of oxidant-catalyzed Cr–S bond fission similar to that reported for another aryl-thiolato complex $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$.[12] This reaction consumes 1 equiv of Np(VI)/mol of Cr(tba) to produce a disulfide which is hypothesized to be the spectrophotometrically detected reaction intermediate. The observed reaction stoichiometry of 1.5 can be rationalized by a scheme in which one aromatic ring of the disulfide is further oxidized *via* a coupling reaction. All observations on the Np(VI) oxidation of Cr(tba) may be understood by considering these two successive reactions as well as slower further oxidation of the aromatic rings.

Summary

Under properly controlled conditions the Np(VI) oxidation of free thiols occurs by 1-equiv oxidation at sulfur to yield disulfides. Deprotonation of the sulfhydryl group strongly promotes this oxidation, presumably by favoring formation of a neptunium(VI)–sulfur bond; in thioglycolic acid deprotonation of the carboxyl group is also effective. Equivalent chemistry is observed for the complex Cr(OH_2)(tga) which has a free sulfhydryl group and for Cr(tba) which behaves as though it has a free thiol group because of oxidant-catalyzed Cr–S bond fission.

In complexes containing chelated alkyl thiols, Np(VI) oxidation proceeds by a multiequivalent process often involving oxidation of the thiol carbon backbone. Ancillary ethylenediamine ligands are not oxidized by Np(VI). Chromium(III)-thiolato complexes are oxidized much more rapidly than analogous cobalt(III) complexes and coordinated tga is oxidized more rapidly than coordinated cys or tpa. Thus, of the alkyl-thiolato complexes investigated, Cr(tga) is oxidized the most rapidly and gives the simplest product mixture, while Co(cys) does not react at all with Np(VI). Further studies are planned to elucidate the factors responsible for these effects.

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Registry No. tga, 68-11-1; Np, 7439-99-8; Me(tga), 2365-48-2; dtdga, 505-73-7; Cr(tga), 41212-24-2; Co(tga), 51911-41-2; Cr(cys), 41777-30-4; Co(cys), 40330-50-5; Cr(tpa), 51911-43-4; Cr(tba), 51922-74-8; Cr(OH_2)(tga), 51922-34-0; Cr(en), 14023-00-8.

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Gas-Phase Composition and Structure of Metal Oxide Tetrafluorides[1]

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The composition of the gaseous equilibrium vapors over the solids $MoOF_4$, WOF_4, and $ReOF_4$ have been studied by mass spectrometry. In each case the principal component is the respective monomeric species; $MoOF_4$ and WOF_4 vapors contain in addition a few per cent of oligomers. The infrared spectra of the vapors at room temperature have been recorded in the region 2000–400 cm^{-1} using a 10-m multipass cell. All three molecules have similar monomer spectra with one M=O stretch, ν_1, near 1050 cm^{-1} and two M–F stretches, ν_2 and ν_7, near 700 cm^{-1}. Analysis of the spectra strongly supports a C_{4v} molecular symmetry.

Introduction

The molecular stereochemistry of transition metal fluoride and oxide fluoride compounds is diverse and of considerable interest due to the expected structural differences among the solid, liquid, and gaseous states. In addition, several of these molecules have potential for stereochemically nonrigid structures or Jahn–Teller distortions. Vibrational spectroscopy should be a sensitive probe for these stereochemical deviations.

The structural systematics in metal oxide tetrafluorides are of special interest. Currently only seven have been reported to exist: MOF_4, M = Cr,[2] Mo,[3] W,[3] Tc,[3] Re,[3,4] Ru,[3] and Os.[5] Each compound is a crystalline solid at room temperature and only $CrOF_4$ has a vapor pressure greater than 0.5 Torr at 23°. At least three different solid-state structure types have been discovered and all contain oligomeric units. The $CrOF_4$,[2] $MoOF_4$,[6,7] $TcOF_4$,[7] and $ReOF_4$[7,8] structures (monoclinic cell, VF_5 type) consist of octahedra of light atoms joined in endless chains by cis-bridging fluorine atoms. A metastable structure based on a trimeric unit containing bridging fluorine atoms also has been reported for $ReOF_4$[9] and $TcOF_4$.[10] The WOF_4[11,12] structure (monoclinic cell, NbF_5 type) consists of light-atom octahedra linked into a tetrameric array by cis-bridging fluorine atoms. The solid-state molecular structures of $OsOF_4$ (orthorhombic cell[5]) and $RuOF_4$ have not yet been determined.

(1) This work performed under the auspices of the U. S. Atomic Energy Commission.

(2) A. J. Edwards, *Proc. Chem. Soc., London*, 205 (1963); A. J. Edwards, W. E. Falconer, and W. A. Sunder, submitted for publication in *J. Chem. Soc.*

(3) J. H. Canterford and R. Colton, "Halides of the Second and Third Row Transition Metals," Wiley, New York, N. Y., 1968, pp 214 f, 283 f, 325 f, and references therein.

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Relatively little is known about the liquid-state MOF_4 structures. The boiling points and heats of vaporization, where known, are high (95-186°, 26-33 cal mol^{-1} deg^{-1})[9] which is consistent with a polymeric liquid phase. Solid- and melt-phase Raman spectra of $MoOF_4$ and WOF_4 also have been interpreted to favor the presence of fluoride-bridged polymers.[13]

Falconer and coworkers[14] have found that the equilibrium vapors over solid metal pentafluorides contain significant amounts of oligomers, $(MF_5)_{2-4}$. In view of the obvious polymeric nature of solid and liquid MOF_4 compounds, it would not be surprising if the vapors contained oligomers. Preliminary mass spectrometric analysis of $MoOF_4$ vapors[15] indicates the presence of a small amount of oligomers, but $ReOF_4$ shows no evidence for gaseous oligomers at an estimated detection level of 1 in 10^3.[4]

Because of the extreme reactivity of these compounds, low volatility at room temperature, and potential for association, very few gas-phase studies have been reported. Infrared spectra of $MoOF_4$[6,7,16,17] and WOF_4[7,11,16,17] vapors have been interpreted as supporting C_{4v} symmetry,[16] but these spectra are complicated by the presence of oligomer bands which were not recognized as such. The infrared spectrum of $ReOF_4$ condensed in an argon matrix also suggested a C_{4v} structure.[18] Unfortunately, the collective data from these studies are not of sufficient quality to make possible a definitive molecular symmetry assignment.

We report here mass spectrometric and infrared spectroscopic analyses of the equilibrium vapors over solid $MoOF_4$, WOF_4, and $ReOF_4$. These data enable firm conclusions to be drawn on the molecular symmetry of the monomer species.

Experimental Section

The oxide tetrafluorides were prepared by the slow hydrolysis of the corresponding hexafluorides. Typically, 3 mmol of metal hexafluoride was condensed into a Kel-F reaction tube containing 1.5 mmol of quartz wool (SiO_2) and 5 ml of anhydrous HF. The hydrolysis was complete in 2-4 hr at room temperature. All volatile products were vacuum evaporated and the metal oxide tetrafluoride was collected by vacuum sublimation. The MOF_4 samples were loaded in a drybox into small Kel-F tubes fitted with all-Kel-F valves. The sample could then be attached directly to an infrared cell or to the inlet system of the mass spectrometer.

A Bendix Model MA-2 time-of-flight mass spectrometer was used to record the cracking patterns of the metal oxide tetrafluorides. The Kel-F sample tube containing the solid was connected through two Kel-F valves and a 1/4 × 2 in. (6 × 50 mm) copper tube to the ion source cross housing. This arrangement allowed for direct line-of-sight sampling of the sample beam. All spectra were recorded with sample temperature 25°, source temperature 30°, and ionizing energy 70 or 20 eV. The amount of sample admitted to the spectrometer was controlled by the Kel-F valves, and the ion source pressure was maintained at 8×10^{-6} Torr or lower.

Infrared spectra were obtained with a Perkin-Elmer Model 521 double-beam spectrometer. Vapor bands were measured at about 300 K in a commercial folded-path absorption cell at path lengths of 6.2 and 10 m. Several modifications were made to this cell to make it usable with reactive fluorine compounds: the original aluminum-coated glass mirrors were replaced by a set of similar mirrors made from Dural 2014 low-silicon aluminum alloy,[19] and all nonreflecting surfaces were coated with a thick layer of Teflon. Silver chloride windows were used.

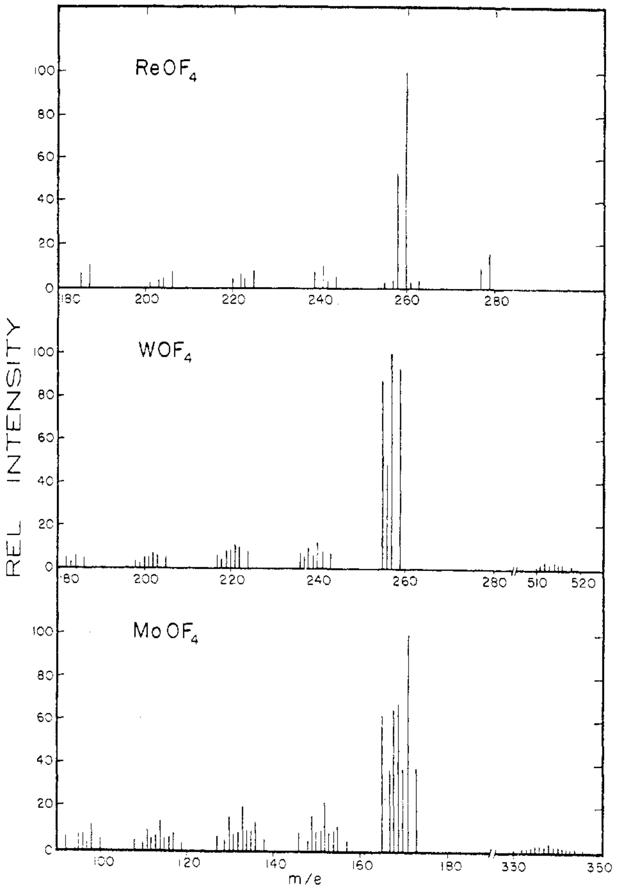

Figure 1. Mass spectra of $MoOF_4$, WOF_4, and $ReOF_4$; sample temperature 25°, source temperature 30°, ionization voltage 70 eV. Each spectrum is normalized to the most intense ion.

Table I. Observed Mass Spectra of MOF_4 Compounds[a]

Ion	M = Mo	M = W	M = Re
$(MOF_3)_2^+$	4	3	0
MOF_4^+	<1	<1	17
MF_4^+	<1	<1	3
MOF_3^+	100	100	100
$MO_2F_2^+$	<1	<1	2
MF_3^+	11	8	5
MOF_2^+	14	10	10
MF_2^+	13	10	9
MOF^+	11	8	6
MF^+	8	6	7
MO^+	8	5	3
M^+	11	6	10

[a] Relative total ion intensities for each polyisotopic ion fragment envelope, normalized to $MOF_3^+ = 100$.

Results

Mass Spectra. The polyisotopic mass spectra of $MoOF_4$, WOF_4, and $ReOF_4$, normalized to the most intense ions, MOF_3^+, are shown in Figure 1. The measured ion intensities are compared in Table I by listing the total ion intensity for each ion fragment envelope normalized to the most intense envelope. The spectra were routinely recorded at 70 eV ionization energy. Spectra recorded at 20 eV showed about 30% greater intensity in the parent ion envelope MOF_4^+, but systematic studies of the ion intensities as a function of

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(18) R. T. Paine, K. L. Treuil, and F. E. Stafford, *Spectrochim. Acta, Part A*, 29, 1891 (1973).

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Table II. Infrared Stretching Fundamentals (cm^{-1}) of Metal Oxide Tetrafluoride Vapors[a]

	$MoOF_4$ (d^0)	WOF_4 (d^0)	$ReOF_4$ (d^1)
ν_1 (A_1 M=O str)	R 1058 Q 1048.6 (0.14) P 1039	R 1065.5 Q 1056.5 (0.33) P 1047	R 1086 Q 1077.0 (0.31) P 1067
ν_2 (A_1 M–F str)		R 744 Q 735.1 (0.21) P 725[b]	R 731 Q 722.3 (0.18)
ν_7 (E M–F str)	Q 720.8[c] (1)	R 705.5 Q 698.7 (1) P 691	R 706.5 Q 700.2 (1) P 693
α_{min}[d]	0.007	0.01	0.005
Oligomer bands	750 w 680 w 542 vw	~740 vw 719 w 556 mw	None

[a] Frequencies of Q-branch maxima are accurate to ±0.5 cm^{-1}; relative peak absorptivities (in parentheses) are accurate to ±0.02. [b] Incompletely resolved. [c] Contour perturbed (see text). [d] α_{min} is the relative peak absorptivity of the weakest vapor band which could have been observed in the region 500–850 cm^{-1}.

ionization voltage were not possible without instrument modification. The ionization process also could not be studied here.

The spectra of the three compounds are similar in several respects. Each spectrum shows a low-intensity parent ion envelope, MOF_4^+, and the most intense envelope corresponds to MOF_3^+. Each spectrum also shows a low-intensity envelope corresponding to $MO_2F_2^+$, which probably results from ionization of MO_2F_2 formed in small amounts by hydrolysis in the sample inlet system. Examination of the spectra reveals one important difference: $ReOF_4$ shows no evidence for ions of the type $(ReOF_x)_{2-4}^+$, but both $MoOF_4$ and WOF_4 provide ions $(MoOF_3)_2^+$ and $(WOF_3)_2^+$ with relative total ion intensities of 4 and 3, respectively. Ions of the type $(MOF_3)_{3-4}^+$ and $(MOF_{1-2})_{2-4}^+$ were not detected; the estimated sensitivity level for these ions in our instrument is ~1 in 10^4.

Although the neutral progenitors of the observed ions have not been determined in this study, the results are consistent with the assumption that the principal neutral species in the MOF_4 vapors are the respective monomers. Apparently both $MoOF_4$ and WOF_4 vapors also contain small amounts (<10 mol %) of oligomeric species [$(MOF_4)_4$?] which on electron impact produce fragment ions $(MOF_3)_2^+$. $ReOF_4$ vapors appear to be free of oligomers at a detection level of 1 in 10^4.

Infrared Spectra. The infrared results are summarized in Table II. Our numbering of the fundamentals is based on C_{4v} symmetry ($\Gamma_{vib} = 3\ A_1 + B_1 + 2\ B_2 + 3\ E$), which, as will be discussed in detail below, the spectra strongly support.

The assignment of the observed bands is straightforward, with the exception of the M-F stretching region of $MoOF_4$. For this molecule, the one observed M-F stretch was asymmetric, with none of the three branches well resolved, and the R branch was considerably broadened. This anomalous contour and the "missing" fundamental can be reasonably explained if it is assumed that ν_2 and ν_7 are nearly coincident in $MoOF_4$. Such a near degeneracy would result in Coriolis interaction between the two fundamentals, and it is known that such an interaction can significantly perturb the contour of the resulting composite band.[20] All other bands attributable to MOF_4 vapor monomers have well-resolved, normal PQR structure; the appearance of these bands is indicated in Figure 2 for $ReOF_4$.

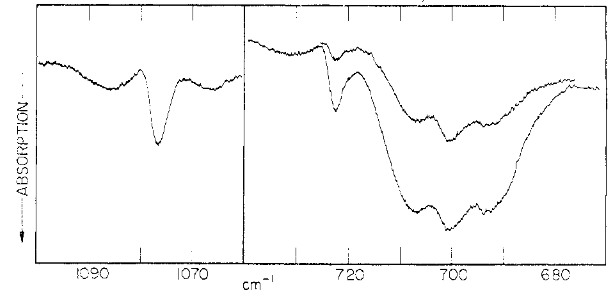

Figure 2. Infrared-active stretching fundamentals of $ReOF_4$ vapor, recorded at 300 K with a path length of 6.2 m; spectral slit widths approximately 1.8 cm^{-1} at 1080 cm^{-1} and 1.5 cm^{-1} at 700 cm^{-1}.

In the case of $MoOF_4$ and WOF_4 several additional very weak bands that lacked any obvious rotational structure were observed in the M-F stretching region. The absorbances of these bands relative to ν_2 and ν_7 were studied as a function of concentration, as the multipass cell was filled and then heated to ~320 K to increase the vapor pressure. The bands were relatively more intense at higher concentrations and hence cannot be due to MOF_4 monomer vapor. They also decreased in intensity faster than the monomer bands when the cell was pumped out and so are probably not due to material deposited on the windows. The fact that they were not observed for $ReOF_4$ suggests strongly that they arise from vapor-phase oligomers. The bands near 550 cm^{-1} seem clearly attributable to fluorine bridges, which have been observed to absorb in this region in the solids.[13,18] In previously published vapor spectra[7,16,17] the distinction between the MOF_4 monomer absorptions and the weaker bands due to oligomers has not always been recognized.

We now consider what information on the structure of these molecules can be extracted from their infrared spectra. The three most likely structures are listed in Table III together with a summary of the appropriate infrared selection rules.

X-Ray studies of $MoOF_4$, WOF_4, and $ReOF_4$[6-8,11] indicate that these molecules have very similar structures in the solid, consisting of light-atom octahedra linked by cis-bridging fluorine atoms. Each octahedron consists of a MOF_4 unit with an additional bridging fluorine trans to the M=O bond; these units would have approximately C_{4v} symmetry except that one of the M–F bonds cis to the M=O is lengthened because it participates in a fluorine bridge to the next unit. The molecular dimensions are very similar in the three molecules: M=O, ~1.65 Å; nonbridging M–F, ~1.84 Å; O=

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Table III. Possible Structures of MOF_4 Molecules[a]

	C_{4v}	C_{3v}	C_{2v}
Structure	Square pyramid, axial O	Trigonal bipyramid, axial O	Trigonal bipyramid, equatorial O
O=M–F angles assumed, deg			
Axial F		180	90
Equatorial F	100	90	120–125
Rotational constants, cm^{-1}	$B = 0.096$ $C = 0.068$	$A = 0.087$ $B = 0.083$	$A = 0.098$ $B = 0.083–0.079$ $C = 0.075–0.078$
Infrared-active M-F stretches (and their P-R spacings, cm^{-1}) at 300 K	1 parallel (18.5) 1 perpendicular ([b])	2 parallel (16.6) 1 perpendicular ([b])	1 type A (15.8) 1 type B (16.2–17.5)[c] 2 type C (17.9)
Band type for M=O stretch	Parallel	Parallel	Type C

[a] Assuming M=O distances of 1.65 A and M–F distances of 1.84 A, as discussed in the text. [b] P-R spacings of the perpendicular bands depend upon the values of the Coriolis constants. [c] Q-Q branch spacings of type B bands, 1.9–0.8 cm^{-1}.

M–F angle, ~100°.[21] For the C_{4v} model, these parameters yield the rotational constants ($B = h/8\pi^2 cI_B$, where I_B is the moment of inertia, etc.) given in Table III. The same lengths were used to calculate rotational constants for the C_{3v} and C_{2v} models. For C_{2v} symmetry we have investigated two slightly different structures: one in which the equatorial O=M–F angle is 120° (*i.e.*, the fluorine and oxygen ligands are equally spaced in the equatorial plane) and a second in which this angle is 125° as it appears to be in the C_{2v} structure suggested[22] for SOF_4. The two models have somewhat different rotational constants *B* and *C*.

With the rotational constants calculated we can now estimate the spacings between the P and R branches of the different bands by standard methods.[23,24] The results are included in Table III.

The infrared data of Table II can be summarized as follows: these molecules each have two M–F stretching modes (except that ν_2 of $MoOF_4$ is missing, as discussed above); the M=O stretch and one of the M–F stretches have similar contours with P-R branch spacings of 18-19 cm^{-1}; the second M–F stretch has a somewhat different contour with a P-R spacing of 13.5-14.5 cm^{-1}. These agree completely with the bands expected for the C_{4v} model (Table III). The P-R spacing in ν_7 corresponds[25] to a Coriolis constant $\zeta_7 = 0.10 \pm 0.03$, which is quite reasonable for a stretching fundamental. (Stretching modes characteristically have small Coriolis constants. It can be shown that for a *pure* stretching mode with no bending character, in which the F atoms move only along their respective M-F axes, the Coriolis constant would be zero.)

On the other hand, there are not enough observed M-F stretches to satisfy the C_{3v} model. Since we could have observed such bands if their intensities were of the order of 0.01–0.005 that of ν_7, it is very unlikely that any such infrared-active fundamentals have been missed. Furthermore, the P-R spacings of the observed M=O stretches are at least 2 cm^{-1} larger than the value expected for parallel bands of a C_{3v} molecule, which is greater than the usual discrepancies between observed and calculated band contours. Of course, our assumption about the structure of the C_{3v} model may not be correct: it has been observed[6,7,26] that ligands trans to multiple M=O bonds have abnormally long bonds to the metal. But increasing the trans M–F bond length will lower the value of *B* and hence *decrease* the predicted P-R spacing, so the discrepancy in the band contours cannot be explained away on these grounds.

For the C_{2v} model, there would have to be two missing M-F stretches for each molecule. In addition, the bands we have identified as ν_7 have P-R spacings which are significantly less than would be expected for any of the three possible band types under C_{2v} symmetry.

In conclusion, the infrared evidence, both as to the number of observed fundamentals and their structure, strongly supports C_{4v} symmetry and cannot easily be reconciled to either of the other two models.

Discussion

At least three barriers may have impeded previous gas-phase structural studies of metal oxide fluoride compounds: uncertainty as to the gas-phase composition, low vapor pressure, and reactivity with most materials at temperatures above about 40°. The present investigation has successfully overcome these problems. We wish to emphasize the importance of using mass spectrometry in conjunction with vapor-phase structural studies of compounds that may associate; obviously no conclusions drawn from the vibrational spectrum can be valid unless one understands what species are present in the vapor phase.

It is interesting that the fragmentation patterns reported here for MOF_4 compounds are similar to molecular beam mass spectra of the corresponding metal oxide tetrachlorides,[27] except that the chlorides showed no evidence of oligomers. The trend to increasing relative intensity of the parent ion MOF_4^+ in the order Mo ~ W << Re is also found in the chloro analogs. This trend has been explained in the chlorides[27] on the basis of the relative magnitudes of the appearance potentials of the principal fragment ions and the ionization potentials of the parent ions. While the same rationale can probably be applied to the fluoride spectra, appearance potential measurements for the MOF_4^+ and MOF_3^+ ions are needed before a definite ionization model can be devised.

The structural results are at first somewhat surprising: the generally successful valence-shell electron-pair repulsion (VSEPR) theory of Gillespie[28] predicts C_{2v} symmetry for

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(21) We have assumed that the oxygen-bridged structure originally reported for WOF_4[11] is actually the fluorine-bridged structure suggested in ref 12 and 13. This brings the bond lengths and angles of WOF_4 into agreement with those of the other two molecules.

(22) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, 51, 2500 (1969).

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(28) R. J. Gillespie, "Molecular Geometry," Van Nostrand-Reinhold, London, 1972.

AOX_4 coordination. SOF_4 does have this structure,[22] and while the VSEPR theory is not always dependable for transition metal compounds, one might expect it to hold at least for the d^0 molecules $MoOF_4$ and WOF_4. However, if just electron-pair repulsions are considered ("points-on-a-sphere" model), the energy difference between the trigonal-bipyramidal (C_{2v}) and square-pyramidal (C_{4v}) symmetries is only slight; in fact, the Berry "pseudorotation" of trigonal-bipyramidal molecules proceeds, *via* a low potential barrier, through just such a C_{4v} intermediate.[29,30] For heavy atoms with large valence shells, the electron-pair interaction may be very small, resulting in a negligible energy difference between the two structures.[28] If ligand repulsions are important in determining the stereochemistry, the C_{4v} structure may then be favored, and the metal oxytetrafluorides appear to be such a case. According to the models of Table III, for C_{2v} symmetry there are two O· · ·F contacts of 2.47 Å (and in the C_{3v} model there are three such contacts), while for C_{4v} symmetry all four O· · ·F distances are 2.68 Å. The four closest F· · ·F distances, on the other hand, are only slightly different: 2.60 Å for C_{2v} *vs.* 2.56 Å for C_{4v}. Another case in which nonbonded interactions are important in determining the stereochemistry of transition metal compounds is that of the chromyl halides,[31] for which the X–Cr–X angles are larger than the O=Cr=O angles, contrary to the predictions of VSEPR theory. For the sulfuryl halides, however, the reverse is true, and their stereochemistry is determined by the electron-pair repulsions alone.

The motion that would convert the C_{4v} structure of the oxytetrafluorides into C_{2v} symmetry is that of the B_2 bending fundamental, ν_6. Because of the apparently small energy difference between the two symmetries, one would expect this mode to have an abnormally small force constant and large amplitude[30] and perhaps to exhibit a perturbed rotational contour. This fundamental is only Raman active, however, and its observation in the vapor phase would be difficult.[32]

Registry No. $MoOF_4$, 52049-90-8; WOF_4, 52049-91-9; $ReOF_4$, 52152-11-1.

[29] E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

[30] R. R. Holmes, *Accounts Chem. Res.*, 5, 296 (1972).

[31] C. D. Garner, R. Mather, and M. F. A. Dove, *J. Chem. Soc., Chem. Commun.*, 633 (1973).

[32] Note Added in Proof. L. E. Alexander, I. R. Beattie, A. Bukovszky, P. J. Jones, C. J. Marsden, and G. J. Van Schalkwyk [*J. Chem. Soc., Dalton Trans.*, 81 (1974)] have recently reported a parallel study of $MoOF_4$ and WOF_4. Vapor density measurements indicated that the gases are essentially monomeric, although there was evidence for polymer formation in WOF_4 (only). Infrared and Raman spectra of the vapor and matrix-isolated species were interpreted as strongly suggesting C_{4v} symmetry. In the Raman spectrum of WOF_4, one band at 328 cm^{-1} was described as weak and broad; this may be the B_2 fundamental that converts C_{4v} symmetry to C_{2v} (see our Discussion). (Alexander, *et al.*, used a numbering system that interchanges the B_1 and B_2 designations relative to our notation. Further confusion arises from their assignment of the 328-cm^{-1} band to B_2 (our B_1) in their text, and to B_1 (our B_2) in their Table 4.)

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The XeF_3^+, $XeOF_3^+$, and XeO_2F^+ Cations. Preparation and Characterization by Fluorine-19 Nuclear Magnetic Resonance Spectroscopy

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The preparation of the salts $XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}^-$, and $XeO_2F^+Sb_2F_{11}^-$ is described. The ^{19}F nmr spectra of solutions of these salts in excess SbF_5 show that the XeF_3^+, $XeOF_3^+$, and XeO_2F^+ ions are present in these solutions. The spectra are consistent with a T-shaped structure of the trigonal-bipyramidal AX_3E_2 type for XeF_3^+ and an AX_4E type structure with the same arrangement of the fluorines and an oxygen replacing one of the equatorial line pairs, for $XeOF_3^+$.

Introduction

Although a large number of complexes of XeF_2 and XeF_6 with fluoride acceptor molecules have been reported[1,2] no such complexes of XeF_4, $XeOF_4$, or XeO_2F_2 had been characterized prior to the work described here. There had been an early report of an unstable xenon tetrafluoride–antimony pentafluoride complex which was believed to have the composition $XeF_4 \cdot 2SbF_5$; however, no analytical or other conclusive evidence in support of this formulation had been published.[3] An early report[4] that XeF_4 interacts with SbF_5 or TaF_5 to form XeF_2 adducts is erroneous. These adducts were most probably obtained because the XeF_4 was contaminated with XeF_2. More recently Martin[5] has claimed the complexes $2XeF_4 \cdot SbF_5$ and $XeF_4 \cdot 4SbF_5$ but again they were not characterized. Bartlett and coworkers have reported that XeF_4 does not form stable adducts with either AsF_5 or IrF_5 in bromine pentafluoride solution[6] or with RuF_5.[7] Consequently, they concluded that the fluoride ion donor ability of XeF_4 is far inferior to that of either XeF_2 or XeF_6. However, as we have shown, XeF_4 does, in fact, readily form the adducts $XeF_4 \cdot SbF_5$ and $XeF_4 \cdot 2SbF_5$, which may be formulated, at least approximately, as the ionic salts $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$. Since our preliminary report[8] of our

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