has been extrapolated to the more polar HF solvent system, in which the successful preparation of pure $FXeOIOF_4$ was accomplished from the reaction of stoichiometric amounts of XeF_2 and IO_2F_3 ($HOIOF_4$) in HF solvent (vide infra).

The ^{129}Xe chemical shifts for the bis isomers of the $-OIF_4O$ group are additive, progressing to lower frequency with increasing cis substitution. For instance, a XeF_2/IO_2F_3 mixture corresponding to a 1:3.53 molar ratio, recorded in SO_2ClF at -5 °C, yields ^{129}Xe chemical shifts of -1866.8 ppm (*trans,trans*-$Xe(OIOF_4)_2$), -1993.2 ppm (*cis,trans*-$Xe(OIOF_4)_2$), and -2109.6 ppm (*cis,cis*-$Xe(OIOF_4)_2$). Substitution of one trans ligand of *trans,trans*-$Xe(OIOF_4)_2$ with one cis ligand results in a shift of the ^{129}Xe NMR resonance 126 ppm to lower frequency, and with substitution of the second trans ligand, the ^{129}Xe NMR resonance is shifted a further 116 ppm to lower frequency. This near-additivity was found to be independent of solvent medium and of temperature. This sequence is consistent with a greater degree of deshielding of the xenon nucleus by the trans ligand and implies the *trans*-OIF_4O group is more electronegative than the *cis*-OIF_4O group. This is further supported by the ^{129}Xe resonance of *trans*-$FXeOIOF_4$, which occurs an average of 117 ppm to high frequency with respect to *cis*-$FXeOIOF_4$ in all solvents and at all temperatures investigated (see Chemical Shift Trends and Group Electronegativities).

Although ^{19}F NMR spectra were recorded on all of the XeF_2/IO_2F_3 mixtures investigated, the mixtures of $-OIF_4O$ derivatives resulted in complex ^{19}F spectra in the F-on-I(VII) region resulting from the partially overlapping multiplet resonances of the cis and trans isomers of $FXeOIOF_4$ and $Xe(OIOF_4)_2$ as well as those of IO_2F_3. However, complete assignments of the ^{19}F NMR spectra for the $-OIF_4O$ derivatives have been made on samples prepared from the pure compounds and are discussed in detail later.

Preparation of *cis,cis*-$Xe(OIOF_4)_2$. Several initial attempts to isolate the pure derivative $Xe(OIOF_4)_2$ were unsuccessful and involved the stoichiometric reaction of either IO_2F_3 or $HOIOF_4$ with XeF_2 in $CFCl_3$ or SO_2ClF solvent. In each case, the reactants were combined at low temperature (−196 °C) and then allowed to react for approximately 10 min at 0 °C. During removal of the solvent at 0 °C, a wet-looking, pale yellow solid separated that detonated violently near dryness. Presumably, the iodine(VII) of the $-OIOF_4$ group is capable of oxidizing chlorine in both $CFCl_3$ and SO_2ClF, generating one or more of the known thermally unstable chlorine oxides, i.e., ClO_2.[33] During removal of the solvent, these unstable species are apparently concentrated and detonate near dryness. Attempts to prepare $Xe(OIOF_4)_2$ by displacement of HF from XeF_2 in HF solvent were also unsuccessful. Stoichiometric amounts (2:1) of $HOIOF_4$ and XeF_2 were allowed to react in HF solvent at 0 °C. Removal of HF under vacuum at 0 °C resulted in a viscous, colorless liquid that was subsequently identified as a mixture of $HOIOF_4$, IO_2F, and IF_5 by recording the ^{19}F NMR spectrum in SO_2ClF solvent at -40 °C.

The successful preparation and isolation of solid *cis,cis*-$Xe(OIOF_4)_2$ was accomplished by the low-temperature displacement of more volatile $HOTeF_5$ (vapor pressure 40 Torr at 0 °C) from $Xe(OTeF_5)_2$ with the stronger protonic acid $HOIOF_4$ according to equilibrium 6. This acid displacement reaction proceeds

$$Xe(OTeF_5)_2 + 2HOIOF_4 \xrightleftharpoons[\text{CFCl}_3\text{ or neat}]{0\text{ °C}} Xe(OIOF_4)_2 + 2HOTeF_5 \quad (6)$$

smoothly at 0 °C as a neat mixture of the two reactants or, alternatively, in $CFCl_3$ solvent. Preparations performed with neat reactants had yields typically over 90%, whereas in $CFCl_3$ solvent, the yields were substantially lower (ca. 50%) owing to redox side reactions that presumably occur between $HOIOF_4$, $F_4OIOXeOTeF_5$, $Xe(OIOF_4)_2$, and $CFCl_3$ solvent.

Table II. ^{129}Xe NMR Parameters for *cis*- and *trans*-$FXeOIOF_4$ and *cis,cis*-$Xe(OIOF_4)_2$ Dissolved in BrF_5 and SO_2ClF

		coupling const, Hz		
species	$\delta(^{129}Xe)$, ppm[a]	^1J-(^{129}Xe–^{19}F)	^3J-(^{129}Xe–^{19}F)	solvent
trans-$FXeOIOF_4$	−1701.5	5893	*b*	SO_2ClF
	−1702.8	5868	37	BrF_5
cis-$FXeOIOF_4$	−1824.4	5851	*b*	SO_2ClF
	−1798.2	5814	41	BrF_5
trans,trans-$Xe(OIOF_4)_2$	−1802.7		*b*	SO_2ClF
	−1871.4		*b*	BrF_5
cis,trans-$Xe(OIOF_4)_2$	−1929.8		*b*	SO_2ClF
	−1929.2		*b*	BrF_5
cis,cis-$Xe(OIOF_4)_2$	−2076.0		*b*	SO_2ClF
	−2059.5		*b*	BrF_5

[a] Spectra were recorded (−40 °C) at 69.56 MHz and were referenced with respect to external neat $XeOF_4$ at 24 °C. [b] Spin–spin coupling was not resolved.

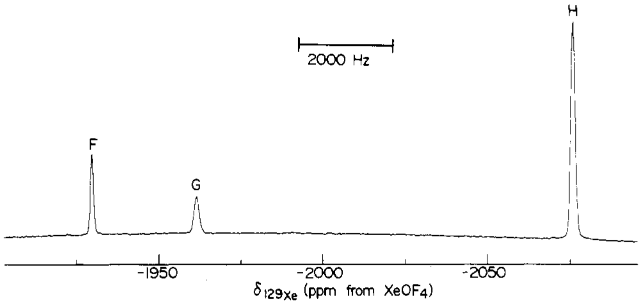


Figure 3. Xenon-129 NMR spectrum obtained at 69.56 MHz of *cis,cis*-$Xe(OIOF_2)_2$ dissolved in SO_2ClF solvent at −40 °C: (F) *cis*-$F_4OIOXeOSO_2F$; (G) *cis,trans*-$Xe(OIOF_4)_2$; (H) *cis,cis*-$Xe(OIOF_4)_2$.

The identity of *cis,cis*-$Xe(OIOF_4)_2$ was established by recording the low-temperature Raman spectrum of the solid and by ^{129}Xe and ^{19}F NMR spectroscopy (vide infra) in BrF_5, $CFCl_3$, and SO_2ClF solvents.

The cis,cis isomer of $Xe(OIOF_4)_2$ is a pale yellow solid at room temperature (white at −196 °C). The compound has a negligible vapor pressure below its decomposition temperature of 0 °C and decomposes rapidly at room temperature under a static vacuum, yielding Xe, O_2, IF_5, and IOF_3 according to eq 7. This decom-

$$Xe(OIOF_4)_2 \rightarrow Xe\uparrow + \tfrac{1}{2}O_2\uparrow + IF_5 + IOF_3 \quad (7)$$

position, which is accompanied by the emission of white light, is thought to proceed by a free-radical mechanism and formation of electronically excited oxygen. This process is presumably accelerated by the buildup of a volatile radical initiator under a static vacuum. Consequently, the compound can be handled under dynamic vacuum near room temperature or under a pressure of dry nitrogen for extended periods of time below 0 °C and can be stored indefinitely, without decomposition, in FEP vessels under dry nitrogen at dry ice temperature.

Characterization of *cis,cis*-$Xe(OIOF_4)_2$ in Solution by ^{129}Xe and ^{19}F NMR Spectroscopy. The structural characterization of *cis,cis*-$Xe(OIOF_4)_2$ by low-temperature ^{129}Xe and ^{19}F NMR spectroscopy was accomplished in BrF_5, $CFCl_3$, and SO_2ClF solvents. The solubility of the pure compound was found to be high in BrF_5 and SO_2ClF solvents at temperatures as low as −40 °C. The ^{129}Xe NMR parameters for the $Xe(OIOF_4)_2$ isomers are summarized in Table II.

The ^{129}Xe NMR spectrum of *cis,cis*-$Xe(OIOF_4)_2$ redissolved in SO_2ClF solvent at −40 °C is depicted in Figure 3. In this

---

[33] Christe, K. O. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 319.

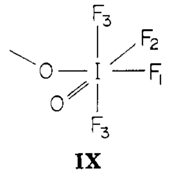
Table III. ^{19}F NMR Parameters for *cis*- and *trans*-$FXeOIOF_4$ and *cis,cis*-$Xe(OIOF_4)_2$ Dissolved in BrF_5 and SO_2ClF

	chem shift, ppm[a]		coupling const, Hz		
species	$\delta(^{19}F)$[b]	$\delta(^{19}F)$[c]	^2J-($^{19}F-^{19}F$)[d]	^1J-($^{19}F-^{129}Xe$)	solvent
trans-$FXeOIOF_4$	−168.5	71.3		5893	SO_2ClF
	−170.1	75.1		5877	BrF_5
cis-$FXeOIOF_4$	−158.5[e]	103.3 (F_1)	284 (1,2)	5852	SO_2ClF
		86.6 (F_2)	240 (1,3)		
		70.3 (F_3)	191 (2,3)		
	−161.7	101.5 (F_1)	280 (1,2)	5816	BrF_5
		85.8 (F_2)	234 (1,3)		
		70.4 (F_3)	193 (2,3)		
cis,cis-Xe-($OIOF_4)_2$		104.1 (F_1)	274 (1,2)		SO_2ClF
		82.4 (F_2)	238 (1,3)		
		74.0 (F_3)	190 (2,3)		
		102.8 (F_1)	287 (1,2)		BrF_5
		81.9 (F_2)	241 (1,3)		
		73.6 (F_3)	191 (2,3)		

[a] Spectra were recorded (−40 °C) at 235.36 MHz and were referenced with respect to external neat $CFCl_3$ at 24 °C. [b] F-on-Xe resonance. [c] F-on-I(VII) resonance. The labels F_1, F_2, and F_3 denote fluorine environments corresponding to structure IX. [d] The numbers in parentheses correspond to different fluorine environments; i.e., (1,2) corresponds to $^2J(F-F)$ between environments F_1 and F_2 as denoted in structure IX. [e] $^4J(F-F)$ = 26 Hz.

spectrum there is evidence for four xenon(II) derivatives, the most abundant species being *cis,cis*-$Xe(OIOF_4)_2$, *cis,trans*-$Xe(OIOF_4)_2$, and *cis*-$F_4OIOXeOSO_2F$ in the ratios 6.3:1.9:1, respectively. A peak corresponding to *trans,trans*-$Xe(OIOF_4)_2$ ($\delta(^{129}Xe)$ = −1802.7 ppm) is also visible (relative intensity 5% of the signal intensity for *cis,cis*-$Xe(OIOF_4)_2$; not shown in Figure 3). Since pure *cis,cis*-$Xe(OIOF_4)_2$ was used to prepare all NMR samples investigated (see below for Raman spectrum), the cis,trans and trans,trans isomers of $Xe(OIOF_4)_2$ must arise from isomerization of the cis ligands in solution. A similar isomer distribution was also observed in $CFCl_3$ and BrF_5 solvents. The ratio of cis to trans isomers was found to vary with the solvent medium and with the temperature at which the spectra were recorded and was consistent with the isomer ratio trends established in the IO_2F_3/XeF_2 systems discussed previously. The mixed derivative $F_4OIOXeOSO_2F$ was also identified in SO_2ClF solvent (equilibrium 4).

Fluorine-19 NMR spectra of samples of pure *cis,cis*-Xe-$(OIOF_4)_2$ were recorded in the same solvent media and under the same temperature conditions as the ^{129}Xe NMR spectra. In all cases, the ^{19}F NMR results were consistent with the conclusions derived from the ^{129}Xe NMR study. The ^{19}F NMR results are summarized in Table III and in Figure 4, which depicts the ^{19}F NMR spectra of *cis,cis*-$Xe(OIOF_4)_2$ recorded at −40 °C in SO_2ClF and BrF_5 solvents. Both spectra display series of partially resolved multiplet resonances, which have been assigned by taking into account known ^{19}F shielding trends and the spin–spin couplings among the fluorines in three magnetically nonequivalent fluorine environments associated with a *cis*-OIF_4O group[34] (structure IX). In general, a fluorine trans to another fluorine resonates at lower frequency than a fluorine trans to a doubly bonded oxygen and to even lower frequency than a fluorine trans to a singly bonded oxygen. The ^{19}F NMR resonances of F_1, F_2, and F_3 in structure IX are therefore expected to occur to lower frequency in the order $F_1 > F_2 > F_3$. Furthermore, under first-order conditions the multiplicity patterns for the three fluorine environments are expected to consist of a doublet of doublets, a doublet of triplets, and a doublet of triplets in the ratio 2:1:1, for F_3, F_2, and F_1, respectively. A *trans*-OIF_4O group will exhibit only one fluorine environment and is expected to yield a singlet resonance near that of F_3.



IX

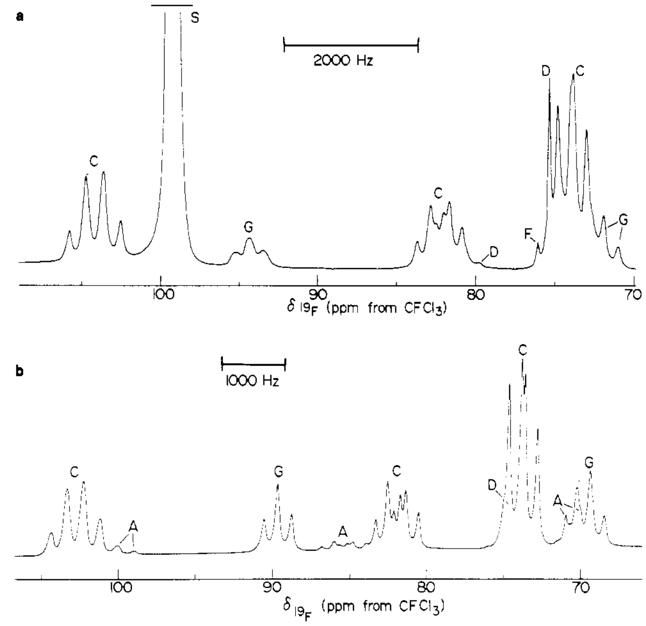


Figure 4. Fluorine-19 NMR spectrum obtained at 235.36 MHz of *cis,cis*-$Xe(OIOF_4)_2$: (a) SO_2ClF solvent at −40 °C, (C) *cis,cis*-Xe-$(OIOF_4)_2$; (D) *cis,trans*-$Xe(OIOF_4)_2$; (F) *trans,trans*-$Xe(OIOF_4)_2$; (G) *cis,cis*-$F_4OIOOIOF_4$; (S) solvent. (b) BrF_5 solvent at −40 °C, (A) *cis*-$FXeOIOF_4$; (C) *cis,cis*-$Xe(OIOF_4)_2$; (D) *cis,trans*-$Xe(OIOF_4)_2$; (G) *cis,cis*-$F_4OIOOIOF_4$.

The ^{19}F NMR spectrum recorded in SO_2ClF solvent and depicted in Figure 4a shows three partially resolved multiplets (C) in the ratio 1:1:2, which are assigned to the three fluorine environments associated with *cis,cis*-$Xe(OIOF_4)_2$, namely, F_1 and F_2, with each environment giving rise to a partially resolved doublet of triplets, and F_3, a partially resolved doublet of doublets. In addition, two singlets of much lower intensity are evident that are assigned to the four equivalent fluorines of *cis,trans*-$Xe(OIOF_4)_2$ and the eight equivalent fluorines of *trans,trans*-$Xe(OIOF_4)_2$. Furthermore, a singlet representing SO_2ClF solvent (S) and an A_2X_2 pattern corresponding to the decomposition product *cis,*-*cis*-$F_4OIOOIF_4O$ (G) are also observed.[35] The ^{19}F NMR chemical shifts reported here for *cis,cis*-$Xe(OIOF_4)_2$ fall within the range of all presently known F-on-I(VII) chemical shifts (170–65 ppm).[34,36–38] In addition, the $^2J(F-F)$ coupling constants are similar to those reported for other iodine(VII) oxide fluorides: IOF_5, 280 Hz;[38] IO_2F_3, 176 Hz;[23] *cis*-$[IO_2F_4]^-$, 204 Hz;[24] *cis*-$HOIOF_4$, 214 Hz.[34]

The ^{19}F NMR spectrum recorded in BrF_5 solvent is essentially the same (Figure 4b), differing only in the ^{19}F chemical shifts and $^2J(F-F)$ coupling constants (Table III) and the appearance of a small amount of *cis*-$FXeOIOF_4$, which presumably results from the dissociation of $Xe(OIOF_4)_2$ according to equilibrium 2. A low-intensity AX_2 pattern arising from IO_2F_3, which is also formed in this dissociation, is partially obscured by the resonances assigned to the *cis*-OIF_4O groups.

Raman Spectrum of *cis,cis*-$Xe(OIOF_4)_2$. Pure *cis,cis*-Xe-$(OIOF_4)_2$ has been characterized in the solid state by low-temperature Raman spectroscopy. The Raman spectrum recorded for the solid at −196 °C is depicted in Figure 5a. Table IV provides a summary of the vibrational frequencies with intensities and assignments.

The *cis*-$Xe-OIOF_4$ fragment of symmetry C_s should possess 18 fundamental modes classified as 12 A′ + 6 A″, all of which

---

(34) Syvret, R. G. Ph.D. Thesis, McMaster University, 1987.

(35) Syvret, R. G.; Schrobilgen, G. J. To be submitted for publication.

(36) Elgad, U.; Selig, H. *J. Inorg. Nucl. Chem., Suppl.* **1976**, 91.

(37) Krasznai, J. P. Ph.D. Thesis, McMaster University, 1975.

(38) Bartlett, N.; Beaton, S.; Reeves, L. W.; Wells, E. J. *Can. J. Chem.* **1964**, *42*, 2531.

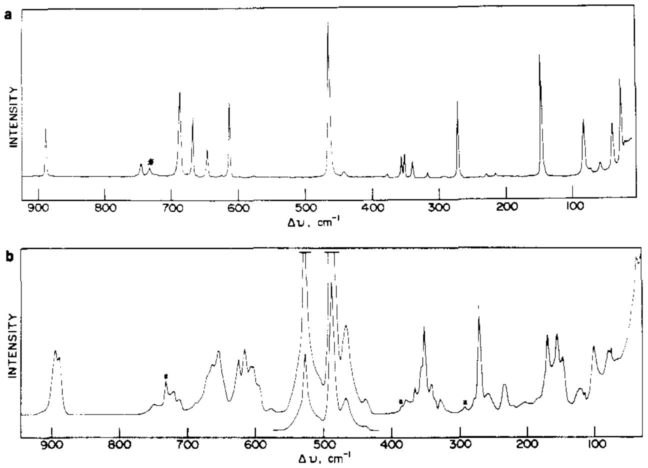


Figure 5. Raman spectra (514.5-nm excitation) of (a) *cis,cis*-$Xe(OIOF_4)_2$ and (b) a mixture of *cis*- and *trans*-$FXeOIOF_4$ recorded in FEP tubes at −196 °C. Asterisks (*) denote bands arising from FEP.

are Raman active. In addition, three modes associated with the O–Xe–O moiety, of which one mode is redundant with a mode in the Xe–$OIOF_4$ fragment, should yield a total of 20 Raman-active bands. With complete intramolecular coupling, a total of 39 Raman-active bands are expected. The spectrum depicted in Figure 5a shows 19 bands (100–900 cm⁻¹), which leads to the conclusion that there is no strong intramolecular coupling between the $-OIF_4O$ groups in the molecule nor among molecules in the unit cell. The high-frequency region of the spectrum (>400 cm⁻¹) can, for the most part, be assigned by comparison with the vibrational spectra for other iodine oxide fluorides, namely, $FOIOF_4$,[24] $[IO_2F_4]^-$,[24] IO_2F_3,[39] and IOF_5.[40,41] Although assignments are given for the low-frequency region (<400 cm⁻¹), these assignments have been made without the benefit of previously assigned $-OIF_4O$ derivative spectra, polarization measurements, and $^{16}O/^{18}O$ isotopic data and therefore must be deemed tentative.

The band at 889 cm⁻¹ is assigned to the I=O stretch of the *cis*-OIF_4O group by comparison with the frequencies of the corresponding modes in IOF_5 (927 cm⁻¹)[40,41] and *cis*-$FOIOF_4$ (914 cm⁻¹).[24] The presence of only one band in the I=O stretching region supports a single $-OIF_4O$ isomer, and the fact that this band shows no splitting or broadening confirms the weakness of factor-group splitting or intramolecular coupling. The bands in the region of the spectrum between 614 and 688 cm⁻¹ are assigned to I–F stretching modes by comparison with the same regions in the spectra of the iodine oxide fluorides cited earlier. Mainly on the basis of intensity arguments, the 614- and 646-cm⁻¹ bands are assigned to the symmetric F_{ax}–I–F_{ax} stretch and antisymmetric F_{ax}–I–F_{ax} stretch, respectively, and the 668- and 688-cm⁻¹ bands to the stretching modes of the two nonequivalent equatorial fluorines, F′ and F″. The bands at 464 and 443 cm⁻¹ are assigned to the strongly coupled symmetric Xe–O–I/XeO_2 and asymmetric Xe–O–I/XeO_2 stretching modes, respectively, by comparison with the positions and relative intensities of the corresponding modes in $Xe(OTeF_5)_2$, which occur at 440 and 428 cm⁻¹.[42] The band at 148 cm⁻¹ is assigned to the O–Xe–O bending mode by analogy with the corresponding band in $Xe(OTeF_5)_2$ (133 cm⁻¹).[43] The band at 272 cm⁻¹ is assigned to the IO_2 bending mode by comparison with the frequency of the F_{ax}—I=O bending mode in IOF_5 at 341 cm⁻¹.[40] The effective mass bonded to the –O—I=O moiety in *cis*-OIF_4O is greater than that of the F—I=O moiety in IOF_5 (i.e., the O—I=O moiety is bonded to $XeOIOF_4$), and as a result, the frequency of the IO_2 bend is expected to occur to low frequency of the F—I=O bend. Further support for this assignment comes from the relative intensity of this band. The IO_2 bending motion in *cis*-OIF_4O is expected to induce a large change in polarizability, resulting in an intense Raman vibration (272 (48) cm⁻¹). In addition, a similar band in the solid-state Raman spectrum of $FOIOF_4$, although not assigned (333 (40) cm⁻¹),[24] also supports our assignment. The bands in the spectrum between 216 and 377 cm⁻¹ are collectively assigned to IF_2, FIO, IO_2, and IF_4 bending modes. It is expected that considerable coupling would occur among these modes, thus resulting in a number of bands in the same region of the spectrum. In comparison, the analogous modes in IOF_5[40] also occur in this region of the spectrum. Finally, the low-frequency vibrations (<100 cm⁻¹) are assigned to external modes (lattice vibrations).

Table IV. Raman Frequencies and Assignments for *cis,cis*-$Xe(OIOF_4)_2$ and *cis*- and *trans*-$FXeOIOF_4$[a]

freq, cm⁻¹		
cis,cis-$Xe(OIOF_4)_2$	*cis*- and *trans*-$FXeOIOF_4$	approx descripn
	894 (15)	ν(I=O), trans
889 (32)	889 (11)	ν(I=O), cis
745 (8)	749 (3)	
	720 (4)	
	712 (2)	
688 (56)		$\nu(IF')_{eq}$
668 (38)	664 (15)	$\nu(IF'')_{eq}$
646 (18)	654 (22)	$\nu(IF_2)_{ax}$, asym
625 (1)	625 (14)	I–F str
614 (54)	616 (17)	$\nu(IF_2)_{ax}$, sym
579 (1)	605 (13)	I–F str
	595 (sh)	
	578 (1)	
	527 (49)	ν(Xe–F)
	488 (100)	ν(Xe–O–I) sym
464 (100)	467 (37)	$\nu(XeO_2)$ sym
443 (3)	438 (3)	ν(Xe–O–I) asym, $\nu(XeO_2)$ asym
377 (3)	379 (3)	IF_2, FIO, IO_2, and IF_4 bends
368 (14)	356 (sh)	
352 (15)	352 (11)	
339 (10)	341 (4)	
317 (4)	328 (2)	
272 (48)	270 (13)	$\delta(IO_2)$
	257 (3)	IF_2, FIO, IO_2, and IF_4 bends
228 (2)	233 (5)	
216 (2)	205 (1)	
	185 (1)	
	170 (12)	δ(F–Xe–O, F–I–O)
	156 (15)	
148 (78)	148 (8)	$\delta(XeO_2)$
82 (35), 73 (3), 58 (6), 39 (28), 26 (46)	122 (4), 101 (11), 80 (6)	external modes

[a] Raman spectra were recorded with FEP sample tubes at −196 °C with use of the 514.5-nm exciting line. Values in parentheses denote intensities; sh denotes a shoulder.

Preparation of $FXeOIOF_4$. The preparation of pure $FXeOIOF_4$ as a mixture of its cis and trans isomers was accomplished in a single-step synthesis involving the reaction of stoichiometric amounts of XeF_2 and IO_2F_3 in HF solvent according to equilibrium 8. As the HF solvent was removed, a light yellow liquid consisting

$$XeF_2 + IO_2F_3 \underset{HF}{\overset{0\ ^\circ C}{\rightleftharpoons}} FXeOIOF_4 \tag{8}$$

of a mixture of *cis*- and *trans*-$FXeOIOF_4$ separated. This preparation differs from that of *cis,cis*-$Xe(OIOF_4)_2$ in a number of respects. The preparation of *cis,cis*-$Xe(OIOF_4)_2$ could only be accomplished by an acid displacement reaction (eq 6) and only in solvents of low polarity in which the formation of *cis,cis*-$Xe(OIOF_4)_2$ is favored, i.e., $CFCl_3$. In HF solvent, the formation

---

(39) Gillespie, R. J.; Krasznai, J. P. *Inorg. Chem.* **1976**, *15*, 1251.

(40) Smith, D. F.; Begun, G. M. *J. Chem. Phys.* **1965**, *43*, 2001.

(41) Holloway, J. H.; Selig, H.; Claassen, H. H. *J. Chem. Phys.* **1971**, *54*, 4305.

(42) Keller, N.; Schrobilgen, G. J. *Inorg. Chem.* **1981**, *20*, 2118.

(43) Sladky, F. *Monatsh. Chem.* **1970**, *101*, 1559.

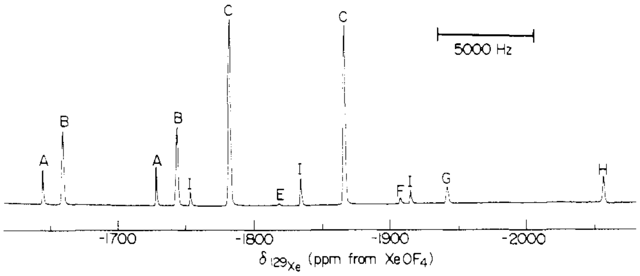


Figure 6. Xenon-129 NMR spectrum obtained at 69.56 MHz at −40 °C of a *cis*- and *trans*-$FXeOIOF_4$ mixture dissolved in SO_2ClF solvent: (A) $FXeOSO_2F$; (B) *trans*-$FXeOIOF_4$; (C) *cis*-$FXeOIOF_4$; (E) *trans,trans*-$Xe(OIOF_4)_2$; (F) *cis*-$F_4OIOXeOSO_2F$; (G) *cis,trans*-$Xe(OIOF_4)_2$; (H) *cis,cis*-$Xe(OIOF_4)_2$; (I) XeF_2.

of $Xe(OIOF_4)_2$ was presumably prevented by the competitive acid displacement represented by equilibrium 9, which lies to the right.

$$Xe(OIOF_4)_2 + HF \rightleftarrows FXeOIOF_4 + HOIOF_4 \qquad (9)$$

In contrast, *cis*- and *trans*-$FXeOIOF_4$ can be formed readily and quantitatively in HF solvent (equilibrium 8).

The mixture of *cis*- and *trans*-$FXeOIOF_4$ is a light yellow liquid at room temperature (mp −5 to 0 °C) that dissociates into XeF_2 and IO_2F_3 under dynamic vacuum at 0 °C and is partially dissociated in BrF_5 and SO_2ClF solvents at −40 °C (vide infra). The compound is thermally stable at room temperature for periods exceeding 1 h and reacts vigorously with organic materials. The compound has been characterized by recording the ^{129}Xe and ^{19}F NMR spectra in SO_2ClF and BrF_5 solvents at −40 °C, and as a solid at −196 °C by Raman spectroscopy.

Characterization of $FXeOIOF_4$ by ^{129}Xe and ^{19}F NMR Spectroscopy. The ^{129}Xe NMR parameters for *cis*- and *trans*-$FXeOIOF_4$ recorded in SO_2ClF and BrF_5 solvents at −40 °C are summarized in Table II. Figure 6 illustrates the ^{129}Xe NMR spectrum of *cis*- and *trans*-$FXeOIOF_4$ in SO_2ClF at −40 °C. The most prominent features of this spectrum are the mono derivatives $FXeOSO_2F$ (A), *trans*-$FXeOIOF_4$ (B), and *cis*-$FXeOIOF_4$ (C). The assignments of these species are based on the ^{129}Xe chemical shifts and ^{129}Xe–^{19}F coupling constants previously recorded for IO_2F_3/XeF_2 systems in SO_2ClF. The integrated ^{129}Xe intensity ratios for the mono derivatives were 1:2.3:5 for $FXeOSO_2F$, *trans*-$FXeOIOF_4$, and *cis*-$FXeOIOF_4$, respectively. As noted previously for the IO_2F_3/XeF_2 system in SO_2ClF, the formation of $FXeOSO_2F$ arises from the reaction of $FXeOIOF_4$ with SO_2ClF solvent (eq 3). In addition to mono derivatives, there is evidence for XeF_2 (I) and the bis derivatives *trans,trans*-$Xe(OIOF_4)_2$ (E), *cis*-$F_4OIOXeOSO_2F$ (F), *cis,trans*-$Xe(OIOF_4)_2$ (G), and *cis,cis*-$Xe(OIOF_4)_2$ (H). The 1:2:1 triplet (I) was assigned to XeF_2 by comparison with the previously reported chemical shift and one-bond xenon–fluorine coupling constant of this species in SO_2ClF solvent ($\delta(^{129}Xe) = -1905$ ppm, $^1J(^{129}Xe-^{19}F) = 5630$ Hz).[29,31] The appearance of a small amount of XeF_2 in this spectrum is consistent with the dissociation of $FXeOIOF_4$ to give XeF_2 and IO_2F_3. The latter point is supported by the presence of both IO_2F_3 and XeF_2 in the ^{19}F NMR spectrum (Figure 7a). The bis derivatives in Figure 6 are assigned by comparison of their ^{129}Xe chemical shifts with those for the IO_2F_3/XeF_2 system in SO_2ClF solvent. The compounds *trans,trans*-, *cis,trans*-, and *cis,cis*-$Xe(OIOF_4)_2$ are presumed to result from the reaction of $FXeOIOF_4$ with IO_2F_3 according to equilibrium 2. The mixed derivative *cis*-$F_4OIOXeOSO_2F$ arises by means of ligand redistribution equilibria involving $FXeOSO_2F$ and/or the reaction of $FXeOSO_2F$ with IO_2F_3 according to equilibrium 4. The ^{129}Xe NMR spectrum for *cis*- and *trans*-$FXeOIOF_4$ recorded in BrF_5 solvent is similar to that shown in Figure 6 except that, in BrF_5, there is no evidence for the fluorosulfate species in the spectrum and the ^{129}Xe chemical shifts occur to low frequency of their counterparts recorded in SO_2ClF. This is consistent with the previously established solvent-dependent shielding trends for Xe(II) chemical shifts.[29,31]

The ^{19}F NMR spectra of *cis*- and *trans*-$FXeOIOF_4$ were also obtained in SO_2ClF and BrF_5 solvents at −40 °C. The ^{19}F NMR parameters for the pure isomers are summarized in Table III. The F-on-I(VII) region of the ^{19}F NMR spectrum recorded in SO_2ClF solvent is depicted in Figure 7a. The most prominent features of this spectrum are the resonances A and B, which represent *cis*-$FXeOIOF_4$ and *trans*-$FXeOIOF_4$, respectively. The assignment of resonance B to *trans*-$FXeOIOF_4$ stems from the fact that a *trans*-OIF_4O group is expected to display a singlet in the F-on-I(VII) region. The three multiplets of *cis*-$FXeOIOF_4$ (A) were assigned by using arguments similar to those already given for *cis,cis*-$Xe(OIOF_4)_2$. While the fluorine environments F_1 and F_3 (structure IX) for *cis*-$FXeOIOF_4$ are shifted to slightly lower frequency of their counterparts in *cis,cis*-$Xe(OIOF_4)_2$, the F_2 resonance is shifted to high frequency of the F_2 resonance of *cis,cis*-$Xe(OIOF_4)_2$ (Table III). The two-bond fluorine–fluorine coupling constants for *cis*-$FXeOIOF_4$ (Table III) are approximately the same magnitude as the two-bond couplings in *cis,cis*-$Xe(OIOF_4)_2$. Figure 7a also shows ^{19}F NMR resonances that can be assigned to the bis derivatives *trans,trans*-$Xe(OIOF_4)_2$ (F), *cis,trans*-$Xe(OIOF_4)_2$ (D), and *cis,cis*-$Xe(OIOF_4)_2$ (C). In addition to Xe(II) species, the weak resonances in Figure 7a labeled E are assigned to IO_2F_3 (AX_2, $\delta(^{19}F) = 107.3$ ppm (X_2), 68.5 ppm (A)), which is formed in the dissociation of $FXeOIOF_4$. The ^{19}F NMR spectrum recorded in BrF_5 solvent was essentially identical. In SO_2ClF and BrF_5 solvents, the differences in chemical shift between environments F_1 and F_2 (15.7 ppm in BrF_5 and 16.7 ppm in SO_2ClF) and environments F_2 and F_3 (15.4 ppm in BrF_5 and 16.3 ppm in SO_2ClF) are approximately equal, implying that the shielding effect on the fluorine environments in *cis*-$FXeOIOF_4$ increases in a near-linear fashion in the order $F_1 < F_2 < F_3$. A similar effect is not observed for the ^{19}F NMR resonances of *cis,cis*-$Xe(OIOF_4)_2$; i.e., in SO_2ClF solvent, $\Delta\delta(F_1-F_2)$ is 21.7 ppm whereas $\Delta\delta(F_2-F_3)$ is only 8.4 ppm. In addition to the resonances assigned to Xe(II) species, there was again evidence for IO_2F_3 dimer in BrF_5 solvent, suggesting that the dissociation of $FXeOIOF_4$ is largely solvent independent.

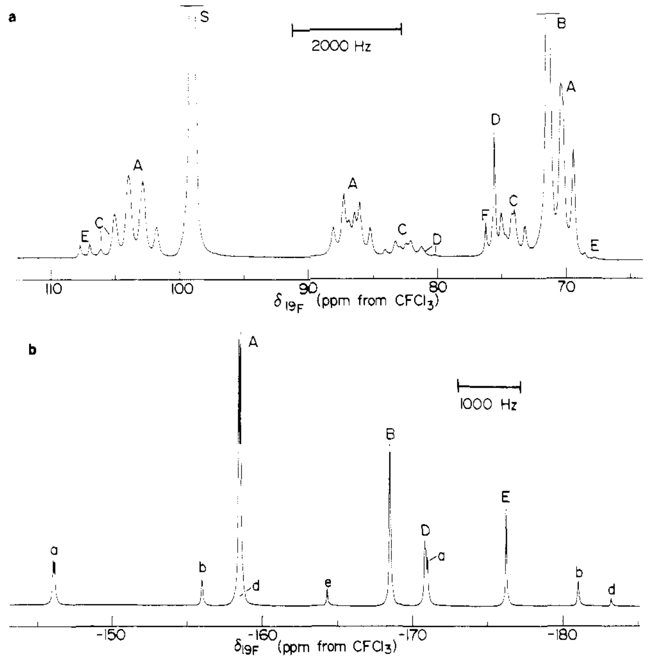


Figure 7. Fluorine-19 NMR spectra obtained at 235.36 MHz at −40 °C of a *cis*- and *trans*-$FXeOIOF_4$ mixture dissolved in SO_2ClF solvent: (a) the F-on-I(VII) region of the spectrum, (A) *cis*-$FXeOIOF_4$, (B) *trans*-$FXeOIOF_4$, (C) *cis,cis*-$Xe(OIOF_4)_2$, (D) *cis,trans*-$Xe(OIOF_4)_2$, (E) IO_2F_3, (F) *trans,trans*-$Xe(OIOF_4)_2$, and (S) solvent; (b) the F-on-Xe(II) region of the spectrum, (A (a,a)) *cis*-$FXeOIOF_4$, (B (b,b)) *trans*-$FXeOIOF_4$, (D (d,d)) $FXeOSO_2F$, and (E (e,e)) XeF_2.

The ^{19}F NMR spectrum of the F-on-Xe(II) region for *cis*- and *trans*-$FXeOIOF_4$ recorded in SO_2ClF solvent at −40 °C (Figure 7b) shows four F-on-Xe(II) resonances with accompanying ^{129}Xe satellites. The assignment of these resonances is based on the relative intensities, with *cis*- and *trans*-$FXeOIOF_4$ expected to be the most intense (also supported by the relative intensities in the ^{129}Xe spectrum), the comparison between the ^{129}Xe satellite spacings and $^1J(^{129}Xe–^{19}F)$ values established in the ^{129}Xe NMR spectrum, and the comparison of the ^{19}F NMR chemical shifts for XeF_2 and $FXeOSO_2F$ reported previously.[44] Resonance A, the most intense resonance in the F-on-Xe(II) region of the spectrum, is assigned to the terminal fluorine on xenon of *cis*-$FXeOIOF_4$. Its accompanying satellites show an additional partially resolved doublet splitting (26 Hz) arising from the four-bond spin–spin coupling of either F_1 or F_2 of the *cis*-OIF_4O group (structure IX) and the terminal fluorine on xenon. It is unclear why none of the other resonances in Figure 7b show such resolved four-bond spin–spin couplings. Such a long-range coupling is not unprecedented and has been noted previously[29] between the terminal fluorine on xenon and the fluorine on sulfur of $FXeOSO_2F$ ($^4J(F–F)$ = 14 Hz). In view of the fact that fluorines cis to the I–O bond (F_3) do not give rise to a resolvable coupling, it is assumed that the remaining cis coupling with F_2 is also not resolved. Consequently, the doublet splitting is attributed to F_1, which is trans to the I–O single bond. Additional corroboration for this observation is found in the ^{129}Xe spectra of *cis*-$FXeOIOF_4$, where the ^{129}Xe resonance appears as a doublet attributed to $^1J(^{129}Xe–^{19}F)$, which, under high resolution, shows additional fine structure on each doublet branch resembling a broadened, partially resolved doublet (41 Hz) with additional unresolved fine structure. Again, the doublet structure on each branch is assumed to arise from $^3J(^{129}Xe–^{19}F)$ involving F_1 whereas the $^3J(^{129}Xe–^{19}F)$ couplings arising from the fluorines cis to the I–O single bond (F_2 and F_3) are presumably not large enough to be resolved but only contribute to the line broadening.

Raman Spectrum of $FXeOIOF_4$. The Raman spectrum of *cis*- and *trans*-$FXeOIOF_4$ was recorded at −196 °C and is illustrated in Figure 5b. The vibrational frequencies and intensities as well as tentative assignments are given in Table IV. The Raman spectrum consists of broad and poorly resolved vibrational bands in comparison to the spectrum of *cis,cis*-$Xe(OIOF_4)_2$. This is likely the combined effect of the fact that we have a mixture of cis and trans isomers with near-coincident vibrational frequencies and the fact that the mixture does not crystallize at −196 °C but forms a glass that would, in turn, give rise to increased librational motions and line broadening.

The *cis*- and *trans*-$FXeOIOF_4$ molecules of symmetry C_s should each possess a maximum of 21 fundamental modes, all Raman active, classified as 14 A′ + 7 A″. The complexity of the spectrum depicted in Figure 5b does not permit a full assignment of all modes associated with the mixture of isomers. When possible, assignments have been made by comparisons with the vibrational spectra of other monofluoro–xenon(II) derivatives and $-OIOF_4$ derivatives.

The high-frequency bands at 889 and 894 cm^{-1} are assigned to I═O stretches by analogy with the I═O stretching frequency determined for *cis,cis*-$Xe(OIOF_4)_2$ (889 cm^{-1}). These bands are assigned to the cis and trans isomers, respectively, by comparison with the frequencies for the I═O stretches in *cis*-$FOIOF_4$ (914 cm^{-1}),[24] *trans*-$FOIOF_4$ (924 cm^{-1}),[24] and *cis,cis*-$Xe(OIOF_4)_2$ (889 cm^{-1}). Moreover, the observation of two bands in the I═O stretching region supports a cis, trans mixture. The vibrational bands in the region 578–664 cm^{-1} are most certainly I—F stretches; however, a detailed assignment of this region cannot be made for these bands since the I—F stretches of both *cis*- and *trans*-$FXeOIOF_4$ are expected to occur in this region and may, in some cases, be coincident. The broad, intense band at 527 cm^{-1} is assigned to the overlapping Xe—F stretches of the cis and trans isomers by analogy with the corresponding frequencies in $FXeOSO_2F$ (521, 527, 532, and 539 cm^{-1}),[45] $FXeOSO_2CF_3$ (534 cm^{-1}),[16] and $FXeOTeF_5$ (520 cm^{-1}).[13] The bands at 467, 488, and 438 cm^{-1} are assigned to the strongly coupled I—O and Xe—O stretches by analogy with the corresponding modes in $FXeOTeF_5$ (457 cm^{-1}),[13] $FXeOSO_2F$ (434 cm^{-1}),[45] $Xe(OTeF_5)_2$ (440 cm^{-1}),[42] and *cis,cis*-$Xe(OIOF_4)_2$ (464 cm^{-1}). The vibrational bands below 400 cm^{-1} correspond to bending and/or torsional modes. The intense bands at 156 and 170 cm^{-1} are assigned to F—Xe—O and F—I—O bending modes by analogy with the corresponding O—Xe—O mode in *cis,cis*-$Xe(OIOF_4)_2$ (148 cm^{-1}). The vibrations in the spectral region 185–380 cm^{-1} are assigned to the IF_2, IF_4, IO_2, and/or IOF bends by analogy with the corresponding modes in *cis*- and *trans*-$[OIOF_4]^-$,[24] IOF_5,[40,41] and *cis,cis*-$Xe(OIOF_4)_2$. It is important to note that, in Figure 5b, there is no evidence for XeF_2, which is expected to have a strong stretching vibration at 496 cm^{-1}, and no evidence for IO_2F_3, which is expected to show a moderately strong vibration at 920 cm^{-1}.[39] These results indicate that IO_2F_3 and XeF_2 observed in the ^{19}F NMR spectra, discussed above, result from the dissociation of $FXeOIOF_4$ in SO_2ClF and BrF_5 solvents at −40 °C and $FXeOIOF_4$ is not appreciably dissociated in the solid state.

Chemical Shift Trends and Group Electronegativities. It has been shown in previous studies[16,29,31,44,46,47] that ^{129}Xe and ^{19}F NMR chemical shifts and xenon–fluorine coupling constants can be correlated with the ionic characters of xenon–ligand bonds. That is, a decrease in ^{19}F chemical shift and increase in $^{129}Xe–^{19}F$ coupling constant are consistent with a greater degree of ionic character in the terminal Xe–F bond and a decrease in ^{129}Xe chemical shift is indicative of an increasingly more covalent xenon–ligand atom bond. These parameters can be correlated with the electron-withdrawing ability or group electronegativity of a substituent group. The ^{129}Xe and ^{19}F NMR studies of the xenon(II) derivatives FXeL and XeL_2, where L = $-OIF_4O$, $-OSO_2F$, $-OTeF_5$, can therefore be used to assess the group electronegativity trends for the series $-OSO_2F$, $-OTeF_5$, and $-OIF_4O$.

The mixed xenon(II) derivatives containing one $-OSO_2F$ and one $-OIF_4O$ group provide a means by which the relative shieldings of the xenon nucleus can be compared for these two groups under the same solvent and temperature conditions. From the ^{129}Xe NMR studies on the IO_2F_3/XeF_2 system performed in SO_2ClF, it was evident that the ^{129}Xe chemical shifts of the fluorosulfate derivatives occur consistently to high frequency of those for the $-OIF_4O$ group derivatives (Table I). The average chemical shift differences are 16 ppm between $FXeOSO_2F$ and *trans*-$FXeOIOF_4$ and 33 ppm between *trans*-$F_4OIOXeOSO_2F$ and *trans,trans*-$Xe(OIOF_4)_2$, implying the electronegativity of the $-OSO_2F$ group is greater than that of the *trans*-OIF_4O group. Furthermore, the ^{129}Xe chemical shifts for the bis isomers of $-OIF_4O$ were found to be approximately additive, progressing to lower frequency with increasing cis substitution. This near-additivity trend was found to be independent of temperature and concentration, allowing the effective group electronegativity order *cis*-OIF_4O < *trans*-OIF_4O < $-OSO_2F$ to be deduced. Further support is obtained by recording the ^{19}F NMR spectra of the monofluoro derivatives in SO_2ClF solvent at −5 °C (Table I). The ^{19}F chemical shift for $FXeOSO_2F$ ($\delta(^{19}F) = -170.9$ ppm) occurs to low frequency of the chemical shifts of both *trans*-$FXeOIOF_4$ ($\delta(^{19}F) = -168.4$ ppm) and *cis*-$FXeOIOF_4$ ($\delta(^{19}F) = -158.7$ ppm). These findings can likewise be interpreted in terms of the ionic characters of the terminal Xe–F bonds, which, in turn, are related to the group electronegativity. Thus, the high electron-withdrawing ability of the fluorosulfate group, as compared to that of *cis*- or *trans*-OIF_4O, results in the $FXeOSO_2F$ molecule having substantially more XeF^+ character than in either *cis*- or *trans*-$FXeOIOF_4$. The increased XeF^+ character is reflected in a low-frequency (more shielded) ^{19}F chemical shift for the fluorosulfate derivative. Moreover, it follows that the covalency of the Xe–O bond is greater in *cis*- or *trans*-$FXeOIOF_4$ than in $FXeOSO_2F$.

In order to compare the electronegativities of the $-OIF_4O$ and $-OTeF_5$ groups, the series of mixed derivatives $(F_4OIO)_xXe$-

---

(44) Gillespie, R. J.; Netzer, A.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 1455.

(45) Gillespie, R. J.; Landa, B. *Inorg. Chem.* **1973**, *12*, 1383.

(46) Holloway, J. H.; Schrobilgen, G. J. *Inorg. Chem.* **1980**, *19*, 2632.

(47) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 765 and references therein.

Table V. Xenon-129 Chemical Shifts for the $Xe(OTeF_5)_2$/*cis,cis*-$Xe(OIOF_4)_2$ System Recorded in $CFCl_3$ Solvent

species	$\delta(^{129}Xe)$, ppm[a]	temp, °C
$Xe(OTeF_5)_2$	−2423.2	5
	−2428.2	24
cis-$F_4OIOXeOTeF_5$	−2298.7	5
	−2315.7	24
cis,cis-$Xe(OIOF_4)_2$	−2219.5	5
	−2236.4	24
trans-$F_4OIOXeOTeF_5$	−2205.3	5
	−2217.5	24
cis,trans-$Xe(OIOF_4)_2$	−2119.8	5
	−2131.3	24

[a] Referenced with respect to neat $XeOF_4$ at 24 °C.

$(OTeF_5)_{2-x}$ were prepared in $CFCl_3$ and studied by ^{129}Xe NMR spectroscopy at 5 and 24 °C. The ^{129}Xe NMR parameters for this system are summarized in Table V. From inspection of Table V, the ^{129}Xe chemical shifts for the mixed derivatives $(F_4OIO)_xXe(OTeF_5)_{2-x}$ progress to higher frequency with increasing $-OIF_4O$ substitution. These frequency shifts are not additive, however, as was found for the cis and trans isomers of $Xe(OIOF_4)_2$. For instance, a frequency shift of 125 ppm was found on substitution of one $-OTeF_5$ group of $Xe(OTeF_5)_2$ for one *cis*-OIF_4O ligand, and with the substitution of the second $-OTeF_5$ group, the frequency was shifted a further 79 ppm to higher frequency. In comparison, the frequency shift associated with substituting one $-OTeF_5$ group of $Xe(OTeF_5)_2$ for one *trans*-OIF_4O group was 218 ppm. The ^{129}Xe chemical shift is observed to decrease in the order *trans*-OIF_4O > *cis*-OIF_4O > $-OTeF_5$, and it may be inferred that the relative group electronegativities increase in the opposite sense. Thus, the NMR parameters for the xenon(II) mixed derivatives containing *cis*-OIF_4O, *trans*-OIF_4O, $-OTeF_5$, and $-OSO_2F$ suggest the group electronegativities increase in the order $-OTeF_5$ < *cis*-OIF_4O < *trans*-OIF_4O < $-OSO_2F$.

Previous ^{129}Xe NMR and ^{129}Xe Mössbauer studies have clearly shown the group electronegativity of $-OTeF_5$ is less than that of fluorine.[32] However, the ordering of group electronegativities for −F, $-OIF_4O$, and $-OSO_2F$ is not as straightforward. In the present work, ^{129}Xe NMR spectra of *cis*- and *trans*-$FXeOIOF_4$ recorded in BrF_5 solvent at −40 °C yielded chemical shifts of −1798 and −1703 ppm, respectively. In a prior ^{129}Xe NMR study,[48] ^{129}Xe chemical shifts of XeF_2 and $FXeOSO_2F$ were similarly determined in BrF_5 solvent at −40 °C, yielding values of −1708 and −1666 ppm, respectively. On the basis of shielding of the central xenon nucleus in these examples, the apparent group electronegativity order has been deduced: $-OTeF_5$ < *cis*-OIF_4O < −F < *trans*-OIF_4O < $-OSO_2F$, where −F is clearly anomalous. On the other hand, ^{19}F NMR results in this work have shown that the fluorine nuclei of FXe–L species become increasingly more shielded in the order *cis*-OIF_4O < *trans*-OIF_4O < $-OSO_2F$ < −F. Furthermore, if one considers the Xe–F stretching frequency of the mono derivatives to be a reflection of the ionic character of the Xe–F bond, then the frequency is expected to increase as the xenon–ligand atom bond becomes more ionic, i.e., more XeF^+ character. The stretching frequencies of the terminal Xe–F bonds, which are not strongly coupled to the Xe–O stretch, increase in the order of increasing group electronegativity, i.e., $-OTeF_5$ (520 cm^{-1})[13] < *cis*- and *trans*-OIF_4O (527 cm^{-1}) < $-OSO_2F$ (530 cm^{-1}).[12] With the exception of the ^{129}Xe chemical shift of XeF_2, the following group electronegativity order appears to be consistent with the majority of the spectroscopic data:

$-OTeF_5$ < *cis*-OIF_4O < *trans*-OIF_4O < $-OSO_2F$ < −F

Experimental Section

Apparatus and Materials. The air- and moisture-sensitive natures of the precursors and products required that all manipulations be carried out under anhydrous conditions on a vacuum line or in a nitrogen-filled drybox (Vacuum Atmospheres Model DLX). Air-sensitive samples of low volatility, i.e., XeF_2, $HOIOF_4$, *cis*- and *trans*-$FXeOIOF_4$, and *cis,cis*-$Xe(OIOF_4)_2$, were transferred in a drybox. The vacuum line used to transfer more volatile substances was constructed from 316 stainless steel, nickel, Teflon, Kel-F, and FEP.

NMR samples were prepared and vacuum-sealed either in glass tubes (5 or 10 mm o.d.) or in FEP tubes (4 or 9 mm o.d.) heat-sealed at one end and flared (SAE 45°) at the other.

The preparation and/or purification of HF,[44] SO_2ClF,[48] BrF_5,[44] $CFCl_3$,[34] XeF_2,[34] and $Xe(OTeF_5)_2$[34] has been described in detail elsewhere.

$HOIOF_4$ and IO_2F_3.[49] Fluorosulfuric acid solvolysis of H_5IO_6 was used to prepare $HOIOF_4$ in this work. The crude acid was titrated with 65% oleum, yielding HSO_3F-wetted IO_2F_3, which was purified with dry K_2SO_4. Addition of a stoichiometric amount of anhydrous HF to purified IO_2F_3 yielded good-quality $HOIOF_4$.

IO_2F_3/XeF_2 Mixtures. In a typical experiment, IO_2F_3 (1.338 g, 6.20 mmol) was vacuum-transferred into a 10 mm o.d. glass NMR tube. Solvent (ca. 2.5 mL) was then distilled onto IO_2F_3. An appropriate amount of XeF_2, depending on the desired IO_2F_3:XeF_2 ratio, was weighed and then transferred to the NMR tube, while cold (−196 °C), in the inert atmosphere of a drybox.

***cis,cis*-$Xe(OIOF_4)_2$.** Pure *cis,cis*-$Xe(OIOF_4)_2$ was prepared according to eq 6. In a typical preparation, $HOIOF_4$ (0.8810 g, 3.74 mmol) was transferred in a drybox into a 9 mm o.d. FEP NMR tube equipped with a Kel-F valve. The tube was cooled to −196 °C, and a preweighed amount of $Xe(OTeF_5)_2$ (1.0740 g, 1.77 mmol) was added. After the transfer was complete, the valve was reassembled and the tube was quickly removed from the drybox and immersed in a Dewar filled with liquid nitrogen. In preparations where solvent was used, the solvent (ca. 4 mL) was vacuum-transferred to the tube at this point. The tube and contents were then warmed to 0 °C in an ice–water bath for ca. 15 min. For reactions performed with neat $HOIOF_4$, the temperature was raised to ca. 10 °C in order to liquefy the $HOIOF_4$ and initiate reaction. After the reaction was deemed complete (ca. 10 min), the volatiles were removed under vacuum at 0 °C for 1 h and then between 0 °C and room temperature for 24 h. After the pumping cycle, a pale yellow free-flowing solid remained, the identity and purity of which were confirmed by Raman spectroscopy.

***cis*- and *trans*-$FXeOIOF_4$.** A homogeneous mixture of *cis*- and *trans*-$FXeOIOF_4$ was prepared according to eq 1 in HF solvent. In a typical preparation, IO_2F_3 (2.6848 g, 12.44 mmol) and XeF_2 (2.1361 g, 12.62 mmol) were combined in a 9 mm o.d. FEP NMR tube at −196 °C in a drybox. After the reaction tube was removed from the drybox while being kept cold, HF (ca. 10 mL) was added and the tube evacuated at −196 °C. The contents of the tube were allowed to react between −10 and 0 °C for $^1/_2$ h. The tube was frequently agitated during the course of the reaction to solubilize the reactants and periodically cooled in liquid nitrogen to control the rate of reaction. The solvent and volatiles were removed under vacuum at −50 °C, resulting in a white solid that, upon warming, yielded a light yellow liquid (mp 0 to −5 °C).

Nuclear Magnetic Resonance Spectroscopy. All NMR spectra were recorded unlocked (field drift <0.1 Hz h^{-1}) with the use of a Bruker WM-250 spectrometer equipped with a 5.8719-T cryomagnet and an Aspect 2000 computer. For variable-temperature measurements, samples were kept cold (−196 or −78 °C) until immediately prior to their placement in the probe. Samples were generally warmed only enough to liquefy and solubilize or partially solubilize the contents and were then quickly placed in the precooled NMR probe. Prior to data accumulation, the tubes were allowed to equilibrate in the probe for several minutes while spinning. Temperatures were periodically checked by placing a copper–constantan thermocouple into the sampling region of the probe and were considered to be accurate to within ±1 °C.

The 5.8719-T ^{19}F and ^{129}Xe spectra were obtained on the same 10-mm probe (broad-banded over the frequency range 23–103 MHz) tuned to 69.56 MHz for ^{129}Xe. Fluorine-19 spectra with 10 mm o.d. tubes were obtained with the use of the proton decoupler coils retuned to 235.36 MHz as the observe coils. Fluorine-19 spectra with 5 mm o.d. tubes were obtained with the use of a combination $^1H/^{19}F$ probe and a fixed-frequency transmitter.

All spectra were obtained on natural-abundance compounds. Xenon-129 spectra were obtained in 400–10 000 scans at a spectral width

---

(48) Schrobilgen, G. J.; Holloway, J. H.; Granger, P.; Brevard, C. *Inorg. Chem.* **1978**, *17*, 980.

(49) The detailed synthesis of $HOIOF_4$ and IO_2F_3 can be found in ref 34. In addition, the details of these syntheses form the basis of a separate publication: Syvret, R. G.; Schrobilgen, G. J. $HOIOF_4$ and IO_2F_3: Improved Syntheses and Definitive Solution Structure of IO_2F_3 by High-Field ^{19}F NMR Spectroscopy. To be submitted for publication in *Inorg. Chem.*

of 50 kHz (16K, 6.1 Hz/data point, 0.164-s acquisition time; 32K, 3.1 Hz/data point, 0.328-s acquisition time) or 100 kHz (32K, 6.1 Hz/data point, 0.164-s acquisition time). Fluorine-19 spectra were obtained in 64–1600 scans at a spectral width of 100 kHz (16K, 12.2 Hz/data point, 0.082-s acquisition time; 32K, 6.1 Hz/data point, 0.164-s acquisition time) or 150 kHz (32K, 9.2 Hz/data point, 0.109-s acquisition time). In some instances ^{19}F free induction decays, accumulated at a spectral width of 100 kHz and in a 32K memory, were zero-filled to 64K for processing. Pulse widths corresponding to bulk magnetization tip angles, $\theta = 90°$, were 2 (^{19}F) and 22 μs (^{129}Xe). Line-broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data point resolutions. In some cases, resolution was further enhanced by transforming the free induction decays from a time to a frequency domain with use of a Gaussian fit rather than the conventional Lorentzian fit. In these instances, a Gaussian broadening between 0.1 and 0.5 and a line broadening equal to the negative of the respective data point resolution were applied to the free induction decays prior to Gaussian multiplication and Fourier transformation.

The respective nuclei were referenced with respect to neat samples of $XeOF_4$ (^{129}Xe) and $CFCl_3$ (^{19}F) at 24 °C. A positive chemical shift was assigned to any resonance occurring to high frequency of the reference substance.

Raman Spectroscopy. A Coherent Model Innova 90 argon ion laser giving up to 3.5 W at 514.5 nm was used to excite the Raman spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with holographic gratings (1800 grooves mm^{-1}). Slit widths depended on the scattering efficiency of the sample but were typically set between 50 and 100 μm. The scanning rate used was 0.5 $cm^{-1}\ s^{-1}$. The typical laser power range used was between 0.4 and 1 W. All Raman shifts quoted are believed to be accurate to $\pm 2\ cm^{-1}$. Cylindrical sample tubes were mounted vertically. The angle between the laser beam and sample tube was 45°, and Raman-scattered radiation was observed at 45° to the laser beam or 90° to the sample tube. Low-temperature spectra were recorded by mounting the sample vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen. All spectra were obtained directly in either FEP or glass reaction vessels.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this work and the Ontario Ministry of Education for the award of a scholarship (R.G.S.).

Registry No. I, 101410-65-5; II, 101470-51-3; III, 101410-66-6; IV, 101470-52-4; V, 101470-53-5; VI, 25519-01-1; VII, 119365-61-6; VIII, 119327-31-0; XeF_2, 13709-36-9; $HOIOF_4$, 34618-93-4; HF, 7664-39-3; SO_2ClF, 13637-84-8; $Xe(OTeF_5)_2$, 25005-56-5; IO_2F_3, 25402-50-0; H_5IO_6, 10450-60-9; ^{129}Xe, 13965-99-6; *cis*-$F_4OIOXeOTeF_5$, 119327-30-9; *trans*-$F_4OIOXeOTeF_5$, 119365-60-5; fluorosulfuric acid, 7789-21-1; oleum, 8014-95-7.

Contribution from the Department of Chemistry,
University of Oregon, Eugene, Oregon 97403

Polyoxoanions Derived from A-β-$SiW_9O_{34}^{10-}$: Synthesis and Crystallographic and ^{183}W NMR Characterization of $Si_2W_{18}Zr_3O_{71}H_3^{11-}$, Including Its Organic Solvent Soluble Bu_4N^+ Salt

Richard G. Finke,* Brian Rapko, and T. J. R. Weakley*,†

Received August 3, 1988

The reaction of A-β-$SiW_9O_{34}^{10-}$ and "ZrO^{2+}" ions in aqueous solution, under conditions initially designed to give "$SiW_9Zr_3O_{40}^{10-}$", instead yields the new heteropolytungstate anion $Si_2W_{18}Zr_3O_{71}H_3^{11-}$, isolated as its Bu_4N^+, Me_4N^+, and Me_3NH^+ acid salts. These have been characterized by means of elemental analysis, TGA, IR spectroscopy, ^{29}Si and ^{183}W NMR spectroscopy, and, for the Bu_4N^+ salt, FAB mass spectroscopy. Structural questions left unanswered by the solution NMR studies were answered by a single-crystal X-ray structural analysis of the Me_3NH^+ salt, $(Me_3NH)_{10}H(Si_2W_{18}Zr_3O_{71}H_3)\cdot 10H_2O$ (monoclinic, $P2_1/n$, $a = 13.452$ (3) Å, $b = 43.416$ (7) Å, $c = 18.331$ (4) Å, $\beta = 102.17$ (2)°, $Z = 4$, Mo radiation, $R = 0.055$ for 8755 independent data with $I \geq 3\sigma(I)$). The crystallographic analysis shows the anion to have the composition $[Zr_3(OH)_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{11-}$, with approximate D_{3h} symmetry. The equatorially placed Zr atoms are linked by OH atoms. Each Zr is also bonded to two oxygens of an edge-sharing pair of WO_6 octahedra in each SiW_9O_{34} unit and each trigonal-prismatic ZrO_6 group [average Zr–O = 2.11 (4) Å] is enlarged by two long Zr–O–(Si,W) bonds [average Zr–O = 2.83 (7) Å] normal to the prism faces. Possible reasons for the formation of $Si_2W_{18}Zr_3$, rather than SiW_9Zr_3, are discussed.

Designed, high-yield synthetic pathways to heteropolyanions containing more than one metal in oxidation states ≤4 are not generally available.[1] However, the factors leading to the several possible classes of such substituted polyoxoanions and thus to their rational synthesis should become increasingly clear now that new methods for the rapid characterization of such polyoxoanions,[2] including their less widely investigated, organic solvent soluble R_4N^+ salts,[1c,2b–f,3c–e,4] are available.

As part of a program[3] aimed initially at preparing two series of triply metal-substituted polyoxoanions $SiW_9M_3O_{40}^{n-}$ and $P_2W_{15}M_3O_{62}^{m-}$ (M = V^{5+}, Nb^{5+} and Ti^{4+}, Zr^{4+}), we have investigated the synthesis and characterization of the M^{4+} = Ti and Zr members of this series. In addition to the fundamental interest in such heteropolyanions, they are of interest as possible soluble metal oxide support systems for transition-metal catalysts.[3,5]

Herein we report that synthetic conditions of $3ZrO^{2+} + SiW_9O_{34}^{10-}$, chosen initially with the goal of preparing the unknown zirconium-containing heteropolytungstate "$SiW_9Zr_3(OH_2)_3O_{37}^{4-}$" instead yield anions of the formula $Si_2W_{18}Zr_3O_{71}^{14-}$. This new, Zr-substituted polyoxoanion has been characterized as its H_2O-soluble, Me_4N^+ and Me_3NH^+ salts, by methods that include multinuclear NMR spectroscopy and a single-crystal X-ray

---

† Previous address: Chemistry Department, University of Dundee, Dundee DD1 4HN, U.K.

(1) (a) For the most recent summary of this area see: Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer-Verlag: New York, 1983. (b) This statement applies to multiple, M_x-containing, compounds possessing the Keggin ($XW_{12-x}M_xO_{40}$) and Dawson ($X_2W_{18-x}M_xO_{62}$) structures. (c) For an exception to this statement see: Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

(2) Two of the most powerful new methods are 1- and 2-D ^{183}W NMR spectroscopy;[2a–f,3] FABMS[2g–h] (fast atom bombardment mass spectroscopy) is another new method: (a) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *Inorg. Chem.* **1984**, *23*, 1478. Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 2748. Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627. Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 3159. Jorris, T. L.; Kozik, M.; Casan-Pastor, N.; Domaille, P. J.; Finke, R. G.; Miller, W. K.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 7402. (b) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677 and references therein. (c) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198. (d) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, *4*, 62. (e) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274. (f) Finke, R. G.; Rapko, B.; Domaille, P. J.; Saxton, R. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 2947. For the original synthesis of A-β-$SiW_9O_{34}^{10-}$, see ref 16. (g) Finke, R. G.; Droege, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750. (h) Suslick, K. S.; Cook, J. C.; Rapko, B.; Droege, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241.