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Acid Properties of the Oxytetrafluorides of Molybdenum, Tungsten, and Uranium toward Some Inorganic Fluoride Ion Donors

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The behavior of $MoOF_4$, WOF_4, and UOF_4 has been studied in the presence of ion donors of various strength: FNO, $ClOF_3$, ClF_3, ClF_5, and HF. For both $MoOF_4$ and WOF_4 in HF solutions, evidence for a partial ionization into $Mo_2O_2F_9^-$ and $W_2O_2F_9^-$ has been shown. From the equilibrium constant values, WOF_4 is found to be a stronger Lewis acid than $MoOF_4$, whereas no direct comparison with the strength of UOF_4 is possible because of its quasiinsolubility in HF. Lewis acid properties of the oxytetrafluorides studied are also demonstrated by the ionic structures found for the adducts with the strong bases FNO and $ClOF_3$. The new adducts $NOMo_2O_2F_9$, $NOW_2O_2F_9$, $ClOF_2Mo_2O_2F_9$, $ClOF_2MoOF_5$, $(NO)_2MoOF_6$, and $(NO)_2WOF_6$ were prepared. Their vibrational spectra and, for some of them, X-ray powder diffraction patterns are given. The unit cell parameters of the adducts $NOMoOF_5$, $NOWOF_5$, and $(NO)_2WOF_6$ have been determined. A study of the HF solutions of the nitrosyl salts has been made by Raman and ^{19}F NMR spectroscopy. This, together with data on propylene carbonate solutions of the same adducts, allowed the identification of the species in the oxytetrafluoride–FNO–HF system. Depending on the F^- concentration the anions $M_2O_2F_9^-$, MOF_5^-, and MOF_6^{2-} (M = Mo or W) are formed, which are in equilibrium with the solvent. The mechanisms of these equilibria are proposed. The results obtained with the F^- donor fluorinating agents indicate that ionic intermediary steps occur in the fluorination process of the oxytetrafluorides to the corresponding hexafluorides.

Introduction

Ionic complexes containing oxypentafluoromolybdate(VI) or oxypentafluorotungstate(VI) anions have already been reported through reactions between organic bases,[1-3] N_2O_4,[4] or alkali fluorides in the presence of moisture or SO_2[5,6] and the corresponding hexafluorides.

Reaction between NF_3 and WO_3[7] is reported to give $NOWOF_5$ while reaction between KF, WO_3, and SeF_4 gives $KWOF_5$.[8] $NaWOF_5$ has been obtained from reaction between tungsten hexacarbonyl and moist sodium iodide in the presence of IF_5.[6] Reactions between $MoOF_4$ or WOF_4 and organic bases[9-11] give solutions from which structural information on the present species has been obtained by NMR spectroscopy. As no systematic study regarding the behavior of the oxytetrafluorides of molybdenum, tungsten, and uranium toward inorganic fluoride donors has yet been reported, it was interesting to try to rationalize their fluoride acceptor ability. The use of fluoride donors of various strength should allow knowledge of the fluorination step expected to take place with some of them.

Experimental Section

Materials and Apparatus. Nonvolatile solid samples were transferred in a dry glove box and volatile materials were manipulated in a vacuum line. This line is made, for its most part, of Monel metal tubing equipped with valves purchased from F.W. Co. and with differential gauges from "Etudes et Constructions Aéronautiques". To allow observation, part of the apparatus is equipped with Kel-F tubes and Kel-F valves purchased from Viennot Co. Before working, the vacuum line was passivated with ClF_3 and the compound to be handled. The starting materials MoF_6, WF_6, UF_6, HF, F_2, ClF_3, and ClF_5, were purchased from "Société des Usines Chimiques de Pierrelatte". NO was obtained from "Air Liquide" and HNO_3 from "Prolabo". UOF_4 was prepared by hydrolysis of UF_6 in HF according to the process described by Wilson.[12] $MoOF_4$ and WOF_4 were prepared by reaction of fluorine with the corresponding trioxides at 300°. FNO was obtained by reaction between F_2 and NO at −196° and $ClOF_3$ was prepared by the process of Pilipovich et al.[13]

Prior to use, the volatile fluorides were purified by fractional condensation, and all compounds were checked for purity by Raman and infrared spectroscopy, powder X-ray diffraction patterns, and microsublimation, whenever the physical state of the sample allowed these methods to be used. Propylene carbonate and acetonitrile used as solvents were purchased in their purest grade from Koch-Light Laboratories and Prolabo, respectively. Prior to use they were stored over 5-A molecular sieves from Union Carbide International Co.

Spectra. Infrared spectra were recorded with a Beckman Model IR 9. Spectra of gases were recorded using a 10 cm long Monel-body gas cell equipped with AgCl windows sealed with Teflon gaskets. Powders were pressed between two thin plates of AgCl.

Raman spectra were recorded with a Coderg Model T 800 using as exciting light the 514.5-nm line of a Model 165 Spectra Physics laser. The samples were handled in 4-mm o.d. Kel-F or FEP Teflon tubing (from Viennot and Penntube Plastics, respectively), attached to a Kel-F valve. X-Ray diffraction powder patterns were taken using a 114-mm diameter Philips camera with copper Kα radiation (0.15418 nm). The samples were loaded in the dry nitrogen atmosphere of the glove box into quartz capillaries (~0.5 mm).

^{19}F NMR spectra were recorded at 56.4 MHz using a Varian NV 14 spectrometer equipped with a variable-temperature probe. As external reference $CFCl_3$ was used and the spectrometer was locked on this resonance. Double-resonance experiments were carried out by irradiating the fluorine atoms of the HF or ClF_3 solvent with increasing field intensity while the fluorine signal due to the dissolved species was being observed. These experiments readily show up even slow chemical exchanges.[14]

Reactions. Unless otherwise specified, solutions or reactions between the compounds studied were achieved by condensing an excess of the most volatile compound onto the other one maintained at −196° in a Kel-F tube. The resultant mixture was then warmed up to room temperature and examined by Raman and NMR spectroscopy. Following this the volatile materials were pumped off and checked by infrared spectroscopy and microsublimation. When a solid residue remained, the removal of the volatile materials was stopped when the equilibrium dissociation pressure of the adduct, if any, was reached. When possible, a material balance was obtained by weighing the compounds before and after reaction.

Reactions of the Oxytetrafluorides. With Nitrosyl Fluoride. Due to the greatly different volatilities of the FNO and $MoOF_4$ starting materials, HF was tested as a common solvent, to ensure a good contact between the reactants. However as will be seen below this method did not give reproducible results. Thus, FNO itself was used as the liquid phase at room temperature but, due to its high vapor pressure, a Monel reactor was used in place of a Kel-F tube.

After a reaction time of several days between 3 g of $MoOF_4$ and a large excess of FNO (18 g), the reactor was cooled at −78° and the excess FNO was removed at this temperature. The white solid residue had a dissociation pressure of about 2.5, 5, or 20 mm at −30, −15, or 0°, respectively.

Due to fast decomposition during the transfers at room temperature it was necessary to start from large quantities; otherwise the fraction of decomposed product seriously interfered with the identification of the original adduct.

The composition of a sample of the product was deduced from the weight loss during pumping at room temperature.

The solid residue and the gas removed were found to be $NOMoOF_5$ and FNO, respectively, so that the composition $(NO)_2MoOF_6$ was established for the initial compound; the decomposition can be written as

$$(NO)_2MoOF_6 \rightarrow FNO + NOMoOF_5 \qquad (I)$$

The analytical results for the solid residue from (I) are as follows. Anal. Calcd for $NOMoOF_5$: NO, 12.7; F, 40.1; Mo, 40.5. Found: NO, 13.3; F, 39; Mo, 40.4. When $NOMoOF_5$ was heated to 70° or treated with HF, i.e., HF was added to $NOMoOF_5$ and pumped off again with this procedure being repeated several times, a new stable white solid was produced having the composition $NOMo_2O_2F_9$. Anal. Calcd for $NOMo_2O_2F_9$: NO, 7.1; F, 40.2; Mo, 45.2. Found: NO, 7.1; F, 39; Mo, 45.5.

Using the same experimental conditions as for the FNO–$MoOF_4$ system, two new adducts were obtained for the FNO–WOF_4 system, in addition to $NOWOF_5$,[4,7] $(NO)_2WOF_6$, and $NOW_2O_2F_9$ which were characterized. Anal. Calcd for $(NO)_2WOF_6$: NO, 16; F, 30.5; W, 49.2. Found: NO, 15; F, 29; W, 49.1. Calcd for $NOW_2O_2F_9$: NO, 4.5; F, 28.5; W, 61.2. Found: NO, 5; F, 27; W, 60.

The most volatile WOF_4 adduct is $(NO)_2WOF_6$ having a dissociation pressure of only 1 mm at room temperature. Therefore, it could be handled more easily than the corresponding $MoOF_4$ adduct. Nevertheless transformations were also observed with these adducts, i.e., adding of HF or heating resulted in removal of FNO.

In the UOF_4–FNO system, ionic adducts were formed under the same experimental conditions as those used for the $MoOF_4$ and WOF_4–FNO system but, owing to a fast decomposition, no clear-cut determination of their composition has yet been made. The final decomposition product is $NOUF_6$.

With Chlorine Oxide Trifluoride, Chlorine Trifluoride, and Chlorine Pentafluoride. All these reactions were achieved according to the general reaction procedure described above, i.e., condensation of an excess of the most volatile material (approximately 10 mmol) onto the oxytetrafluoride (from 1 to 2 mmol) followed by slow warming up to room temperature. The mixture was then kept at the temperature for periods related to the observed reaction rate as briefly mentioned for each system.

The only stable adducts formed through these reactions were those obtained between $ClOF_3$ and $MoOF_4$. From material balance and vibrational analysis, their compositions are $ClOF_2^+MoOF_5^-$ and $ClOF_2^+Mo_2O_2F_9^-$, respectively. Anal. Calcd for $ClOF_2MoOF_5$: Cl, 12; F, 44.9; Mo, 32.4. Found: Cl, 10.9; F, 44; Mo, 31.7. Calcd for $ClOF_2Mo_2O_2F_9$: Cl, 7.3; F, 43.1; Mo, 39.6. Found: Cl, 6.6; F, 40; Mo, 39.7. Hereafter these adducts will be referred to as the 1/1 and 1/2 compounds, respectively.

As for the FNO–MOF_4 systems, the 1/1 adduct was transformed into the 1/2 adduct, either by heating at 75–80° and pumping or by treatment with HF. Melting of the 1/1 $ClOF_3$ adduct was observed to occur around 75° and the Raman spectrum of this molten salt showed the presence of bands of the 1/2 adduct and some $ClOF_3$. When the melt is cooled the 1/1 adduct is recovered almost unchanged. The amount of 1/2 adduct observed upon cooling is increased when the 1/1 adduct is pumped on while molten. This observation is best explained in terms of the equilibrium

$$2ClOF_2{}^+MoOF_5{}^- \rightleftarrows ClOF_3 + ClOF_2{}^+Mo_2O_2F_9{}^- \qquad (II)$$

Warming to higher temperature leads to a mixture of $MoOF_4$ and the same adduct found by reaction of ClO_2F with $MoOF_4$.

Results and Discussion

The $MoOF_4$–HF System. The HF solution of $MoOF_4$ was studied by both ^{19}F NMR and Raman spectroscopy. Using this latter technique, in addition to the bands due to dissolved $MoOF_4$, a pronounced shoulder was seen for the Mo–O stretching band (1041 cm^{-1}) on the lower frequency side. The HF solution was studied with $MoOF_4$:HF molar ratios running from 2.6×10^{-1} to 1.5×10^{-2}. The Raman spectra were digitized every 0.1 cm^{-1} over 80 cm^{-1} on a PD 8/1 computer connected to the Benson LNC 610 reading system. After adjustments for coincidence at the maximum intensity and subsequent adjustment of the (intensity, frequency) couple values, the values of the intensities for the spectrum corresponding to the most concentrated solution were subtracted on an IBM 360 computer from the corresponding data of the other spectra. Doing so, it turned out that a peak emerged at 1022 cm^{-1} the intensity of which was increased with dilution. This rules out its attribution to associated $MoOF_4$. From the comparison with the HF solutions of the FNO adducts (see below) this extra band was assigned to the dimeric anion $Mo_2O_2F_9^-$.

The ^{19}F NMR spectroscopy of this solution gave results shown in Table I; the homonuclear double-resonance experiment showed that an exchange takes place between HF and the dissolved species. From the observations made through Raman spectroscopy and by analogy with the reported equilibrium for a Lewis acid such as SbF_5[15,16] the following process can account for this exchange

$$2MoOF_4 + 2HF \leftrightarrows Mo_2O_2F_9{}^- + H_2F^+ \qquad (III)$$

The ion H_2F^+ or rather its solvated form[17] $(HF)_nH^+$ has not been observed probably because its concentration is too low and it exchanges rapidly with the solvent HF.

The WOF_4–HF System. Using the same experimental method, the ionization of WOF_4 was observed in HF. This indicates that equilibrium III is also valid with W written in place of Mo. It is worth saying that for an equivalent concentration the intensity of the extra band seen at 1040 cm^{-1} for $W_2O_2F_9^-$ was more intense than the corresponding band in the molybdenum system. For example with an MOF_4:HF molar ratio of 1.5×10^{-2}, the relative intensities of the $M_2O_2F_9^-$ bands were found to be 0.03 and 0.13 for $MoOF_4$ and WOF_4, respectively. No attempts were made to estimate the equilibrium constant for III, since the extent of ionization of MOF_4 is small and, therefore, is more easily influenced by trace impurities. Nevertheless, as HF of the same purity was used for the solutions of $MoOF_4$ and WOF_4, the above result shows that in HF solution WOF_4 is a stronger Lewis acid than $MoOF_4$.

The $MoOF_4$–FNO and WOF_4–FNO Systems. Compared to some of the other strong fluoride donors used in this work, FNO is not a very powerful fluorinating agent. Furthermore the NO^+ cation gives a simple vibrational spectrum which does not interfere with the identification of the anion bands. The Raman lines of $(NO)_2MoOF_6$ are listed in Table II. Owing to its thermal instability, neither the X-ray diagram nor the infrared spectrum were obtained for this adduct.

Table I. ^{19}F NMR Data and Evolution of Two Characteristic Raman Frequencies as Functions of the F^- Concentration for $MoOF_4$ and WOF_4 and Their Nitrosyl Adducts Dissolved in HF or HF–FNO Mixtures

Sample	Solvent	Initial mole ratio, sample: solvent %	Temp, °C	δ ($CFCl_3$ ext),[a] ppm (solute; solvent)	Assignment[b] of the solute line (main constituents)	Characteristic Raman frequencies of the solute, cm^{-1}: M–O	Characteristic Raman frequencies of the solute, cm^{-1}: Sym in-plane M–F str	Species evidenced[b] by the Raman band
$MoOF_4$	HF	0.2	10	−142.7 (35); 197.9 (37)	$MoOF_4$	1041, 1022 sh	706	$MoOF_4 + Mo_2O_2F_9^-$
	FNO, 2.7 HF	Satd	10	99.6 (600); 158.8 (320)	$MoOF_5^-$	1005	676	$MoOF_5^-$
$NOMoOF_5$	HF	0.2	15	−134.5 (12); 198.6 (2)	$[MoOF_4, Mo_2O_2F_9^-]$	1043, 1024	702, 695 sh	$MoOF_4 + Mo_2O_2F_9^-$
	FNO, 3 HF	5	15	~108; 162.7 (870)	$MoOF_5^-$	1007	677	$MoOF_5^-$
$(NO)_2MoOF_6$	FNO, 3 HF	Satd	10	101.2; 149.1 (1160)	$MoOF_5^-$	1006	675	$MoOF_5^-$
	FNO, 2.7 HF	Satd	10	90; 147.0 (500)	$MoOF_5^-$	998, 962	672, 595 sh	$MoOF_5^- + MoOF_6^{2-}$
WOF_4	HF	1.4	10	−61.9 (70); 191.3 (258)	WOF_4	1054, 1040 sh	722	$WOF_4 + W_2O_2F_9^-$
	FNO, 3 HF	~2	10	−54 (975), 109.3 (228); 164.9 (1200)	$W_2O_2F_9^-, WOF_5^-$	1013	695	WOF_5^-
$NOWOF_5$	HF	1.4	15	−54.4 (10) $J_{F-W} = 84$ Hz; 196.9 (34)	$W_2O_2F_9^-$	1034, 1009 sh	709	$W_2O_2F_9^- + WOF_5^-$
	FNO, 3 HF	7.1	15	107.1 (130); 164.2 (450)	WOF_5^-	1010	693	WOF_5^-
$(NO)_2WOF_6$	HF	1.6	0	−54.8 (13), $J_{F-W} = 83$ Hz; 194.6 (100)	$W_2O_2F_9^-$	1020	703	$[W_2O_2F_9^- + WOF_5^-]$
	FNO, 3 HF	4.6	10	−54.1 (800), 112.4 (150); 166.5 (520)	$W_2O_2F_9^-, WOF_5^-$	1010	693	WOF_5^-
	FNO, 2.7 HF	5.4	0	86.8 (68); 147.0 (480)	WOF_5^-	996, 982 sh	689, 613	$WOF_5^- + WOF_6^{2-}$
	HF		15	199.6 (2)				
	FNO, 3 HF		15	162.1 (15)				
	FNO, 2.7 HF		10	151.3 (19)				

[a] Values in parentheses refer to the line widths in hertz at half-height. [b] Species in brackets stand for alternative assignments or mixtures of these species.

The X-ray diffraction pattern of $NOMoOF_5$ was identical with that reported by Ralston and Musil[18] and prepared by reaction between MoF_6 and N_2O_4. This powder diffraction pattern could be indexed in a tetragonal unit cell, the parameters of which are $a = 5.191 \pm 0.003$ Å and $c = 9.731 \pm 0.008$ Å (see Table III). Concerning the vibrational spectra shown in Table II, an important remark can be made about the respective position of the axial Mo–F vibration and that one due to the in-phase symmetric Mo–F stretching. In line with a more ionic character of the axial Mo–F bond, and as already reported by Sawodny and Beuter,[19] the former appears at a lower frequency than the other does. As can be seen from Table II this observation is also valid for WOF_5^- and is further supported by the NMR data on the solutions.

The powder diffraction pattern obtained for $NOMo_2O_2F_9$ gave lines which are listed in Table III. The vibrational frequencies of this adduct are as listed in Table II and are in close agreement with those reported by Beuter and Sawodny[20] for the similar salt $Rb_2Mo_2O_2F_9$.

The powder X-ray diffraction patterns of the adducts prepared with WOF_4 are listed in Table III. As can be seen $NOW_2O_2F_9$ is isomorphous with $NOMo_2O_2F_9$. The diagram of $NOWOF_5$ is indexed in a tetragonal unit cell, the parameters of which are $a = 5.178 \pm 0.005$ Å and $c = 9.807 \pm 0.0014$ Å. Based on a comparison with isotypic K_2TaF_7,[21] the powder X-ray diagram of $(NO)_2WOF_6$ is indexed in a monoclinic (pseudoorthorhombic) unit cell (space group $P2_1/c$) with parameters $a = 5.898 \pm 0.006$ Å, $b = 13.066 \pm 0.012$ Å, $c = 8.397 \pm 0.007$ Å, and $\beta = 90°$. The vibrational spectra of these solids are given in Table II.

To summarize the synthesis and thermal decomposition results on $MoOF_4$ and WOF_4–FNO adducts it is possible to write equilibria IV–VI where M stands for Mo or W.

$$FNO + 2MOF_4 \rightleftarrows NOM_2O_2F_9 \qquad (IV)$$

$$FNO + NOM_2O_2F_9 \rightleftarrows 2NOMOF_5 \qquad (V)$$

$$FNO + NOMOF_5 \rightleftarrows (NO)_2MOF_6 \qquad (VI)$$

A sufficient pressure of FNO is necessary to transform MOF_4 into pure $(NO)_2MOF_6$, while a temperature higher than 70° (M = Mo) or 150° (M = W) and pumping are necessary to decompose the $NOM_2O_2F_9$ adducts to MOF_4.

The UOF_4–FNO System. The NO^+ vibration appeared in the Raman and infrared spectra of the pale yellow solids formed, and the U–O stretching vibration frequency was different from that of UOF_4. From the number and location of the U–O and U–F stretching vibrations it is probable that adducts similar to those obtained with WOF_4 and $MoOF_4$ are obtained with UOF_4.

The Oxytetrafluoride–FNO–HF Systems. From the previous observations on the effect of HF on the nitrosyl salts it was interesting to know the actual species present in HF solutions. As the nature of the species is obviously related to the F^- activity, the adducts were dissolved and studied at several concentrations in HF or in FNO–HF mixtures.

The adducts were also studied in propylene carbonate (4-methyl-2-dioxolone) solution. This solvent was chosen for its strong dielectric constant[22] and its relatively high resistance to fluorination by the compounds studied. Contrary to the HF solutions, the absence or slow rate of chemical exchange in this solvent allowed the observation or the multiplet structures which in turn permitted the unambiguous identification of these species.

A clear-cut identification of the species present in HF or FNO–HF solutions was then obtained by a comparison of their Raman frequencies with those obtained for the solids or the propylene carbonate solutions.

UOF_4 was found to be soluble in an FNO·3HF solution, but again decomposition and production of $NOUF_6$ prevented

Table II. Vibrational Spectra[a,b] for the Solid Adducts of $MoOF_4$ and WOF_4 with FNO and $ClOF_3$

1/1 adducts					1/2 adducts						2/1 adducts		Main assignments	
$ClOF_2MoOF_5$[c]	$NOMoOF_5$		$NOWOF_5$		$ClOF_2Mo_2O_2F_9$		$NOMo_2O_2F_9$		$NOW_2O_2F_9$		$(NO)_2MoOF_6$[c]	$(NO)_2WOF_6$[c]	For $ClOF_2^+$ in point group C_s	For anions MOF_5^- in point group C_{4v}
Raman	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Raman		
					145 (0.8)						112 (0.5)			
161 (0.7)	158 (1.3)		163 (1.1)		185 (0.3)		196 sh				145 (0.7)			
186 (0.7)	200 (0.7)		200 sh		214 } (1.3)		220 (1.3)		210 (0.7)			190 br (1.9)		
266 (2.6)					221							235 sh		
282 sh							306 sh							
306 sh	293 (1)		292 sh		306 } (4.4)									
316 } (8.6)	317 (6.2)		327 (5.9)		316		317 (7.6)							
319					324 (6.3)		330 sh		318 (5.8)		322 (5)	335 br (4.2)		$\nu_9(e)$, $\delta(MOF_4)$ or $\nu_{10}(e)$, $\delta(FMF_4)$
361 (1)														
[382] (1.1)					[381] (0.6)								$\nu_6(a'')$	
[411] (1.1)					[402] (1.5)						375 (0.6)	380 (0.6)	$\nu_4(a')$	
		436 ms		455 ms		438 ms		420 ms		435 ms	392 (0.6)	415 (0.5)		$\nu_3(a_1)$, ν(axial MF)
[503] (1.7)					[502] (0.9)	[500] ms					467 (0.3)		$\nu_3(a')$	
548 (1)	557 (0.6)	550 sh	591 (0.4)		536 (1.1)	540 ms	566 (1)	556 sh			487 (0.3)	482 (0.3)		$\nu_5(b_1)$, ν(sym out-of-phase MF_4)
561 (1.2)									594 (0.5)	598 sh	528 (0.3)	528 (0.1)		
					627 (1)									
650 (6)		650 vs, br		610 vs, br	641 (1.9)	643 vs, br		650 vs, br		635 vs, br				$\nu_8(e)$, ν(asym in-plane MF_4)
					664 (2.2)									
680 (10)	665 (7.2)		684 (3.5)	680 sh	696 (3.5)		680 (10)		699 (6)	703 sh	592 (6.4)	607 (4.6)		$\nu_2(a_1)$, ν(sym in-plane MF_4)
					[790] sh								$\nu_5(a'')$	
[724] (5)					[740] (3.8)	[750] sh	*d*	*d*					$\nu_2(a')$	
1011 (10)	985 (10)	990 s	1001 (10)	1003 s	1020 (10)	1020 s	1025 (9.1)	1026 s	1041 (10)	1040 s	976 (10)	978 (10)		$\nu_1(a_1)$ ν(MO)
[1305] sh					[1321] (0.4)	[1320] sh							$\nu_1(^{37}Cl)(a')$	
[1314] (2.5)					[1333] (1.3)	[1330] ms							$\nu_1(^{35}Cl)(a')$	
		1970 w							[2332] (0.5)	[2338] m	[2306] (2)	[2315] (2.9)	$\nu(NO^+)$	
	[2321] (1.3)	[2320] m	[2327] (1.2)	[2320] m			[2330] (0.7)	[2333] m			[2322] (1.5)	[2326] (2.4)	$\nu(NO^+)$	

[a] Frequencies are given in cm^{-1}. [b] Figures in brackets refer to cation bands, and those in parentheses, to the uncorrected relative intensities. Abbreviations used: sh, shoulder; br, broad; (a)sym, (a)symmetric; M = Mo, W; (v)s or (m)s, (very or middle) strong; m, medium; w, weak. [c] No representative ir spectrum was obtained due to decomposition of these adducts under the experimental conditions. [d] In ir spectrum weak bands are observed at 910, 935, 967, 973, and 983 cm^{-1}; the last one could be due to a slight amount of $NOMoOF_5$ and is sometimes observed as a weak Raman band.

Table III. X-Ray Data for the Nitrosyl Salts

$NOMoOF_5$

hkl	*d*, Å Calcd	*d*, Å Obsd	Intens
100	5.19	5.20	s
002	4.86	4.87	m
101	4.57	4.56	s
110	3.67	3.67	m
102	3.55	3.56	s
111	3.43	3.43	m
112	2.93	2.93	mw
103	2.749	2.751	w
200	2.593	2.596	vw
201	2.506	2.508	vvw
004	2.431	2.436	vw
113	2.429		
210	2.320	2.321	vw
211	2.256	2.257	m
104	2.201	2.207	vvw
212	2.094	2.094	m
114	2.026	2.027	ms
203	2.025		
218	1.886	1.886	m
220	1.834	1.833	mw
221	1.802	1.804	vvw
204	1.774	1.779	vvw
115	1.718	1.719	w
222	1.716		
301	1.702	1.704	vw
214	1.678	1.681	w
310	1.640	1.642	vw
006	1.621	1.620	w
311	1.618		
312	1.554	1.555	mw, br
205	1.556		
303	1.526	1.528	vw
215	1.491	1.491	vw, br
116	1.484		
313	1.465	1.465	mw
224	1.464		

Tetragonal
$a = 5.191 \pm 0.003$ Å
$c = 9.731 \pm 0.008$ Å

$NOWOF_5$

hkl	*d*, Å Calcd	*d*, Å Obsd	Intens
100	5.18	5.18	s
002	4.89	4.87	ms
101	4.57	4.57	s
110	3.66	3.67	m
102	3.56	3.56	s
111	3.42	3.41	m
112	2.93	2.94	m
103	2.762	2.766	mw
200	2.587	2.590	w, br
201	2.502	2.499	mw
004	2.450	2.450	w
113	2.437		
210	2.314	2.296	vvw
211	2.252	2.244	m
104	2.215	2.218	w
212	2.092	2.100	m
114	2.036	2.034	s, br
203	2.028		
213	1.888	1.886	ms
105	1.833	1.835	w
220	1.829		
204	1.779	1.783	w, br
115	1.728	1.726	vw
300	1.725		
222	1.714	1.704	vw
301	1.699		
214	1.682	1.685	vw
310	1.636	1.634	vw
006	1.634		
311	1.614	1.614	w, br
223	1.596	1.589	
205	1.562	1.564	m
312	1.552	1.550	w
303	1.525	1.527	m
116	1.491	1.496	m
215	1.495		
224	1.466	1:467	m, br
313	1.463		

Tetragonal
$a = 5.178 \pm 0.005$ Å
$c = 9.807 \pm 0.014$ Å

$NOMo_2O_2F_9$		$NOW_2O_2F_9$	
d_{obsd}, Å	Intens	d_{obsd}, Å	Intens
5.33	m	5.37	m
4.98	ms, br	5.00	ms, br
3.81	s	3.86	s
3.63	m	3.60	ms, br
3.56	m		
3.50	w	3.49	w
2.78	s	2.79	vw
2.72	mw	2.73	w
2.634	vvw	2.673	vw
2.562	w	2.561	w
		2.479	w
2.453	vw	2.415	w
2.382	vw	2.378	vw
2.279	ms, br	2.288	mw
2.210	w	2.199	mw
2.174	w		
2.125	w, br	2.135	mw, br
2.013	vw	2.008	w
1.942	w	1.935	m
1.912	w, br	1.894	vw
1.826	w	1.823	vw
1.786	vvw		
1.745	m	1.762	mw, br
1.687	w, br	1.694	w, br
1.656	m	1.667	mw
1.608	w	1.606	mw

$(NO)_2WOF_6$

hkl	*d*, Å Calcd	*d*, Å Obsd	Intens
110	5.379	5.37	m
021	5.206	5.14	s
111	4.529	4.52	ms
002	4.198	4.18	m
130	3.502	3.52	mw
102	3.421	3.41	mw
112	3.309	3.30	ms
131	3.234	3.23	m
200	2.949	2.944	mw
220	2.715	2.694	w
132	2.705		
023	2.599	2.563	ms, br
042	2.575		
221	2.556		
051	2.494	2.476	mw
113	2.483		
202	2.414	2.413	w
150	2.389	2.398	w
142	2.363	2.362	vw
123	2.358		
231	2.345		
151	2.298	2.303	vw
133	2.209	2.188	mw
240	2.190		
241	2.118	2.110	ms
232	2.112		
061	2.108		
004	2.099		
152	2.076	2.076	vw
014	2.073		
160	2.043	2.040	mw
242	1.941	1.942	ms
223	1.939		
311	1.894	1.891	m
124	1.893		
233	1.840	1.836	w
321	1.837		
162	1.837		
071	1.8226	1.824	vw
153	1.8172		
134	1.8011	1.797	vw
330	1.7925		
252	1.7730	1.765	w
044	1.7660		
312	1.7641		
260	1.7522	1.746	w
171	1.7409		
293	1.7245	1.718	m
322	1.7180		
214	1.6922	1.695	w
144	1.6922		

Monoclinic $P2_1/c$
Pseudoorthorhombic[21]
Isotype of K_2TaF_7
$a = 5.898 \pm 0.006$ Å
$b = 13.066 \pm 0.012$ Å
$c = 8.397 \pm 0.007$ Å
$\beta = 90°$

Table IV. ^{19}F NMR Spectral Data of the Propylene Carbonate Solutions of $MoOF_4$ and WOF_4 and Their Nitrosyl Adducts

Sample	Initial mole ratio, % sample: solvent	Temp, °C	δ ($CFCl_3$ ext), ppm	Multiplet structure[a]	Coupling const, Hz	Assignments[b]
$MoOF_4$	6.0	16	−145.9	I		$MoOF_4$
WOF_4	6.1	15	−65.2	I + S(2)	$J_{W-F} = 69$	WOF_4
WOF_4 + HF	6.0	15	−65.2	I + S(2)	$J_{W-F} = 69$	WOF_4
			−61.8	II + S(4)	$J_{F-F} = 58, J_{W-F} = 70$	$F_4OW\text{-}(F^-)\text{-}WOF_4$
			144.5	IX + S(*n*)	$J_{F-F} = 58$	$(F_4)OW\text{-}F^-\text{-}WO(F_4)$
			188.7	I		HF
$NOMo_2O_2F_9$	3.6	10	−146.0	I		$MoOF_4$
			−140.7	II + S(12)	$J_{F-F} = 55, J_{Mo-F} = 68$	$F_4OMo\text{-}(F^-)\text{-}MoOF_4$
			133.6	IX + S(*n*)	$J_{F-F} = 55$	$(F_4)OMo\text{-}F^-\text{-}MoO(F_4)$
$NOW_2O_2F_9$	5	10	−65.3	I + S(2)	$J_{F-W} = 68$	WOF_4
			−62.	II + S(4)	$J_{F-F} = 58, J_{W-F} = 70$	$F_4OW\text{-}(F^-)\text{-}WOF_4$
			−51.6	I (weak)		$WOF_4(F^-)$
			145.5	IX + S(*n*)	$J_{F-F} = 58$	$(F_4)OW\text{-}F^-\text{-}WO(F_4)$
			149.7	I		HF_2^-
$NoMoOF_5$	5	10	−145.2	I (weak)		$MoOF_4$
			−140.4	II	$J_{F-F} = 55$	$F_4OMo\text{-}(F^-)\text{-}MoOF_4$
			35.5	I (weak)		Unidentified
			134.5	IX	$J_{F-F} = 55$	$(F_4)OMo\text{-}F\text{-}MoO(F_4)$
			188.8	II	$J_{H-F} = 474$	HF
$NOWOF_5$	3.4	10	−65.1	I (weak)		WOF_4
			−62.0	II + S(4)	$J_{F-F} = 57.5, J_{F-W} = 70$	$F_4OW\text{-}(F^-)\text{-}WOF_4$
			−49.2	I + S(2)	$J_{F-W} = 70$	$WOF_4(F^-)$
			145.7	IX + S(*n*)	$J_{F-F} = 57.5, J_{F-W} = 55$	$(F_4)OW\text{-}F^-\text{-}WO(F_4)$
			188.1	II	$J_{H-F} = 475$	HF
$(NO)_2MoOF_6$	5.8	10	−127.0	II	$J_{F-F} = 50$	$MoOF_4(F^-)$
			47.1	V	$J_{F-F} = 50$	$MoO(F_4)F^-$
$(NO)_2WOF_6$	6.1	10	−50	II + S(4)	$J_{F-F} = 53, J_{F-W} = 70$	$WOF_4(F^-)$
			80.9	V + S(*n*)	$J_{F-F} = 53, J_{F-W} = 58$	$WO(F_4)F^-$
$(NO)_2MoOF_6$ + FNO[c]		10	−128.6 (−127.9)	II	$J_{F-F} = 49$	$MoOF_4(F^-)$
			68.2 (69.5)	V	$J_{F-F} = 49$	$MoO(F_4)F^-$
			100.2 (133.4)	I		HF_2^-, HF

[a] The multiplet structures are given with the following abbreviations: I, II, V, and IX refer to a singlet, doublet, quintet, and nonet, respectively. The extreme lines of the nonet were not observed owing to their low intensity, but the intensity ratios of the seven lines observed agree with the calculated ratio for the seven central lines of a nonet. S(2), S(4), and S(12) give the total number of satellites for the multiplet; S(*n*) means that the relative intensity and F–F coupling prevent a clear-cut determination of the number of satellites. [b] Symbol(s) in parentheses refer to the atoms not concerned by the chemical shift. For assignment references see text. [c] From the process used to mix extra FNO, the concentration in unknown. Figures in parentheses refer to the data obtained for a 24 hr old solution.

proper observation of the other species. Therefore the following description is restricted to the adducts obtained from $MoOF_4$ and WOF_4.

The ^{19}F NMR results obtained for the propylene carbonate solutions are given in Table IV. The species were identified by their multiplet structures, the spin–spin coupling, and the chemical shift values and are compared for identification with those previously reported.[1,2,9,10,23]

It can be seen that, by the action of the solvent, FNO is partly removed from the initial solid complexes, producing for instance $MoOF_4$ and $Mo_2O_2F_9^-$ from $NOMo_2O_2F_9$ or $NOMoOF_5$ and $MoOF_5^-$ from $(NO)_2MoOF_6$.

For some samples, HF was produced owing to the action of FNO on the solvent. Depending on the amount of F^-, either the HF participated in a slow-exchange mechanism through formation of HF_2^- ion or no exchange occurred allowing even the observation of proton–fluorine spin coupling.[24,25] The ionization of WOF_4 in HF solution above reported to give the $W_2O_2F_9^-$ ion was confirmed by the presence of this ion in a propylene carbonate solution of a sample of WOF_4 containing a small amount of HF.

An attempt to observe the $MoOF_6^{2-}$ ion in propylene carbonate has been made by shaking a $MoOF_5^-$ solution with liquid FNO for a few hours at room temperature. This process was ineffective in the sense that no new multiplet structure attributable to the $MoOF_6^{2-}$ ion was seen. The main effect was the appearance of a broad line whose resonance was strongly dependent on both the age of the solution and its temperature.

From similar treatment of propylene carbonate with FNO and results on the other solutions, this line was assigned to the (HF, F^-) exchanging species. In addition to this new line, the quintet assigned to $MoOF_5^-$ was considerably shifted toward upfield (at 10° δ is 68.2 ppm compared to δ 47.1 ppm for untreated propylene carbonate solution) indicating that the shielding of the axial fluorine atom appears to be very sensitive to the F^- activity of the solvent.

In agreement with previously reported data[1,2,3,9,10,23] the dimeric anions $Mo_2O_2F_9^-$ and $W_2O_2F_9^-$ in propylene carbonate give spectra corresponding to an AX_8 type, i.e., a fluorine bridge between two metal atoms, each of them being bonded to four other equivalent fluorine atoms. Based on its AX_4 type spectrum, the WOF_5^- ion possesses an octahedron of the light elements around the tungsten atom. Our data suggest that $MoOF_5^-$ has the same type of structure. As expected for a partial charge transfer from the added F^- to the equatorial fluorine atoms, the shielding of these atoms is found to increase in the following order: $MOF_4 < M_2O_2F_9^- < MOF_5^-$ (M = Mo, W). For the axial fluorine atom the two ions give the same trend. In addition it can be seen that the latter are more shielded than the equatorial ones so that, in agreement with the vibrational data on the solids, the negative charge in these ions is mainly localized on the axial fluorine–metal bond. The NMR data obtained for some of the HF or FNO–HF solutions of the oxytetrafluorides and their nitrosyl salts are shown in Table I.

Chemical exchange between dissolved species and the solvent is evident from the disappearance of the fluorine–fluorine coupling multiplet structure, from the change in the solvent and solute line widths with temperature, and as mentioned above from the double-resonance experiments.

The overall results suggest that the following equilibria exist

$$HF + FNO \rightleftarrows HF_2^- + NO^+ \tag{VII}$$

$$HF + M_2O_2F_9^- \rightleftarrows HF_2^- + 2MOF_4 \tag{VIII}$$

$$HF + 2MOF_5^- \rightleftarrows HF_2^- + M_2O_2F_9^- \tag{IX}$$

$$HF + MOF_5^{2-} \rightleftarrows HF_2^- + MOF_5^- \tag{X}$$

In these equations M stands for Mo or W.

Concerning equilibrium VII, a rapid exchange through fluoride ion transfer has been proved previously by NMR spectroscopy,[26,27] whereas from conductivity measurements[27] FNO was found to be dissociated in HF (0.25 *M*) as a 1/1 electrolyte. From our own observation on the Raman spectrum of an FNO·3HF mixture, NO^+ is apparent from a strong band at 2320 cm^{-1} [28] and FNO is apparent from the shoulder at about 550 cm^{-1} [28] on the high-frequency side of the strong diffuse band which extends from 800 cm^{-1} up to the Rayleigh line and from a very broad band around 1750 cm^{-1}.[28] Another broad band centered around 1500 cm^{-1} was assigned to HF_2^- [28] or, rather, as this band is Raman active, to an asymmetric form of the bifluoride ion, which is probably solvated. For a solution enriched in FNO by pumping on the FNO·3HF mixture at room temperature, and for which Seel[27] gave the composition FNO·2.67HF, the intensities of the bands at 1750 and 1500 cm^{-1} were increased. It was shown that equilibria VIII–X are shifted to the left by increasing the F^- concentration through further addition of FNO to the solutions. Starting, for instance, from a solution of $MoOF_4$ in HF, it was established that the addition of FNO gave a decrease in the intensity of the Raman band due to $MoOF_4$ and an increase of that one due to $Mo_2O_2F_9^-$. As can be seen from Table I, mixtures enriched in FNO were necessary to get successive growth of the bands due to the $MoOF_5^-$ and $MoOF_6^{2-}$ ions.

Conversely these equilibria were established by the nature of the species found in the solutions of the pure salts in HF; e.g., both $NOMoOF_5$ and $NOMo_2O_2F_9$ give a mixture of $MoOF_4$ and $Mo_2O_2F_9^-$ whereas $(NO)_2MoOF_6$ gives a mixture of $MoOF_5^-$ and $Mo_2O_2F_9^-$. It was possible to get an estimate of the equilibrium constant corresponding to (VIII) by dissolving $NOMo_2O_2F_9$ in HF. The value of

$$K_{\mathrm{VIII,Mo}} = \frac{[HF_2^-][MoOF_4]^2}{[HF][Mo_2O_2F_9^-]} \tag{1}$$

was estimated from the $MoOF_4$:$Mo_2O_2F_9^-$ integrated area ratio of the corresponding Raman bands (1041 and 1022 cm^{-1}, respectively). Moreover, the assumptions were made that 1 mol of dimer gives twice the area of 1 mol of monomer and that, at the used concentration, the HF_2^- produced through (VIII) is not consumed through (VII). For the $NOMo_2O_2F_9$:HF initial molar ratios equal to 4×10^{-3} and 2×10^{-3}, the integrated area ratios were found to be 0.78 and 1.13, respectively, so that, taking $[HF_2^-] = {}^1/_2[MoOF_4]$, $K_{\mathrm{VIII,Mo}}$ is found to be 4.8×10^{-4} and 2.5×10^{-4} mol kg^{-1}.

Starting with $NOMoOF_5$ in place of $NOMo_2O_2F_9$, the $MoOF_5^-$ concentration is too low to be seen in the Raman spectrum, indicating that (IX) is totally shifted to the right. Initial molar concentration ratios of $NOMoOF_5$:HF equal to 4×10^{-3} and 2×10^{-3} gave $MoOF_4$:$Mo_2O_2F_9^-$ integrated area ratios equal to 0.54 and 0.91. From these data $K_{\mathrm{VIII,Mo}}$ is found to be 2×10^{-4} and 1.3×10^{-4} mol kg^{-1} consistent with the above values. The major part of the inaccuracy probably comes from the approximation made about the Raman scattering coefficients. Owing to the very low concentration of WOF_4 in HF solutions of $NOWOF_5$ or $NOW_2O_2F_9$, no such quantitative data were obtained for $K_{\mathrm{VIII,W}}$. Nevertheless this latter result is consistent with the above statement that WOF_4 is a better F^- acceptor than $MoOF_4$.

Several conclusions can be drawn from the NMR data shown in Table I. First, the bridging fluorine atom in the dimeric anions appears to undergo a rapid exchange with the solvent. This is mainly apparent from the results on the WOF_4 adducts in HF solutions. Even taking into account the chemical shift difference due to the nature of the solvent, the value observed for the $W_2O_2F_9^-$ ion (−54.4 ppm) is by no means the weighted-average value between axial and equatorial fluorine chemical shifts (145.5 and −62 ppm, respectively, in propylene carbonate). Moreover, the Raman data show that the amount of WOF_4 in this solution was, if present at all, too low to account for this shift value. The −54.4-ppm line is then assigned to the equatorial fluorine atoms of $W_2O_2F_9^-$. The disappearance of the axial fluorine line in HF solution is easily explained by a rapid exchange with the solvent together with the relative number of fluorine atoms on the corresponding exchanging sites. Further proof of these conclusions are given by the spin–spin coupling observations. In HF solutions, the F_{axial}–$F_{\mathrm{equatorial}}$ coupling is averaged out whereas one of the ^{183}W–F couplings is not, its value being 84 Hz in HF vs. 70 Hz ($F_{\mathrm{in\text{-}plane}}$) and 55 Hz ($F_{\mathrm{axial}}$) in propylene carbonate solution. Consequently the −54.4-ppm line in HF solutions which is flanked by these satellites arises from only one type of F, i.e., the equatorial ones. On the other hand, as proved by a double-resonance experiment, a slow exchange takes place between HF and WOF_4 or the equatorial fluorines of $W_2O_2F_9^-$. It is then possible to propose two mechanisms, one involving a rapid exchange between the bridging fluorine atom and HF, probably via rupture of the dimer, and the other being a very slow exchange of an equatorial fluorine with the solvent. This latter mechanism probably occurs via formation of WOF_5^- and WOF_6^{2-} and subsequent interchanging of the types of F. This viewpoint is supported by the line width increase of the −54.4-ppm line with the increase in F^- concentration which according to (IX) and (X) favors WOF_5^- and WOF_6^{2-} ion formation. The latter ion has not been observed in the NMR spectra. This might be due either to its low concentration or to a possible fast-exchange rate with the solvent.

The broad line observed around 100 ppm, the location of which is very dependent on the F^- concentration, is assigned from the Raman data to the WOF_5^- ion in exchange with the solvent. As a consequence of this exchange this line, when compared to the propylene carbonate solution data, is significantly shifted upfield. The above description restricted for convenience to the WOF_4 derivatives can be, apart from the metal–fluorine coupling satellite observation, extended to the $MoOF_4$ adduct solutions, as can be seen from Table I. To complete the results on the species of the oxytetrafluoride–FNO–HF system, a diagram is given in Figure 1 showing some

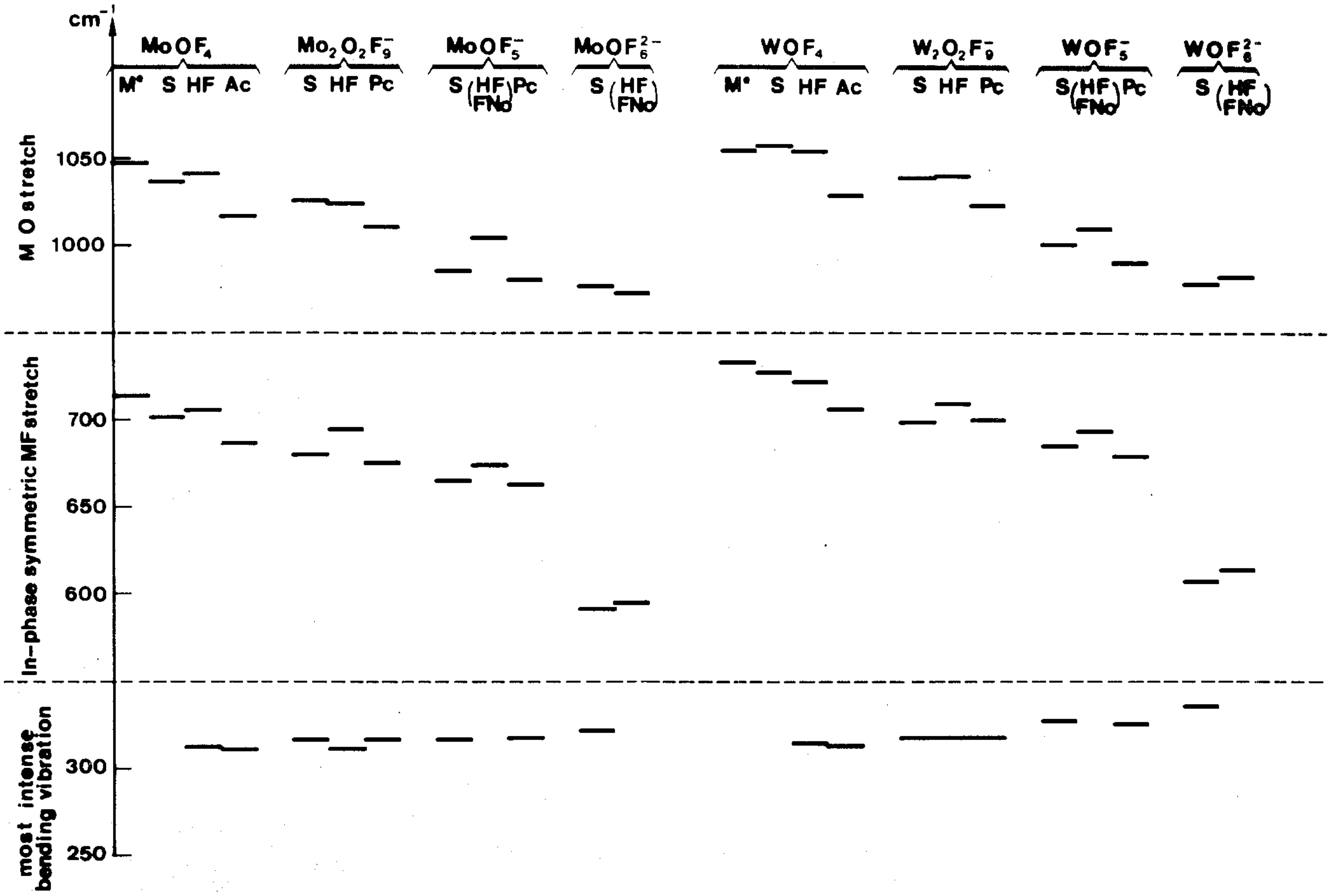

Figure 1. Trends observed for three characteristic Raman frequencies of the oxytetrafluorides and their derived anions in several media. Abbreviations used: M^e, monomer (values reported from ref 29); HF, (HF, FNO), PC, and Ac refer to HF, HF-FNO mixture, propylene carbonate, and acetonitrile solutions, respectively. Data are given for the ions associated with the nitrosyl cation. The deep color formed by the propylene carbonate-oxytetrafluoride solution prevented its Raman observation, whereas decomposition of the complexes occurs in acetonitrile solutions so that only the suitable solution data are given.

characteristic vibrational frequencies observed for the solids and for various solutions together with the values reported[29] for the monomeric form of MOF_4 (M = Mo, W). Apart from the frequency shifts due to the nature of the media, some general trends are seen. Consistent with an increase of the ionic character of the bonds, the frequencies of both the M–O and the in-phase symmetric M–F stretching vibrations decrease with the number of atoms bonded to the metal, whereas the reverse effect occurs for the most intense bending vibrations. This latter fact is probably connected with the stiffer configuration produced by the increased number of atoms around the metal.

The $MoOF_4$–$ClOF_3$ System. $ClOF_3$ is known to be a good fluoride donor.[30,34] Furthermore it is able to act both as a fluorinating and/or oxygenating[35] agent. When, for instance, it was allowed to react with MoF_5, both MoF_6 and $MoOF_4$ were produced with subsequent formation of adducts of the latter. Vibrational spectra of $ClOF_2^+MoOF_5^-$ and $ClOF_2^+$-$Mo_2O_2F_9^-$ are listed in Table II.

Due to fast attack of the capillaries, no X-ray patterns have been obtained for the pure adducts. Likely due to symmetry lowering[36] the anion spectra of $ClOF_2^+$ salts are more complex than those of the FNO adducts. It was noticed that Raman spectra of HF solutions of the $ClOF_3$ adducts showed the presence of $MoOF_4$, $Mo_2O_2F_9^-$, and $ClOF_2^+$ while ^{19}F NMR spectra indicate a fast exchange between $ClOF_2^+$ and HF. At 10° a common line is observed for these two species at 190 ppm from $CFCl_3$ whereas at −20°, probably from the decrease in solubility,[37] the chemical shift is increased toward the pure HF line. Fluorine-on-molybdenum species appeared as a single line at −136 ppm. Homonuclear double resonance showed exchange between these fluorines-on-molybdenum and the HF–$ClOF_2^+$ exchanging species.

The WOF_4–$ClOF_3$ and UOF_4–$ClOF_3$ Systems. No stable ionic product was isolated with theses systems and the oxytetrafluorides were transformed into the corresponding hexafluorides and ClO_2F according to

$$ClOF_3 + MOF_4 \rightarrow ClO_2F + MF_6 \quad (M = W, U) \qquad (XI)$$

The $MoOF_4$–ClF_3 System. When ClF_3 is removed from a ClF_3 solution of $MoOF_4$ after a contact time of a few days at room temperature, no stable adduct is found and $MoOF_4$ is recovered unchanged. However after a contact time of a few months, $MoOF_4$ was totally converted into MoF_6. Both Raman and NMR spectra of the fresh ClF_3 solution show interesting features. In addition to lines of $MoOF_4$ and ClF_3, $Mo_2O_2F_9^-$ (1025 cm⁻¹) and ClF_2^+ (780 cm⁻¹)[38] are seen in the Raman spectrum.

In the NMR spectrum, broadenings of both lines due to $MoOF_4$ and ClF_3 are observed as the temperature is decreased: for F-on-molybdenum species, δ −143.5 ppm, half-width line Δ = 20 Hz at 10°; δ −141 ppm, Δ = 80 Hz at −75°; for F-on-chlorine species, δ −80.6 ppm, Δ = 90 Hz at 10°; δ −72.2 ppm, Δ = 450 Hz at −75°. For these two species, slowing down of the exchange process can account for appearance of different types of fluorine atoms: i.e., $MoOF_4$ and $Mo_2O_2F_9^-$; ClF_3 and ClF_2^+. It is noteworthy that the exchange process in this solution is yet too fast at −75° to allow observation of separate signals for the two types of fluorine atoms in ClF_3. From this set of results the following equilibrium is suggested

$$ClF_3 + 2MoOF_4 \rightleftarrows ClF_2^+ + Mo_2O_2F_9^- \tag{XII}$$

The WOF_4–ClF_3 and UOF_4–ClF_3 Systems. For both of these systems, a reaction much faster than for the preceding system occurs at room temperature. From the products found after reaction, it is possible to write the equation

$$ClF_3 + MOF_4 \rightarrow ClF + MF_6 + {}^1/_2O_2 \quad (M = W, U) \tag{XIII}$$

A small amount of ClO_2F is also produced.

The $MoOF_4$–ClF_5, WOF_4–ClF_5, and UOF_4–ClF_5 Systems. No reaction occurs between $MoOF_4$ and ClF_5 at room temperature within a period of a few days. For the two other oxytetrafluorides, the overall reaction can be written as[39]

$$ClF_5 + 2MOF_4 \rightarrow ClO_2F + 2MF_6 \quad (M = W, U) \tag{XIV}$$

which in turn can be written as the result of the reaction

$$ClF_5 + MOF_4 \rightarrow ClOF_3 + MF_6 \quad (M = W, U) \tag{XV}$$

followed by (XI). But no proof was found for the presence of $ClOF_3$ as an isolable product. This can be easily rationalized by the higher reactivity of $ClOF_3$ when compared to that of ClF_5.

In summary, this study has demonstrated the fluoride ion acceptor ability (Lewis acid character) of the oxytetrafluorides of Mo, W, and U. In HF solution, three types of anions are formed depending on the F^- concentration. Both a rapid exchange of F^- and a slow internal rearrangement can take place. Depending on the fluorinating strength of the Lewis base, fluorination can compete with the formation of ionic adducts. It is tempting to explain the primary mechanism of the fluorination as first formation of ionic species like MOF_6^{2-} (M = Mo, W, U), followed by both oxygen and electron transfers to give MF_6. This viewpoint is supported for instance by the results on the $MoOF_4$–ClF_3 system, in which, prior to fluorination, ionization occurs. Further, if the assumption is made that both WOF_4 and UOF_4 are better F^- acceptors than $MoOF_4$, then compared to the behavior of the latter, the faster reaction obtained between WOF_4 or UOF_4 and ClF_3, $ClOF_3$, or ClF_5 is consistent with ionic intermediates. Such an intermediary step has been observed[40] for the pentavalent uranium complex $ClOF_2^+UF_6^-$ from which UF_6 is slowly formed either from the solid adduct or from the HF solution. As it was suggested by one of the referees, additional support for such an ionic oxidation mechanism can be derived from the following general considerations. (i) Cations are stronger fluorinating oxidizers than the corresponding parent molecules.[41] (ii) Anions are more readily oxidized than the corresponding parent molecules.[42] (iii) The ionic mechanism requires only low activation energies as shown for the following example of an oxidative fluorination of MF_5 by XF_3. The first step would be the transfer of an F^- to MF_5 which can proceed even at low temperature, i.e.

$$XF_3 + MF_5 \rightarrow XF_2^+ + MF_6^-$$

The second step, i.e., oxidation of MF_6^- to MF_6, involves only the transfer of one electron without breakage of a bond or change of the geometry of the MF_6 species and requires again a very low activation energy, i.e.

$$MF_6^- \rightarrow MF_6 + e^-$$

Therefore, we propose that such an ionic mechanism should be quite general and underlies many inorganic oxidative fluorination reactions.

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Registry No. $NOMoOF_5$, 55124-60-2; $NOWOF_5$, 18460-17-8; $NOMo_2O_2F_9$, 55124-61-3; $NOW_2O_2F_9$, 55156-11-1; $(NO)_2MoOF_6$, 55124-47-5; $(NO)_2WOF_6$, 55124-65-7; $ClOF_2MoOF_5$, 55124-62-4; $ClOF_2Mo_2O_2F_9$, 55124-63-5; $MoOF_4$, 14459-59-7; WOF_4, 13520-79-1; FNO, 7789-25-5; $ClOF_3$, 30708-80-6; HF, 7664-39-3.

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