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ON THE SYNTHESES OF XENON(VI) FLUOROPLUMBATES(IV) AND FLUOROSTANNATES(IV)

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SUMMARY

The new xenon(VI) fluorometallates $4XeF_6.PbF_4$, $3XeF_6.4PbF_4$, $XeF_6.4PbF_4$, $4XeF_6.3SnF_4$, $3XeF_6.4SnF_4$ and $XeF_6.4SnF_4$ have been isolated and characterized.

On the basis of Raman and infrared spectra the 4:1 compounds can be confidently formulated as $(Xe_2F_{11}^+)$ salts, while the 1:4 compounds are XeF_5^+ salts with polymeric anions. The 4:3 and 3:4 compounds are apparently intermediate compounds with both $Xe_2F_{11}^+$ and XeF_5^+ cations present.

INTRODUCTION

Of the reactions of xenon hexafluoride with Group IVa fluorides, only those of germanium and tin tetrafluorides have so far been reported [1,2]. The analogous reaction with lead tetrafluoride, however, has not been studied, although taking into consideration the increasing stability of xenon(VI) fluorometallates(IV) along the group IV fluorides, the existence of xenon(VI) fluoroplumbates(IV) seemed to be quite likely. Indeed, we found that the reaction of excess of xenon hexafluoride with lead difluoride yields three new compounds, $4XeF_6.PbF_4$, $3XeF_6.4PbF_4$ and $XeF_6.4PbF_4$. In addition, the system XeF_6 - SnF_4 was re-investigated and a whole set of new compounds ($4XeF_6.3SnF_4$, $3XeF_6.4SnF_4$, $XeF_6.4SnF_4$) was isolated and characterized, in addition to the known $4XeF_6.SnF_4$.

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RESULTS AND DISCUSSION

To favour the formation of xenon hexafluoride rich complexes, we set out by treating lead difluoride and tin difluoride with a large excess of liquid xenon hexafluoride. Xenon hexafluoride oxidized Pb(II) and Sn(II) forming xenon(VI) fluoroplumbate(IV) and fluorostannate(IV):

$$MF_2 + nXeF_6 \xrightarrow{60^\circ C} 4XeF_6.MF_4 + XeF_4 + (n-5)XeF_6$$

M = Pb, Sn

Removal of the excess of xenon hexafluoride and the xenon tetrafluoride formed yielded Pb(IV) and Sn(IV) salts, $(Xe_2F_{11}^+)_2MF_6^{2-}$, which were also prepared using other starting materials such as the tetrafluorides, oxides, and ammonium or hydrazinium fluorometallates.

The adducts $4XeF_6.MF_4$ (M = Pb, Sn) lose xenon hexafluoride under vacuum at elevated temperatures, yielding xenon(VI) fluoroplumbates(IV) and fluorostannates(IV) with a mole ratio $4 > XeF_6/MF_4 \geqslant 0.25$. Treatment of these complexes with excess of liquid xenon hexafluoride at 60°C again yielded $4XeF_6.MF_4$.

Xenon(VI) fluoroplumbates(IV) and fluorostannates(IV) are white solids at room temperature with negligible vapour pressure. They are extremely sensitive to traces of moisture and their reaction with water is vigorous. In the presence of traces of moisture, xenon(VI) fluoroplumbates(IV) turn immediately from white to yellow then brown and finally dark brown consistent with hydrolysis.

The vibrational spectra of xenon(VI) fluoroplumbates(IV) and fluorostannates(IV) were assigned by comparison with earlier data. As may be seen from the Raman data given in Table 1, the complexes $4XeF_6.PbF_4$ and $4XeF_6.SnF_4$ contain essentially the same cation as $(Xe_2F_{11}^+)_2PdF_6^{2-}$ [3] and may, therefore, be confidently formulated as $(Xe_2F_{11}^+)_2PbF_6^{2-}$ and $(Xe_2F_{11}^+)_2SnF_6^{2-}$.

Infrared and Raman data indicate that $XeF_6.4PbF_4$ and $XeF_6.4SnF_4$ are XeF_5^+ salts (Table 2), the plausible anion being the fluorine bridged polymer $(M_4F_{17})_x^{x-}$.

TABLE 1

Vibrational spectra (cm^{-1}) of $4XeF_6.MF_4$ (M = Pb, Sn, Pd)

	$4XeF_6.PbF_4$		$4XeF_6.SnF_4$		$4XeF_6.PdF_4$ [a]	Assignment
	R	IR	R	IR	R	
Cation lines						$Xe_2F_{11}^+$
	664 (m) 650 (vs)	663 (sh) 650 (sh)	674 (w) 657 (vs)	672 (sh)	668 (w) 651 (vs)	ν XeF_{ax}
	630 (m) 620 (m-s)	633 (sh) 616 (vs)	638 (w) 629 (m) 617 (vw)	640 (s) 617 (vs)	630 (m)	$\nu_{deg}XeF_4$
	607 (sh) 600 (m)		608 (sh) 602 (sh) 599 (w)	605 (sh) 597 (sh)	615 (w) 610 (m) 606 (w)	$\nu_{as}XeF_4$
	585 (s) 574 (s) 571 (sh)	594 (sh) 577 (m)	b	578 (w-m)	591 (s) 583 (m)	$\nu_s XeF_4$
	405 (w)	410 (w)	416 (w)	412 (m)	412 (vw) 396 (vw)	δF_4XeF
	365 (w)		372 (w)		375 (w)	
	302 (w)		311 (w)		296 (w)[b]	$\delta_s XeF_4$
	245 (sh)		267 (w)		270 (w)[b]	$\delta_s XeF_4$ (in plane)
Anion lines						MF_6^{2-}
	539 (s)		578 (vs)		568 (s)	ν_1
		503 (sh) 473 (vs)		550(w-m)(sh) 530 (vs)		ν_3
	228 (w)		458 (w)		546 (w)	ν_2
					245 (w)[b]	ν_5

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[a] K. Leary, A. Zalkin and N. Bartlett, Inorg. Chem., 13, 775 (1974)

[b] Obscured by anion feature

TABLE 2

Vibrational spectra (cm^{-1}) of $XeF_6.4MF_4$ (M = Pb, Sn)

	$XeF_6.4PbF_4$		$XeF_6.4SnF_4$		Assignment
	R	IR	R	IR	
Cation lines					XeF_5^+
	675 (m)		680 (m)	680 (sh)	ν_1
	667 (m)	666 (vs)	669 (sh)	664 (vs)	ν_7
		643 (s)		635 (vw)	
	621 (m-s)	616 (w)	620 (m)	616 (w)	ν_2
	612 (m-s)		610 (s)		ν_4
	408 (w)	420 (w)	404 (w)		ν_8
	291 (w-m)		298 (w)		ν_3
	232 (w)		235 (vw)		ν_5
Anion lines					M - F
			604 (vs)		
	562 (vvs)	565 (vs)		554 (vs)	
		536 (s)			
		511 (sh)			
	491 (w)	484 (vs)	490 (w)	495 (sh)	
	440 (w)	453 (sh)	435 (vw)		
	253 (w)				

$4XeF_6.3SnF_4$ does not have an analogous compound in the series of xenon(VI) fluoroplumbates(IV). The reason for this is probably the lower stability of xenon(VI) fluoroplumbates(IV) in comparison to xenon(VI) fluorostannates(IV). For example, $3XeF_6.4PbF_4$ can be prepared by pyrolysis of $4XeF_6.PbF_4$ at 45°C in vacuo, while the analogous tin compound can be prepared by pyrolysis of $4XeF_6.SnF_4$ at 105°C in vacuo. The spectra of the ($Xe_2F_{11}^+$) salts are very like those of the corresponding XeF_5^+ salts but the ($Xe_2F_{11}^+$) ion is characterized by 'bridge stretching' vibrations at ca. 360 cm^{-1} [4]. The adduct $4XeF_6.3SnF_4$ has a Raman line at 378 cm^{-1} (Table 3) which can most probably be attributed to the $Xe_2F_{11}^+$ cation. Infrared and Raman data indicate that $4XeF_6.3SnF_4$ is a salt containing both $Xe_2F_{11}^+$ and XeF_5^+, a plausible anion being the fluorine bridged polymer $(Sn_3F_{15})_x^{3x-}$ [5]. The tin atom is considered to be octahedrally coordinated to fluorine atoms (4 uniquely, 2 bridging).

TABLE 3

Vibrational spectrum (cm^{-1}) of $4XeF_6.3SnF_4$

	R	IR	Assignment
Cation lines			XeF_5^+
	655 (vs)		ν_1
	634 (w) 621 (w-m)	630 (vs)	ν_7
	a	583 (sh)	ν_2
	580 (sh)		ν_4
	422 (w)	420 (m)	ν_8
	378 (w)		
	307 (w)		ν_3
	286 (w)		ν_6
Anion lines			Sn - F
	590 (vs)		
	568 (s)	568 (sh)	
		535 (vs)	
	490 (w)	484 (w)	
	446 (m)	457 (vw)	
	268 (vw)		

[a] Obscured by anion feature

$3XeF_6.4PbF_4$ has a shoulder at 370 cm^{-1}, while the analogous tin compound has a Raman line at 369 cm^{-1}, thus again suggesting the possible presence of $Xe_2F_{11}^+$ as well as XeF_5^+ (Table 4). A plausible anion is the fluorine bridged octamer $M_8F_{36}^{4-}$, or a puckered sheet polymer, $(M_4F_{18})_x^{2x-}$ [6]. In each case each metal atom is considered to be octahedrally coordinated to the fluorine atoms (3 uniquely, 3 bridging).

The X - ray diffraction patterns of $3XeF_6.4PbF_4$ and analogous $3XeF_6.4SnF_4$ are similar thus,confirming the presence of $Xe_2F_{11}^+$ cation also in the lead compound. Namely, the Raman spectrum of $3XeF_6.4PbF_4$ has no very significant feature for $Xe_2F_{11}^+$ cation.

TABLE 4

Vibrational spectra (cm^{-1}) of $3XeF_6.4MF_4$ (M = Pb, Sn)

	$3XeF_6.4PbF_4$		$3XeF_6.4SnF_4$		Assignment
	R	IR	R	IR	
Cation lines					XeF_5^+
	655 (vs)	660 (sh)	648 (vs)	666 (sh)	ν_1
		641 (vs)	643(vw,sh)	645 (vs)	ν_7
	635 (sh)	634 (sh)		625 (sh)	
		614 (sh)			
	605 (sh)		618 (sh)		ν_4
	595 (s)	597 (sh)	[a]		ν_2
	417 (w)	420 (m)	416 (w)	420 (m-s)	ν_8
	392 (w-m)				
	370 (sh)		369 (w)		
	300 (w)		302 (w-m)		ν_3
	230 (w)		235 (w)		ν_5
Anion lines					M - F
	560 (vvs)	567 (sh)	593 (vvs)		
		543 (sh)		570 (vs)	
	520 (vw)		520 (w)	535 (sh)	
		498(vs,vb)	500 (w)		
	465 (w)	470 (sh)	461(m)		
	437 (sh)	453 (sh)			
	253 (w)				

[a] Obscured by anion feature

EXPERIMENTAL

General apparatus and techniques

The products were synthesized in argon-arc welded nickel pressure and weighing vessels, equipped with Teflon packed nickel valves. The volume of the reaction vessels was about 10^{-4} m^3. Vessels for manipulating solid materials were tested hydrostatically up to 20 MPa. Transfer of all materials was carried out either in the atmosphere of a dry box, or by distillation under vacuum in well dried apparatus.

Raman spectra were recorded using a Spex 1401 double monochromator instrument. As exciting radiation, the 514.5 nm line of an Ar^+ laser (Coherent Radiation) was used. Powdered samples were loaded into quartz capillaries in a dry box and temporarily plugged with Kel-F grease. They were sealed with a small flame outside the dry box.

Infrared spectra were recorded using a Zeiss UR-20 spectrometer. A 10 cm path length nickel cell with silver chloride windows (A.D. McKay, Inc.) was used for gas phase work. Spectra of the solids were obtained by dusting samples onto silver chloride plates which were later sandwiched in a leak-tight brass holder.

X-ray powder photographs were obtained by the Debye-Scherrer method on an ENRAF apparatus (Delft, Holland) using graphite monochromated CuK_α radiation. Finely powdered samples were sealed in 0.5 mm thin-walled quartz capillaries.

Reagents

Lead(II) fluoride was prepared by the reaction between lead(II) oxide and excess of hydrogen fluoride at 110°C. The last traces of hydrogen fluoride were pumped off at 140 - 150°C. Chemical analysis of lead(II) fluoride: Calcd. for PbF_2 : Pb, 84.50; F, 15.50. Found: Pb, 84.7; F, 15.5 %. Tin(II) fluoride, 99.99 %, was from Ventron Alfa Products (ultrapure).

Xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride as catalyst at 120°C [7].

Preparation

The compounds $4XeF_6.MF_4$ (M = Pb, Sn) were prepared by reaction between the corresponding metal difluoride and excess of xenon hexafluoride at 60°C. After the reaction ceased, the excess of xenon hexafluoride and the xenon tetrafluoride formed were pumped away at room temperature.

The compound $4XeF_6.3SnF_4$ was prepared by pumping $4XeF_6.SnF_4$ in dynamic vacuum at 40°C. The compounds $3XeF_6.4MF_4$ (M = Pb, Sn) were prepared by pumping $4XeF_6.3SnF_4$ in a dynamic vacuum at 105°C and by pumping $4XeF_6.PbF_4$ in dynamic vacuum at 45°C.

The compounds $XeF_6.4MF_4$ (M = Pb, Sn) were prepared by pumping $3XeF_6.4MF_4$ in dynamic vacuum at 80°C in the case of lead, or at 155°C in the case of tin. The stoichiometry of the reactions was also followed by weighing the reactants and products with an accuracy of ± 1 mg throughout the experiments (Table 5).

TABLE 5

Mass analysis of xenon(VI) fluorostannates(IV) and fluoroplumbates(IV)

Compound	Mass of MF_2 (g)	Mass of the product		Difference (%)
		Calcd.(g)	Found (g)	
$4XeF_4.SnF_4$	0.4844	3.6352	3.5983	1.0
$4XeF_6.3SnF_4$	0.4478	1.4911	1.4721	1.3
$3XeF_6.4SnF_4$	0.4478	1.0822	1.0773	0.5
$XeF_6.4SnF_4$	0.4019	0.6567	0.6490	1.2
$4XeF_6.PbF_4$	0.9268	4.7793	4.7406	0.8
$3XeF_6.4PbF_4$	0.9268	1.7658	1.7636	0.1
$XeF_6.4PbF_4$	0.9906	1.3919	1.3815	0.7

The xenon(VI) fluoroplumbates(IV) and fluorostannates(IV) obtained were examined by X-ray powder photography, Raman and infrared spectroscopy and were chemically analysed (Table 6 and Table 7).

TABLE 6

Chemical analyses of xenon(VI) fluoroplumbates(IV)

	% Pb		% F	
	Calcd.	Found	Calcd.	Found
$4XeF_6.PbF_4$	16.39	16.5	42.08	42,6
$3XeF_6.4PbF_4$	44.35	44.4	34.57	35.0
$XeF_6.4PbF_4$	60.14	60.0	30.33	30.3

TABLE 7

Chemical analyses of xenon(VI) fluorostannates(IV)

	% Sn		% F	
	Calcd.	Found	Calcd.	Found
$4XeF_6.SnF_4$	10.09	10.0	45.24	45.2
$4XeF_6.3SnF_4$	22.75	22.5	43.70	43.5
$3XeF_6.4SnF_4$	31.34	31.4	42.65	42.5
$XeF_6.4SnF_4$	46.36	46.4	40.82	40.7

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