cluded, and a non-Poisson-contribution weighting scheme with an instability factor of $P = 0.08$ was used in the final stages of refinement. The maximum peak in the final difference Fourier had a height of 0.397 e Å^{-3}.

The space group of **2** was determined as for **1**. Data were collected in the *hkl* octant between 2θ values of 3.0 and 44.0°. The In, Li, and P atoms were refined anisotropically as were the carbon atoms of the phenyl rings. The atoms of the THF molecules were refined isotropically. Hydrogen atoms were not located, but their contributions were included in the refinements.[10] Data with intensities less than $3\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a non-Poisson-contribution weighting scheme with $P = 0.08$ was used. The maximum peak in the final difference Fourier had a height of 0.462 e Å^{-3}.

The unit cell parameters for **3** were determined from 25 reflections with 2θ values between 28 and 30°. The triclinic space group $P\bar{1}$ (No. 2) was chosen on the basis of successful refinement of the structure. A hemisphere of data was collected between 2θ values of 3.0 and 44.0°. There was a severe decay in the crystal during the course of data collection. However, this does not appear to have adversely affected the structure. The Ga, As, and C atoms of the phenyl rings were refined anisotropically. The atoms of the THF molecules and Li were refined isotropically. There was a disordered THF molecule also found in the structure that was not bound to Li. The atoms of this unit (O(91) and C(91)–C(98)) were refined isotropically. Hydrogen atoms were not located, but their contributions were included in the refinement.[10] A non-Poisson contribution to the weighting scheme was employed ($P = 0.06$). The maximum peak in the final difference Fourier had a height of 0.505 e Å^{-3}.

Supplementary material for **1–3** is available.[11] Scattering factors were taken from ref 12.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the Texas Advanced Technology Research Program for financial support. R.A.J. thanks the Alfred P. Sloan Foundation for a fellowship (1985–1989).

Registry No. **1**, 114860-65-0; **2**, 114860-67-2; **3**·THF, 114860-70-7.

Supplementary Material Available: Tables of bond lengths, bond angles, positional parameters, and thermal parameters for **1–3** (23 pages); tables of observed and calculated structure factors for **1–3** (38 pages). Ordering information is given on any current masthead page.

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(10) P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the leasth-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4(|F_o|)^2/[\sum(|F_o|)^2]^2$, $[\sum(|F_o|)^2]^2 = [S^2(C + R^2B) + (P(|F_o|)^2)^2]/Lp^2$, S^2 is the scan rate squared, C is the total background count, R^2 is the ratio of scan time to background count squared, and L_p is the Lorentz–polarization factor.

(11) See paragraph at the end of the paper regarding supplementary material.

(12) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Contribution from Rocketdyne, A Division of Rockwell
International, Canoga Park, California 91303

Synthesis and Properties of $XeO_2F^+AsF_6^-$ and $[FO_2XeFXeO_2F]^+AsF_6^-$

Karl O. Christe* and William W. Wilson

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The new compound $XeO_2F^+AsF_6^-$ was prepared from XeO_2F_2 and an excess of AsF_5 with anhydrous HF as a solvent. The compound is a white solid having a dissociation pressure of 7 Torr at 23 °C. On pumping or exposure to a laser beam, it loses AsF_5 and is converted into $[FO_2XeFXeO_2F]^+AsF_6^-$, which was also obtained by the direct combination of XeO_2F_2 with AsF_5 in a 2:1 mole ratio in HF. Both XeO_2F_2 adducts were characterized by Raman spectroscopy. By analogy with the closely related $XeF^+MF_6^-$ and $[FXeFXeF]^+MF_6^-$ salts, $XeO_2F^+AsF_6^-$ exhibits $FO_2Xe\cdots FAsF_5$ bridging and distortion of the AsF_6^- anion, whereas the anion–cation interaction in $[FO_2XeFXeO_2F]^+AsF_6^-$ appears to be minimal.

Introduction

Relatively little is known about the fluoride ion donor properties of XeO_2F_2. To our knowledge, the only previous publications in this area are those by Schrobilgen and co-workers. In 1972, they reported the synthesis of a yellow solid having the composition $XeO_2F_2 \cdot 1.8SbF_5$ by adding SbF_5 to an HF solution of XeO_2F_2. The solid dissolved in SbF_5 to give a yellow-green solution that slowly evolved oxygen. Cooling to 5 °C caused the gas evolution to cease and caused the color of the solution to intensify to a dark green.[1]

In a subsequent paper on the ^{19}F NMR spectrum of XeO_2F^+, it was stated that pure $XeO_2F^+Sb_2F_{11}^-$ is white and that the yellow color was due to its decomposition product $XeF^+Sb_2F_{11}^-$.[2] The Raman spectrum of solid $XeO_2F^+Sb_2F_{11}^-$ was also published;[3] however, of the six fundamental vibrations expected for an XeO_2F^+ cation of symmetry C_s, only four were observed. Furthermore, the complexity of the $Sb_2F_{11}^-$ part of the spectrum did not allow any conclusions about the extent of fluorine bridging and anion distortion frequently encountered with ionic xenon fluoride adducts. Finally, the synthesis of $XeO_2F^+SbF_6^-$ from SbF_5 and a 2-fold excess of XeO_2F_2 in HF solution was briefly mentioned in a paper on ^{129}Xe NMR spectroscopy, but no properties of the salt were given except for its NMR data.[4] In view of the paucity of data available for XeO_2F^+, the convenient XeO_2F_2 synthesis recently discovered by us,[5] and the reluctance of AsF_5 to form stable polyanions, a study of the adduct formation between XeO_2F_2 and AsF_5 was undertaken, the results of which are reported in this paper.

Experimental Section

Materials. Commercial AsF_5 (Ozark Mahoning) was of good quality and was used without further purification after removal of any material noncondensable at −196 °C. Hydrogen fluoride (Matheson) was dried by storage over BiF_5.[6] The synthesis of XeO_2F_2 is described elsewhere.[5]

Caution! The hydrolysis of XeO_2F_2 produces highly explosive XeO_3.

Apparatus. Volatile materials used in this work were handled in a well-passivated (with ClF_3) stainless-steel Teflon–FEP vacuum line.[7] Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Reactions were carried out in either 0.5 in. o.d. sapphire (Tyco) or Teflon–FEP tubes closed by either stainless-steel or Teflon–PFA (Fluoroware Inc.) valves. Raman spectra were recorded on either a Spex Model 1403 or a Cary Model 83 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser or the 488-nm exciting line of an Ar ion laser, respectively. Sealed melting point capillaries or the sapphire reactors were used as sample containers in the transverse-view-

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ing–transverse-excitation mode. A previously described[8] device was used for the recording of the low-temperature spectra. The ^{19}F NMR spectra of HF solutions of the samples contained in heat-sealed, 5 mm o.d. Teflon–FEP tubes (Wilmad Glass Co.) were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer equipped with a variable temperature probe.

Preparation of $XeO_2F^+AsF_6^-$. A sample of XeO_2F_2 (1.095 mmol) was freshly prepared[5] from N_2O_5 and $XeOF_4$ in a 0.5 in. o.d. Teflon–FEP ampule. The ampule was cooled to −196 °C, and anhydrous HF (1 mL of liquid) was condensed in. XeO_2F_2 was dissolved in the HF, and AsF_5 (3.56 mmol) was added at −196 °C. The mixture was briefly warmed to room temperature and then cooled to −78 °C. Unreacted AsF_5 and HF solvent were pumped off on warm-up of the ampule from −78 toward 0 °C. After pumping at 0 °C for 30 min, the ampule was weighed and found to contain 408 mg of a white solid (weight calculated for 1.095 mmol of $XeO_2F^+AsF_6^-$ = 406.5 mg) that was identified by Raman spectroscopy as $XeO_2F^+AsF_6^-$.

Preparation of $[FO_2XeFXeO_2F]^+AsF_6^-$. This preparation was carried out as described above for $XeO_2F^+AsF_6^-$ except for using a sapphire reactor and a different ratio of starting materials, XeO_2F_2 (0.626 mmol) and AsF_5 (0.313 mmol). Again, a white solid product was isolated whose weight (177 mg, weight calcd for 0.313 mmol of $[FO_2XeFXeO_2F]^+AsF_6^-$ = 179 mg) and Raman spectrum were in agreement with the composition $[FO_2XeFXeO_2F]^+AsF_6^-$.

Results and Discussion

Synthesis and Properties. The reaction of XeO_2F_2 with an excess of AsF_5 in anhydrous HF as a solvent produces $XeO_2F^+AsF_6^-$ according to

$$XeO_2F_2 + AsF_5 \xrightarrow{HF} XeO_2F^+AsF_6^-$$

This 1:1 salt is a white solid that is stable at 0 °C and has a dissociation pressure of about 7 Torr at 23 °C. The gas above the solid was identified by its infrared spectrum as AsF_5. On prolonged pumping or exposure to a laser beam during the recording of the Raman spectra, $XeO_2F^+AsF_6^-$ is slowly converted to $[FO_2XeFXeO_2F]^+AsF_6^-$ according to

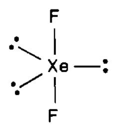
$$2XeO_2F^+AsF_6^- \rightarrow [FO_2XeFXeO_2F]^+AsF_6^- + AsF_5$$

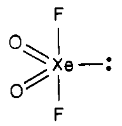
The latter compound can also be prepared by the direct combination of XeO_2F_2 and AsF_5 in a 2:1 mole ratio in anhydrous HF solution:

$$2XeO_2F_2 + AsF_5 \xrightarrow{HF} [FO_2XeFXeO_2F]^+AsF_6^-$$

The $[FO_2XeFXeO_2F]^+AsF_6^-$ salt is a white solid that is stable at room temperature. Both XeO_2F_2–AsF_5 adducts did not show any color or noticable tendency to lose O_2 with either XeF^+ or $Xe_2F_3^+$ formation at room temperature in either the solid state or HF solution. The ^{19}F NMR spectra of their HF solutions exhibited only a single broad resonance due to rapid exchange between the HF and both the anions and cations. This is in agreement with a previous study[4] which concluded that a more acidic solvent, such as SbF_5, is required for the observation of a separate XeO_2F^+ signal.

The tendency of XeO_2F_2 to form both 1:1 and 2:1 adducts with AsF_5 is not surprising in view of the facts that XeO_2F_2 is structurally closely related to XeF_2 and that XeF_2 is well-known for forming both XeF^+ and $[FXeFXeF]^+$ salts[9] with AsF_5. The molecular structures[10,11] of both XeF_2 and XeO_2F_2 can be derived from trigonal bipyramids in which the two fluorine atoms occupy the axial positions and either three free valence-electron pairs or one free valence-electron pair and two doubly bonded oxygen atoms, respectively, occupy the equatorial positions.





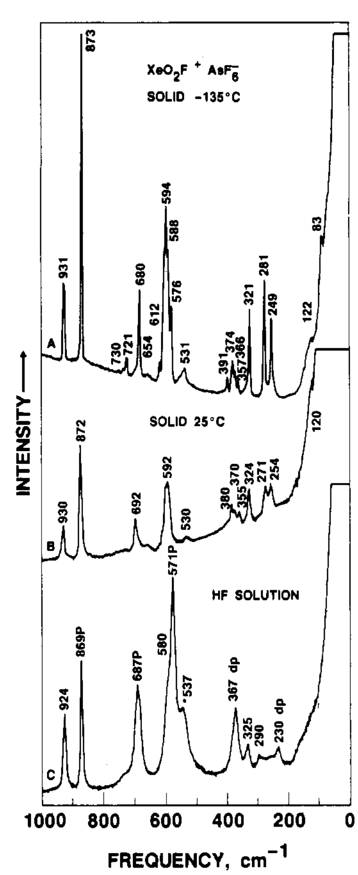
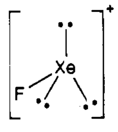


Figure 1. Raman spectra of $XeO_2F^+AsF_6^-$: trace A, solid at −135 °C; trace B, solid at 25 °C in a sapphire tube containing 200 Torr of AsF_5; trace C, HF solution at 25 °C in a sapphire tube.

Since trigonal-bipyramidal structures are energetically less favorable than either tetrahedral or octahedral ones,[12,13] they generally are both strong fluoride ion donors and acceptors. Thus, both XeF_2 and XeO_2F_2 show a pronounced tendency to form pseudotetrahedral



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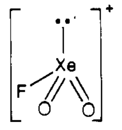
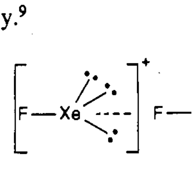
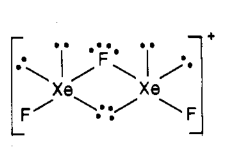
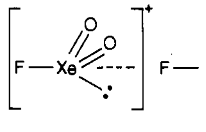


cations, respectively. Since the xenon central atom in XeF^+ is coordinatively unsaturated, it is capable of forming in its solid salts a bridge to one of the fluoride atoms of either the anion or a second XeF_2 molecule, resulting in either a strong distortion of the anion or the formation of a $[FXeFXeF]^+$ polycation, respectively.[9]

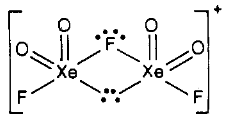




On the basis of the above-mentioned close structural relationship between XeO_2F_2 and XeF_2, the formation of the analogous



and



cations appears likely. Convincing evidence for the validity of

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Table I. Raman Spectra of $XeO_2F^+AsF_6^-$ Compared to Those of $XeF^+AsF_6^-$ and SeO_2F^-

obsd freq, cm^{-1} (rel intens)					assignments (point group)	
	$XeO_2F^+AsF_6^-$					AsF_6^-
	solid					
$XeF^+AsF_6^-$ [a]	−135 °C	25 °C	HF soln	SeO_2F^- [c]	XO_2F^+ (C_s)	(O_h) → (C_{4v}) → (C_s)
	931 (23)	930 (29)	924 (38)	903 (100)	ν_5 (A″), $\nu_{as}(XO_2)$	
	873 (100)	872 (100)	869 (65) p	888 (45)	ν_1 (A′), $\nu_{sym}(XO_2)$	
731 (5)	730 (1.5)					ν_3 (F_{1u}) — E — A″
724 (5)	721 (5)	725 (1)				A′
667 (4)	654 (1)	655 (0+)				A_1 — A′
678 (20)	680 (26)	692 (28)	687 (48) p			ν_1 (A_{1g}) — A_1 — A′
609 (100)	594 (54)	592 (59)	571 (100) p	424 (25)	ν_2 (A′), ν(XF)	
	588 (10)					
	576 (20)					
586 (10)	612 (5)		580 sh			ν_2 (E_g) — A_1 — A′
	531 (5)	530 (4)				B_1 — A′
417 (5)	391 (4)					ν_4 (F_{1u}) — A_1 — A′ E — A′ A″
387 (6)	374 (10)	380 (15)	367 (34) dp			ν_5 (F_{2g}) — E — A′
	366 (6)	370 (9)				A″
	357 (3)	355 (9)				B_2 — A″
339 (21) [b]						
	321 (26)	324 (29)	325 (12)	324 (10)	ν_3 (A′), $\delta_{sciss}(XO_2)$	
	281 (35)	271 (25)	290 (7)	283 (10)	ν_4 (A′), $\delta_{sym}(FXO_2)$	
	249 (24)	254 (20)	230 (9) dp	238 (2)	ν_6 (A″), $\delta_{asym}(FXO_2)$	
155 (15) [b]						
146 sh						
	122 sh	120			lattice modes	
	83 (20)					

[a] Reference 17. [b] These bands were assigned in ref 17 to the stretching and deformation modes of the Xe···FAs bridge. [c] Reference 16.

these predictions was obtained by Raman spectroscopy.

Raman Spectra. Figure 1 shows the spectra of the 1:1 adduct of XeO_2F_2 with AsF_5. The observed frequencies together with their assignments are listed in Table I. Because of the marginal stability of $XeO_2F_2{\cdot}AsF_5$ at room temperature and its tendency to form the 2:1 adduct in the laser beam (see above), it was necessary to either maintain an AsF_5 pressure of several hundred Torr above the sample during the recording of the spectrum at ambient temperature or cool the sample.

As can be seen from trace A of Figure 1 and Table I, the low-temperature Raman spectrum of solid $XeO_2F_2{\cdot}AsF_5$ is in excellent agreement with our expectations for a predominantly ionic $XeO_2F^+AsF_6^-$ adduct in which an $FO_2Xe{\cdots}FAsF_5$ bridge distorts the AsF_6^- anion from O_h to either C_{4v} or C_s symmetry. The six fundamentals predicted for an XeO_2F^+ cation of symmetry C_s can be readily assigned on the basis of their frequencies and relatively high intensities and by comparison with those of similar XO_2F species, such as ClO_2F,[14] BrO_2F,[15] and SeO_2F^-.[16] The assignments for $XeO_2F^+AsF_6^-$ are further supported by a comparison with those previously given[17] for $XeF^+AsF_6^-$. Unfortunately, the published[17] Raman spectrum of $XeF^+AsF_6^-$ has a relatively low signal to noise ratio and resolution; therefore, it does not show as much detail as that of $XeO_2F^+AsF_6^-$. However, these spectra leave little doubt that $XeF^+AsF_6^-$ and $XeO_2F^+AsF_6^-$ are structurally closely related.

The room-temperature spectrum of $XeO_2F^+AsF_6^-$ (Figure 1, trace B) is similar to the low-temperature spectrum but, as expected, shows line broadening and loss of resolution. The spectrum of the HF solution (Figure 1, trace C) shows the bands expected for the isolated ions, XeO_2F^+ and octahedral AsF_6^-.[18,19] A weak band at 537 cm^{-1} was of variable relative intensity and, at higher intensity, it was accompanied by weaker bands at 900, 850, and 310 cm^{-1}, which are characteristic of free XeO_2F_2.[20] Furthermore, HF solutions containing $XeO_2F^+AsF_6^-$ and excess XeO_2F_2 showed only the bands characteristic of XeO_2F^+ and free XeO_2F_2 but none attributable to $Xe_2O_4F_3^+$. It, therefore, appears that in relatively dilute HF solutions the equilibrium

$$[FO_2XeFXeO_2F]^+AsF_6^- \rightleftarrows XeO_2F^+AsF_6^- + XeO_2F_2$$

is shifted to the right.

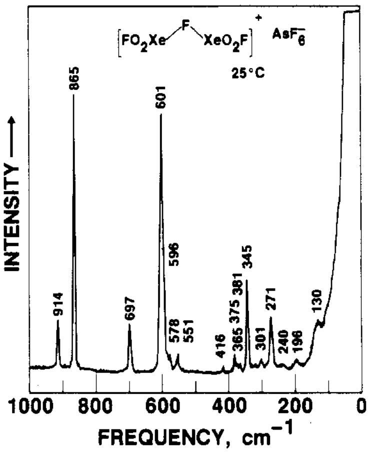

Figure 2. Raman spectrum of solid $[FO_2XeFXeO_2F]^+AsF_6^-$ at room temperature in a glass capillary.

The room-temperature Raman spectrum of the 2:1 adduct, $2XeO_2F_2{\cdot}AsF_5$, is shown in Figure 2, and the observed frequencies and their assignments are given in Table II. The spectrum can be readily assigned in terms of an ionic $[FO_2XeFXeO_2F]^+AsF_6^-$ structure (see Table II) because (i) bands are observed that are

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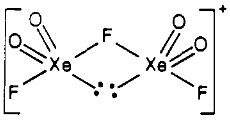
Table II. Raman Spectrum of Solid $[FO_2XeFXeO_2F]^+AsF_6^-$ at 25 °C Compared to That of $[FXeFXeF]^+AsF_6^-$

obsd freq, cm^{-1} (rel intens)		assignments (point group)		
$Xe_2O_4F_3^+$ AsF_6^-	$Xe_2F_3^+AsF_6^-$ [a]	$Xe_2O_4F_3^+$ (C_{2v})	$Xe_2F_3^+$ (C_{2v})	AsF_6^- (O_h)
914 (18)		ν_8 (A_2), ν_{18} (B_2)		
865 (100)		ν_1 (A_1), ν_{12} (B_1)		
697 (17)	681 (20)			ν_1 (A_{1g})
601 (95)	588 (100)	ν_2 (A_1)	ν_1 (A_1)	
596 sh	598 (95)	ν_{13} (B_1)	ν_6 (B_1)	
578 (4) 551 (5)	580 sh			ν_2 (E_g)
416 (2)	417, 401 (<1)	ν_3 (A_1)	ν_2 (A_1)	
381 (7) 375 (2) 365 (2)	367 (17)			ν_5 (F_{2g})
345 (33)		ν_4 (A_1), ν_{15} (B_1)		
301 (3)		ν_{10} (A_2), ν_{20} (B_2)		
271 (18)		ν_5 (A_1), ν_{16} (B_1)		
240 (1)	255 (5) br	ν_{11} (A_2), ν_{21} (B_2)	ν_5 (A_2)	
196 (3)		ν_6 (A_1), ν_{17} (B_1)		
130 (15)	163 (37)	ν_7 (A_1)	ν_4 (A_1)	

[a] Values from ref 17.

characteristic of octahedral AsF_6^-, for which the degeneracies of the E_g and F_{2g} modes have been lifted due to solid-state effects, and (ii) the observed spectrum is analogous to that of $[FXeFXeF]^+AsF_6^-$,[17] whose crystal structure has been established by X-ray diffraction.[21] Consequently, a structure consisting of essentially octahedral AsF_6^- anions and V-shaped



cations is indicated with relatively weak interactions between the anions and cations. For the purpose of vibrational assignments and mode designations (see Table III), it was assumed that the $[FO_2XeFXeO_2F]^+$ cation possesses C_{2v} symmetry, i.e. that the XeO_2 groups are symmetric with respect to the symmetry plane of the FXeFXeF skeleton of the cation. However, a crystal structure determination is required to verify the exact location of these oxygen atoms.

An $[FO_2XeFXeO_2F]^+$ cation of symmetry C_{2v} possesses 21 fundamental vibrations. Their classifications and mode descriptions are given in Table III. The fact that the XeO_2 stretching modes show no signs of splitting indicates minimal in-phase, out-of-phase coupling of the vibrations of each half of the cation. The only band that shows a small splitting possibly due to in-phase, out-of phase coupling is the terminal fluorine–xenon stretching mode at 601 cm^{-1}, which exhibits a shoulder at about 596 cm^{-1}. This is in agreement with our predictions that the relatively high mass of the xenon atoms should reduce any coupling effects and that the coupling should be at a minimum for the oxygen atoms, which are perpendicular to the Xe–F bridge bonds and at a maximum for the terminal fluorine, which is at 180° to these Xe–F bonds. This weakness of the in-phase, out-of-phase coupling reduces the number of bands expected for $[FO_2XeFXeO_2F]^+$ by 7, from 21 to 14. Furthermore, the two XeO_2 torsional modes and the antisymmetric XeFXe stretching mode are expected to be of very low Raman intensity, thereby reducing the number of observable bands to 11. This number is in agreement with our observations for $[FO_2XeFXeO_2F]^+$, and assignments can be made to the fundamental vibrations on the basis of frequency and intensity arguments and by comparison with the spectrum of $[FXeFXeF]^+$, which possesses the same skeleton (see Table III).

Table III. Mode Description for the Fundamental Vibrations of $Xe_2O_4F_3^+$ and $Xe_2F_3^+$ in Point Group C_{2v}[a]

			$[FO_2XeFXeO_2F]^+$	$[FXeFXeF]^+$ [b]
A_1	ν_1	$\nu_{sym}(XeO_2)$, in phase	865	
	ν_2	$\nu(XeF)_t$, in phase	601	582
	ν_3	$\nu_{sym}(XeFXe)$	416	420
	ν_4	$\delta_{sciss}(XeO_2)$, in phase	345	
	ν_5	$\delta_{rock}(XeO_2)$, in phase	271	
	ν_6	$\delta(FXeF)$ in plane, in phase	196	171
	ν_7	$\delta_{sciss}(XeFXe)$	130	161
A_2	ν_8	$\nu_{as}(XeO_2)$, in phase	914	
	ν_9	$\tau(XeO_2)$, in phase	n.o.[c]	
	ν_{10}	$\delta_{wag}(XeO_2)$, in phase	301	
	ν_{11}	$\delta(FXeF)$ out of plane, in phase	240	255
B_1	ν_{12}	$\nu_{sym}(XeO_2)$, out of phase	865	
	ν_{13}	$\nu(XeF)_t$, out of phase	596	591
	ν_{14}	$\nu_{as}(XeFXe)$	n.o.[c]	n.o.[c]
	ν_{15}	$\delta_{sciss}(XeO_2)$, out of phase	345	
	ν_{16}	$\delta_{rock}(XeO_2)$, out of phase	271	
	ν_{17}	$\delta(FXeF)$ in plane, out of phase	196	179
B_2	ν_{18}	$\nu_{as}(XeO_2)$, out of phase	914	
	ν_{19}	$\tau(XeO_2)$, out of phase	n.o.[c]	
	ν_{20}	$\delta_{wag}(XeO_2)$, out of phase	301	
	ν_{21}	$\delta(FXeF)$ out of plane, out of phase	240	255

[a] The choice of B_1 and B_2 is arbitrary and for this table was selected in such a manner that the B_1 modes are symmetric with respect to the plane of the FXeFXeF skeleton. [b] Frequencies for $Xe_2F_3^+SbF_6^-$ from ref 17. [c] Not observed.

A comparison of the vibrational spectra of XeO_2F^+ and $[FO_2XeFXeO_2F]^+$ shows the expected similarity, since the $[FO_2XeFXeO_2F]^+$ cation is simply a polycation formed by the addition of XeO_2F_2 to the XeO_2F^+ cation. As predicted, the frequencies of the XeO_2 stretching modes in the polycation (914 and 865 cm^{-1}) are intermediate between those of XeO_2F^+ (931 and 873 cm^{-1}) and those of solid XeO_2F_2 (882 and 850 cm^{-1})[20] and are well suited for the recognition of polycation formation.

In several instances, assignments of Raman bands to Xe···F bridge modes have been made[22,23] and were summarized in 1976.[22] A closer inspection of this summary reveals numerous discrepancies, which cast doubt on the validity of these assignments. First of all, most of the frequencies are too high for the lengths of the bridge bonds involved. For example, bands in the 233–257-cm^{-1} frequency range were assigned to Xe···F bridges ranging from 2.49 to 2.94 Å[22] in spite of previous model calculations which had shown that weak interactions of this type result in frequencies ≤ 100 cm^{-1} and, if these frequencies are high enough, they would mix with the xenon fluoride bending modes.[9] Secondly, the Xe···F bridge mode for $XeF^+RuF_6^-$ was listed as 390 cm^{-1},[22] but the original work from which this value was quoted does not list a band in this region.[9] Thirdly, the quality of most of the spectra from which these values were taken was relatively poor, and the bands in question were either weak and questionable or fell into the region of the deformation modes of the anions.[17,23,24] Finally, in the case of $XeF^+AsF_6^-$, the relative intensity of the 339-cm^{-1} band assigned to the bridging Xe···F stretching mode[17] is much too high for this type of vibration and is inconsistent with those of the other bands assigned by these authors to similar Xe···F bridges.[22] Futhermore, in our Raman spectrum of $XeO_2F^+AsF_6^-$ (trace A, Figure 1), there is no reasonably intense band in the 150–500-cm^{-1} frequency region that cannot be assigned with confidence to either the anion or the cation. Therefore, the Xe···F bridge modes are of either relatively low frequency or relatively low intensity, or both, contrary to previous assignments.[22,23]

Conclusion. The fluoride ion donor properties and the nature of the Lewis acid adducts of XeO_2F_2 closely resemble those of XeF_2. This is not surprising in view of the fact that the structure

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of XeO_2F_2 can be derived from that of XeF_2 by replacing two free equatorial valence-electron pairs on xenon by two doubly bonded oxygen atoms.

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Registry No. $XeO_2F^+AsF_6^-$, 115117-21-0; $[FO_2XeFXeO_2F]^+AsF_6^-$, 13875-06-4; XeO_2F_2, 13875-06-4; AsF_5, 7784-36-3.

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Potentiometric Determination of the Stabilities of Cobalt(II) Complexes of Polyamine Schiff Bases and Their Dioxygen Adducts

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Potentiometric measurement of hydrogen ion concentration, previously employed for the determination of oxygenation constants of cobalt(II) complexes in aqueous and mixed aqueous solvents, is now extended to the determination of equilibrium constants for Schiff base ligands and for the determination of oxygenation constants for systems in which the ligands and/or their metal complexes are not completely formed in the absence of dioxygen or in the absence of the cobalt(II) ion. The method is illustrated by the potentiometric measurement of oxygenation constants for solutions in 70% dioxane–30% water (v/v) containing cobalt(II) chloride and the following ligand components: 1, salicylaldehyde and *N*,*N*′-bis(2-aminoethyl)dipicolinic acid diamide; 2, salicylaldehyde and *N*,*N*-bis(2-aminophenyl)methylamine; 3, salicylaldehyde, ethylenediamine, and 4-methylpyridine; and 4, 3-fluorosalicylaldehyde, *o*-phenylenediamine, and 4-methylpyridine. The stability constant and dioxygen affinity are also reported for the cobalt(II) complex of a pentadentate ligand, *N*,*N*-bis(2-((2-hydroxybenzyl)amino)phenyl)methylamine, produced by hydrogenation of the Shiff base formed from salicylaldehyde and *N*,*N*-bis(2-aminophenyl)methylamine. The equilibrium parameters obtained provide all the information necessary to calculate the concentrations of all molecular species present in solution at 25.00 °C and 0.100 M ionic strength as a function of p[H] and solution composition. The results are displayed for each system as distribution curves consisting of species concentration profiles vs p[H] at specific concentrations of solution components.

Introduction

The potentiometric determination of hydrogen ion concentration has long been the technique most frequently employed for the determination of metal ion–ligand stability constants.[1] It is also one of the more accurate techniques for that purpose because of improved methods of data processing and the development of improved equipment for the measurement of hydrogen ion concentration. The application of the method to complex formation requires a mobile equilibrium involving dependence of degree of complex formation on hydrogen ion concentration, under conditions such that the concentrations of all species involved in the equilibrium may be determined accurately. During the past decade, this method has also been employed for the determination of dioxygen affinities (oxygenation equilibrium constants) of cobalt complexes of polyamines, amino acids, and related complexes.[2] Although the oxygenation reaction itself does not usually involve hydrogen ion displacement, dioxygen reacts only with the metal ion complex itself, thus producing a shift of prior hydrogen ion dependent equilibria, so that hydrogen ion concentration is sensitive to the degree of oxygenation.

More recently, it has become apparent that the potentiometric method may be extended one step further—the determination of oxygenation constants of metal complexes that are not formed at all, or not fully formed, in the absence of dioxygen. This experimental technique has now been extended one step further—the determination of oxygenation constants of cobalt(II) complexes for which even the ligand itself is not completely formed in the absence of dioxygen. Several examples of this type of reaction, involving salicylaldehyde–polyamine type Schiff bases, have recently been studied in this laboratory, and several examples of such systems are now presented for the first time in this paper.

Because of the nature of the compounds involved, it was not possible to study these compounds in aqueous systems. The organic components of the ligands, as well as the ligands themselves, are not soluble in water but are soluble in mixtures of water with compatible low dielectric constant solvents such as dioxane and tetrahydrofuran. The water–dioxane system was thoroughly investigated as a medium for potentiometric hydrogen ion concentration measurement up to 70% v/v dioxane by Van Uitert et al.[3] The only previous report of the use of the potentiometric method for the determination of Schiff base formation and cobalt dioxygen complex formation is a paper by Motekaitis et al.[4]

In addition to the improved solubility of the aromatic aldehyde components of the systems under investigation, an advantage of using the dioxane–water mixed solvent lies in the favorable reduction in the dielectric constant of the medium relative to pure water, resulting in more complete formation of the Schiff base. A further advantage is its compatibility with the standard glass electrode (both theoretically and practically) so that the required p[H] measurements may be carried out in a manner similar to that employed in purely aqueous systems.

Experimental Section

Dipicolinic Acid Dimethyl Ester. A 16.7-g (0.100-mol) sample of dipicolinic acid (Aldrich), 100 g of anhydrous methanol (MC/B), and 3.0 g (0.030 mol) of 98% sulfuric acid (Baker) were placed in a flask fitted with a reflux condenser, a magnetic stirrer, and a drying tube. H_2SO_4 was added last, through the condenser. After 2-h reflux, about one-fourth of the volume was evaporated off and the solution was allowed to cool, whereupon a colorless crystalline product was isolated: mp 125–128 °C, 12.2 g (62%). Additional material to a total of 90% was obtained from the mother liquor (lit.[5] mp 121 °C). ^{1}H NMR ($CDCl_3$), δ: 4.04 (6 H, CH_3); 8.40 (3 H, m, pyridyl).

Preparation of *N*,*N*′-Bis(2-aminoethyl)dipicolinic Acid Diamide Schiff Base. A 9.8-g (0.050-mol) sample of dimethyl 2,6-pyridinedicarboxylate and 50.0 mL (45 g, 0.75 mol) (1:15) of ethylenediamine were refluxed in an Ascarite-protected flask. Two-hour reflux was followed by 10-h storage at room temperature. The reaction mixture was diluted with methanol, filtered, and stored at 0 °C. All volatile materials were then removed by vacuum distillation. The residual oil was found by titration to be nearly pure diamide. ^{1}H NMR ($CDCl_3$), δ: 3.80 (4 H, sharp multiplet, CH_2NH_2); 7.3 and 6.9 (t's, 4 H, CH_2NHCO, syn and anti); 8.30 (m, 3 H, pyridyl).

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