Thermochimica Acta, 142 (1989) 49–57
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS AND CHARACTERIZATION OF NEW HYDRAZINIUM-(2 +) AND HYDRAZINIUM(1 +) HEXAFLUOROPHOSPHATES AND HYDRAZINIUM(1 +) HEXAFLUOROARSENATE

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(Received 31 May 1988)

ABSTRACT

The reaction between hydrazinium difluoride and excess phosphorus pentafluoride in anhydrous hydrogen fluoride yields $N_2H_6(PF_6)_2$. This is unstable at room temperature and decomposes slowly by releasing hydrogen fluoride and phosphorus pentafluoride. The thermal decomposition in a thermoanalyser proceeds through the intermediates $N_2H_5PF_6$ and NH_4PF_6 to the gaseous components. $N_2H_6(PF_6)_2$ and the intermediates were characterized by their vibrational spectra.

The reaction of hydrazinium(2+) hexafluoroarsenate with hydrazine hydrate yields $N_2H_5AsF_6$; this was also investigated using thermal analysis and vibrational spectra.

The X-ray powder photographs of the new complexes $N_2H_5PF_6$ and $N_2H_5AsF_6$ were indexed on the basis of an orthorhombic cell.

INTRODUCTION

The great interest in hexafluorophosphates is primarily associated with organic compounds which are mainly applied in catalysis, especially photopolymerization. Among the inorganic hexafluorophosphates, $LiPF_6$ and KPF_6 are important as electrolytes in lithium anode batteries. Hexafluorophosphoric acid and its salts are also useful as herbicidal agents.

The soluble, stable organic and inorganic hexafluorophosphates can be prepared by the reaction of hexafluorophosphoric acid with the appropriate base [1]. Another route is the reaction of the metal chloride and PCl_5 with anhydrous HF [2]. Fluorination of the metal or metal chloride and an excess of phosphoric oxide with bromine trifluoride can also be used [3]. Patent literature describes the preparation of the PF_6^- salts by heating a mixture of alkali metal fluoride, elemental phosphorus and anhydrous HF at 180–200 ° C under pressure [4].

0040-6031/89/$03.50

For a synthesis of $N_2H_6(PF_6)_2$, reaction between $N_2H_6F_2$, a stoichiometric amount of P_2O_5 and anhydrous HF in a KelF reaction tube was employed initially. The compound isolated was wet contaminated by the products of hydrolysis of the PF_6^- ion and by H_3PO_4. Therefore, the reaction between $N_2H_6F_2$ and excess PF_5 in anhydrous HF as solvent was used in this study for the preparation of $N_2H_6(PF_6)_2$. This type of reaction was reported initially by Kemmitt et al. [5] for the synthesis of pure $LiPF_6$.

$N_2H_5PF_6$ was obtained as the first step intermediate in the thermal decomposition of $N_2H_6(PF_6)_2$. Several $N_2H_5^+$ compounds which cannot be prepared by direct reactions have been produced in this way [6–8].

Previously, $N_2H_6(AsF_6)_2$ has been prepared and characterized [9]; however, a study of its thermal decomposition has revealed that it decomposes directly to $N_2H_6F_2$ without any intermediate compound. Therefore, the reaction between $N_2H_6(AsF_6)_2$ and $N_2H_4 \cdot H_2O$ was used for the preparation of a new complex, $N_2H_5AsF_6$.

EXPERIMENTAL

Phosphorus pentafluoride was prepared by fluorination of P_2O_5 using elemental fluorine in a nickel can under pressure [10]. Anhydrous HF was purified by a conventional method [11].

For the preparation of $N_2H_6(PF_6)_2$ approximately 3 mmol of $N_2H_6F_2$ were loaded into a nickel reaction vessel. About 10 g of HF were distilled into the vessel and then PF_5 was added stepwise. The molar ratio $N_2H_6F_2 : PF_5$ was 1 : 10. The product was isolated after the volatiles had distilled off at 0 ° C.

$N_2H_5PF_6$ was isolated by decomposition of 200 g of $N_2H_6(PF_6)_2$ in a Mettler thermoanalyser at 75 ° C.

$N_2H_6(AsF_6)_2$ was reacted with an excess of hydrazine hydrate and, after the evaporation of volatiles, $N_2H_5AsF_6$ was isolated.

Hydrazine was determined potentiometrically by potassium iodate titration [12], and ammonium by a Kjeldahl method [13].

Thermal analysis was carried out using a Mettler TA 1 thermoanalyser. The heating rate was $1° C\ min^{-1}$, and the reference sample was α-Al_2O_3. The decomposition was run in a dry argon atmosphere with a flow rate of $5\ l\ h^{-1}$. The DTG range was $10\ mg\ min^{-1}$ and the DTA range was 100 or 200 μV.

IR spectra of powdered $N_2H_6(PF_6)_2$ pressed between AgCl windows were obtained using a Zeiss UR-20 spectrometer. The solid was prepared in a dry box. For the IR spectra of $N_2H_5PF_6$, NH_4PF_6, $N_2H_5AsF_6$ and NH_4AsF_6, CsBr plates and a Perkin–Elmer 521 spectrometer were employed. The Raman spectra of the samples in Pyrex tubes were recorded on a Spex 1401 instrument with a 5145 Å line Ar^+ laser (coherent radiation).

The X-ray powder diffraction data were obtained with a Debye–Scherrer-type camera and Cu *Kα* radiation. The X-ray diffraction photographs were indexed on the basis of a Haendler program [14].

RESULTS AND DISCUSSION

Phosphorus pentafluoride is a strong Lewis acid which gives a number of metal, non-metal and organic hexafluorophosphates [1]; many of them have actual and potential commercial applications. The PF_6^- salts with hydrazinium(2+) and hydrazinium(1+) have not been described previously; therefore we decided to investigate the system $N_2H_6F_2$–PF_5 in anhydrous HF as solvent. PF_5 is only slightly soluble in anhydrous HF in the absence of bases; it reacts with $N_2H_6F_2$ giving a complex $N_2H_6(PF_6)_2$. The product is stable at 0 °C but releases PF_5 and HF at room temperature. It is unstable in air and has to be prepared for thermal analysis and vibrational spectroscopy in a dry box. Before commencing its decomposition on a Mettler thermoanalyser, it was estimated that it lost approximately 19% of its starting weight.

The thermal decomposition of $N_2H_6(PF_6)_2$ is given in Fig. 1. Up to 75 °C the sample loses 36.6% of its weight. The decomposition is endothermic with DTA peaks at 36, 40 and 55 °C, and DTG minima at 35, 41 and 63 °C. The first intermediate is $N_2H_5PF_6$ for which the calculated weight loss amounts to 45.05%. In the next step between 75 and 185 °C the sample loses a further 5.8% of its weight and the second intermediate NH_4PF_6 is formed (theoretical weight loss is 4.64%). This step is exothermic with a DTA peak and a DTG minimum at 182 °C. In the last step up to 330 °C the sample is decomposed to the gaseous components without a residue. In this endothermic step with a DTA peak and a DTG minimum at 295 °C, the sample loses 49.2% of its weight (theoretical weight loss is 50.31%).

$N_2H_6(PF_6)_2$ decomposes according to the equations

$$N_2H_6(PF_6)_2 \xrightarrow{25\text{–}75\,°C} N_2H_5PF_6 + HF + PF_5 \tag{1}$$

$$N_2H_5PF_6 \xrightarrow{75\text{–}185\,°C} NH_4PF_6 + 0.5N_2 + 0.5H_2 \tag{2}$$

$$NH_4PF_6 \xrightarrow{185\text{–}330\,°C} PF_5 + HF + 0.5N_2 + 1.5H_2 \tag{3}$$

Comparison of the thermal decomposition of $N_2H_6(AsF_6)_2$ [9] with that of $N_2H_6(PF_6)_2$ shows that they are different with respect to both thermal stability and thermal behaviour: the former is stable up to 68 °C and loses all its arsenic pentafluoride in the first step giving $N_2H_6F_2$ which decomposes further; the latter decomposes through its $N_2H_5^+$ and NH_4^+ salts. The different behaviour is probably a reflection of the different strengths of the hydrogen bonds of the type N–H · · · F in these structures. In the crystal

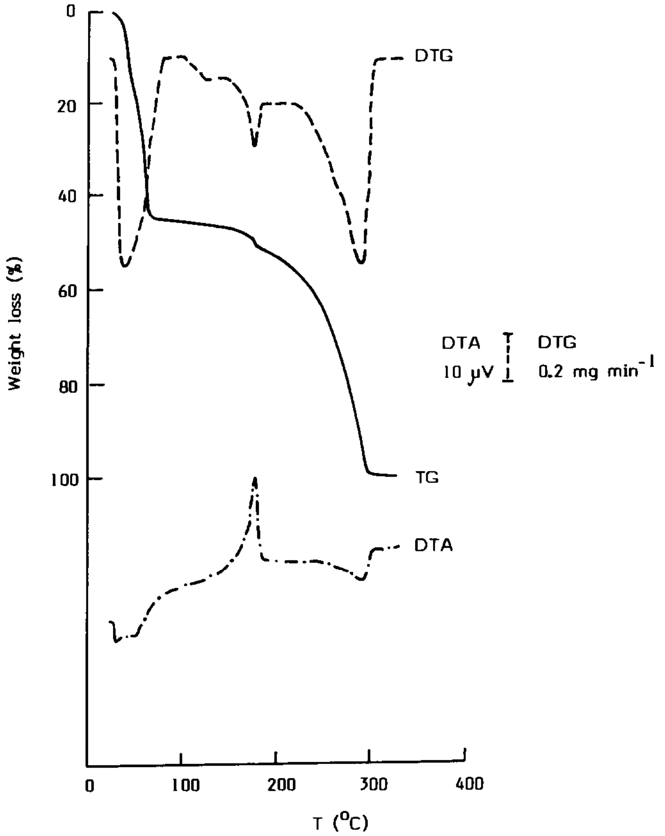

Fig. 1. TG, DTG and DTA curves of $N_2H_6(PF_6)_2$.

structures of the $N_2H_6^{2+}$ fluorometalates [15–19] it has been found that the hydrogen bonds, single or polyfurcated, form a three-dimensional network which holds together the $N_2H_6^{2+}$ and fluorometalate units.

Chemical analysis of the products gives $N_2H_6(PF_6)_2$: N_2H_4 found, 10.0%; N_2H_4 calculated, 9.89%; $N_2H_5PF_6$: N_2H_4 found, 17.9%; N_2H_4 calculated, 18.00%; NH_4PF_6: NH_4 found, 10.6%; NH_4 calculated, 11.07%.

In the absence of any indication of the existence of $N_2H_5AsF_6$ derived from the thermal decomposition of $N_2H_6(AsF_6)_2$, we performed the reaction between the $N_2H_6^{2+}$ salt and hydrazine hydrate. This is also a useful method for the preparation of $N_2H_5^+$ compounds [20]. $N_2H_5AsF_6$ is stable in air and its thermal behaviour was investigated.

The thermal decomposition of $N_2H_5AsF_6$ begins at 185 °C (Fig. 2). In the first step up to 248 °C the sample loses 22.0% of its weight; the gaseous components N_2, H_2, HF and AsF_5 are released (calculated weight loss is 22.30%) and the intermediate product is NH_4AsF_6 (NH_4 found, 14.4%; calculated for NH_4AsF_6: NH_4, 14.44%). This step is accompanied by an endothermic DTA peak at 215 °C, exothermic DTA peaks at 222 and

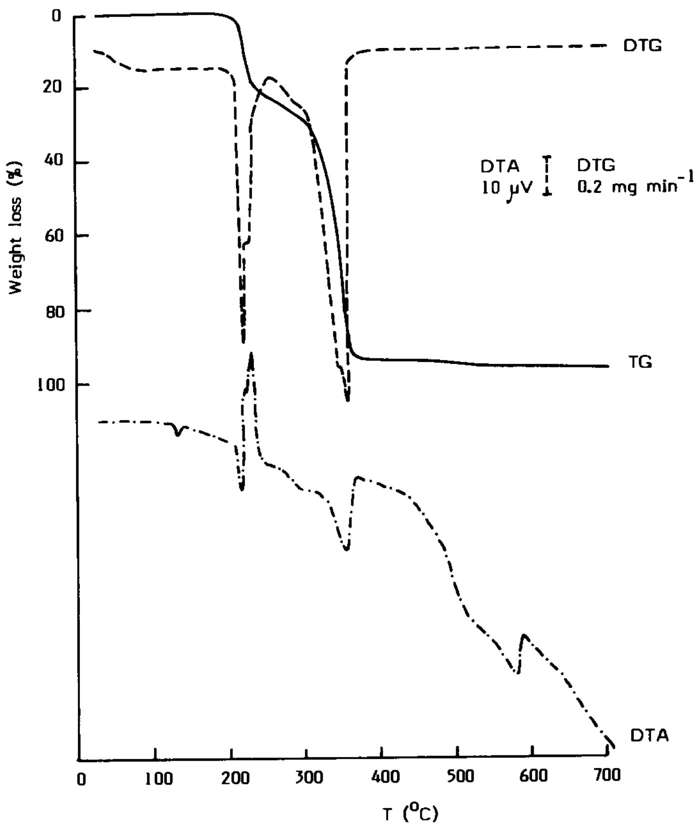

Fig. 2. TG, DTG and DTA curves of $N_2H_5AsF_6$.

230 °C and DTG minima at 221 and 230 °C. With increasing temperature, a complete decomposition occurs yielding gaseous products. Up to 700 °C the decomposition is endothermic with a DTA peak at 357 °C and minima in the DTG curve at 350 and 359 °C.

The thermal decomposition of $N_2H_5AsF_6$ can be described in terms of the following equations

$$6N_2H_5AsF_6 \rightarrow 5NH_4AsF_6 + AsF_5 + HF + 3.5N_2 + 4.5H_2 \tag{4}$$

$$NH_4AsF_6 \rightarrow AsF_5 + HF + 0.5N_2 + 1.5H_2 \tag{5}$$

Chemical analysis of the products gives $N_2H_5AsF_6$: N_2H_4 found, 14.4%; N_2H_4 calculated, 14.44%; NH_4AsF_6: NH_4 found, 8.4%; NH_4 calculated, 8.72%.

The vibrational spectra of $N_2H_6(PF_6)_2$ and $N_2H_5PF_6$ are given in Table 1.

The PF_6^- ion has the phosphorus present as an sp^3d^2 hybrid. An isolated octahedral PF_6^- ion (O_h point group) has six fundamental frequencies: ν_1 (745–780 cm^{-1}), ν_2 (550–580 cm^{-1}) and ν_5 (460–480 cm^{-1}) are Raman

TABLE 1

Vibrational spectra (cm^{-1}) of hexafluorophosphates

$N_2H_6(PF_6)_2$		$N_2H_5PF_6$		NH_4PF_6		Assignment
R	IR	R	IR	R	IR	
168(33.6)				318(10)		
			389w	382(50)	401w	
			447w			
474(25)		468(20.5)	467w	478(27.7)	499sh	$\nu_5(PF_6^-)$
	562m	555(5.2)	550vs		550vs	$\nu_4(PF_6^-)$
576(12.6)		574(10)		572(10)		$\nu_2(PF_6^-)$
662(12.6)						
748(100)		746(100)	739m	748(100)	730s	$\nu_1(PF_6^-)$
	840s		811vs		835s	$\nu_3(PF_6^-)$
			958m			$(N-N)_s$
972(2.4)	980w	971(20.5)	970m			
1046(17)						
			1082m			$(NH_3^+)_r$
		1098(7.6)	1097m			
1120(24)	1105m	1124(7.6)	1122w			
			1148w			
	1240w		1235w			
			1298w			
			1358m			$(NH_2)_r$
			1371s			
		1476(5.8)				
1522(8.4)	1540m	1542(5.8)	1531vs			$(NH_3^+)_d$
1608(14)	1602m		1595vs			
		1613(9.3)	1611m			
1628(14.7)		1634(10.5)	1630m			
					3122w	$\nu_3(NH_4^+)$
					3148w	
				3240(20)	3248w	

active, ν_3 (835–880 cm^{-1}) and ν_4 (550–570 cm^{-1}) are IR active and ν_6 is inactive in both the Raman and IR.

The vibrational data for all three PF_6^- salts are in accordance with the published data for the cations $N_2H_6^{2+}$, $N_2H_5^+$ [21] and NH_4^+ [22], and for the anionic part of the spectrum [23]. The weak bond at 972 cm^{-1} in the Raman and the absorption at 980 cm^{-1} in the IR spectrum of $N_2H_6(PF_6)_2$ (which are characteristic of the N–N stretching vibration of the $N_2H_5^+$ ion) are a consequence of the decomposition of the sample during its handling in the dry box.

The vibrational spectra of $N_2H_5AsF_6$ and NH_4AsF_6 are given in Table 2.

The AsF_6^- ion also has O_h symmetry with six fundamental frequencies: IR active ν_3 (690–710 cm^{-1}) and ν_4 (380–400 cm^{-1}), Raman active ν_1

TABLE 2

Vibrational spectra (cm^{-1}) of $N_2H_5AsF_6$ and NH_4AsF_6

$N_2H_5AsF_6$		NH_4AsF_6		Assignment
IR	R	IR	R	
	118(3)			
287w		288w		
374vs	374(26)	375vs	361(40)	$\nu_5(AsF_6^-)$
402m				
464m				
	587(10)		553(30)	$\nu_2(AsF_6^-)$
683vs	691(100)	688sh	679(100)	$\nu_1(AsF_6^-)$
708vs	715(6)			$\nu_3(AsF_6^-)$
809m				
942vs				$(N-N)_s$
961sh	974(14)	958m		
1082vs	1092(2)			$(NH_3^+)_r$
1135sh	1122(4)	1143m		
1222m	1228(1)			
	1421(2)			$(NH_2)_r$
1483s				
	1543(1)			$(NH_3^+)_d$
1590m	1603(2)			
1610m	1618(4)			
	1641(5)			$(NH_2)_d$
			3140(30)	$\nu_3(NH_4^+)$
		3322m		

TABLE 3

X-ray powder diffraction data for $N_2H_5PF_6$

h k l	$d_{calcd.}$	$d_{obs.}$	*I*	*h k l*	d_{calcd}	d_{obs}	*I*
0 1 0	5.90	5.86	m	2 1 1	2.260	2.233	w
1 0 0	5.14	5.14	s	2 0 2	2.158	2.168	w
1 0 1	4.32	4.27	vs	2 2 0	1.938	1.947	m
0 0 2	3.97	3.87	s	2 2 1	1.883	1.885	m
1 1 0	3.87	3.77	s	—	—	1.810	w
1 1 1	3.48	3.50	s	3 1 0	1.646	1.640	w
0 1 2	3.29	3.34	m	1 3 3	1.509	1.510	w
1 0 2	3.14	3.13	m	3 2 0	1.482	1.487	w
0 2 0	2.95	2.98	s	0 4 0	1.475	1.469	w
2 0 1	2.446	2.466	w	3 0 3	1.439	1.443	w
0 1 3	2.415	2.411	w	0 3 4	1.397	1.401	vw
1 0 3	2.354	2.349	w	3 2 2	1.388	1.386	vw

Indexed on the basis of an orthorhombic cell with $a = 5.14(1)$ Å, $b = 5.90(2)$ Å, $c = 7.94(3)$ Å and $V = 241$ Å^3.

TABLE 4

X-ray powder diffraction data for $N_2H_5AsF_6$

h k l	$d_{calcd.}$	$d_{obs.}$	*I*	*h k l*	$d_{calcd.}$	d_{obs}	*I*
0 1 0	6.06	5.95	w	0 3 1	1.958	1.943	w
1 0 0	5.21	5.22	s	2 2 1	1.918	1.918	w
1 0 1	4.36	4.34	vs	1 3 1	1.833	1.841	w
0 0 2	3.98	3.95	m	3 0 0	1.738	1.744	w
1 1 0	3.95	4.00	m	1 3 2	1.703	1.705	vw
1 1 1	3.54	3.56	m	3 1 0	1.670	1.669	w
0 1 2	3.33	3.40	w	1 3 3	1.536	1.537	vw
1 0 2	3.16	3.18	w	0 4 0	1.515	1.516	vw
0 2 0	3.03	3.03	m	0 4 1	1.489	1.495	vw
1 1 2	2.80	2.74	vw	1 1 5	1.476	1.470	vw
1 2 0	2.62	2.57	vw	3 0 4	1.308	1.308	vw
2 1 0	2.394	2.382	w	0 1 6	1.295	1.295	vw
1 1 3	2.202	2.202	w	1 4 3	1.276	1.276	vw
2 2 0	1.976	1.976	w	1 1 6	1.257	1.259	vw

Indexed on the basis of an orthorhombic cell with $a = 5.21(1)$ Å, $b = 6.06(1)$ Å, $c = 7.95(2)$ Å and $V = 251$ Å^3.

(680–695 cm^{-1}), ν_2 (570–590 cm^{-1}) and ν_5 (370–390 cm^{-1}) and inactive ν_6. The vibrational spectra of $N_2H_5AsF_6$ and NH_4AsF_6 are assigned to $N_2H_5^+$, NH_4^+ and AsF_6^- according to the literature [21–23].

The X-ray powder diffraction data for $N_2H_5PF_6$ and $N_2H_5AsF_6$ are given in Tables 3 and 4. Both are indexed on the basis of an orthorhombic cell with the cell parameters $a = 5.14(1)$, $b = 5.90(2)$ and $c = 7.94(3)$ Å for $N_2H_5PF_6$ and $a = 5.21(1)$, $b = 6.06(1)$ and $c = 7.95(2)$ Å for $N_2H_5AsF_6$.

ACKNOWLEDGEMENTS

We thank Miss B. Sedej for chemical analysis. This work was financed through the Research Community of Slovenia.

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