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Synthesis and studies on pyridinium pentafluorozirconate and pyridinium oxotetrafluoroniobate

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Abstract

Pyridinium pentafluorozirconate, $(C_5H_5NH)ZrF_5$, and pyridinium oxotetrafluoroniobate, $(C_5H_5NH)NbOF_4$, have been synthesised by the reaction of pyridinium poly(hydrogen fluoride), PPHF, with $ZrOCl_2$ and Nb_2O_5, respectively. These new complexes have been characterised by chemical analysis, thermal analysis, X-ray diffraction and infrared spectra.

Introduction

PPHF is a good fluorinating and pyridinium salt-forming reagent as seen in its reaction with titanium tetrachloride [1]. In the present study it was of interest to see the extent of fluorination and complexation of pyridinium fluoride in the case of zirconium oxochloride and niobium oxide.

Experimental

Materials and methods

All reagents were AR/Analar grade. PPHF was prepared by mixing pyridine and HF in a molar ratio (3:7) [2] and stored at −5 °C in polyethylene bottles. Infrared spectra were recorded on a FTS-7 Bio-Rad spectrometer between 4000–400 cm^{-1} (KBr disc) and 600–200 in Nujol mulls between CsI discs. X-Ray diffractograms were recorded on a vertical goniometer Philips MDL PW 1050/70 diffractometer, using Cu $K\alpha$ and Co $K\alpha$ targets. Thermal analysis was carried out in air using a ULVAC SINKU-RICO TA1500 thermal analyser.

Synthesis

PPHF (30 ml) was introduced into a polyethylene flask fitted with a sodium fluoride guard tube (to absorb entrained HF vapour and avoid the entry of excess moisture) and the solution stirred with a Teflon-coated magnetic pellet. The reactant, PPHF, was cooled in an alcohol–liquid nitrogen slush bath (−10 °C to −20 °C). The compound [$ZrOCl_2 \cdot 8H_2O$ (8.0 g), Nb_2O_5 (7.5 g)] was added in small portions over a period of 10–15 min. After addition was complete, stirring was continued, the contents allowed to warm up to room temperature and stirred for a further 0.5 h. On completion of the reaction, two distinct zones had separated, the bottom containing a white precipitate and the top being liquid PPHF. The reactant solution was treated with chloroform in a polyethylene separating funnel, the bottom layer separating below the chloroform layer was treated with dried acetone. In the case of zirconium, it led to a white precipitate which settled rapidly and thus allowed the liquid above to be decanted. The precipitate thus obtained was washed several times with dry acetone to remove all traces of PPHF. In the case of niobium, the product was soluble in acetone in the presence of PPHF. Precipitation was achieved by use of an ether/acetone mixture (15:1 ratio) and the solid obtained was dried *in vacuo* and stored under nitrogen. The products [$pyHZrF_5$ (6.34 g) and $pyHNbOF_4$ (7.11 g); py = C_5H_5N] were soft white powders. The yields of the zirconium and niobium salts (based on the amounts of $ZrOCl_2 \cdot 8H_2O$ and Nb_2O_5 taken) were 96% and 95%, respectively. The niobium salt slowly changes colour to blue on exposure to air.

Characterisation

Analysis

The pyridine content was determined volumetrically [3], while the fluoride content was obtained using a fluoride ion selective electrode [4] (Orion model 94-09 with an Orion model 90-01 single junction reference) after hydrolysing the compound with boiling sodium hydroxide (2 mol l^{-1}).

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TABLE 1. Infrared vibrational frequencies for pyridinium pentafluorozirconate and pyridinium oxotetrafluoroniobate

Frequencies (cm^{-1})		Assignments
$pyHZrF_5$	$pyHNbOF_4$	
3298 (s); 3196 (m); 3151 (m); 3105 (s); 3082 (sh); 2995 (w); 2928 (w)	3262 (s); 3177 (s); 3082 (s); 2981 (m); 2924 (m)	C−H and N−H stretching vibrations
1636 (m); 1609 (s); 1542 (s); 1493 (s)	1636 (m); 1611 (s); 1540 (s); 1487 (s)	in-plane ring deformation, result of C=C and C=N interactions
1375 (w); 1337 (w); 1248 (w); 1200 (vw); 1174 (w); 1053 (w); 1025 (m)	1334 (w); 1249 (w); 1204 (w); 1172 (w); 1055 (w); 1020 (w)	aromatic in-plane hydrogen deformations
1000 (w); 884 (w)	998 (w)	C−H out-of-plane and ring vibrations
	797 (s)	ν_{Nb-O}
746 (vs); 674 (vs)	745 (s); 676 (s)	C−H out-of-plane and ring vibrations
600 (s); 516 (s) 442 (vs)	580 (s)	ν_{M-F}
319 (m); 232 (m)	316 (m); 246 (m)	δ_{M-F}

Thermal studies

During preliminary attempts to measure the melting points, it was found that these compounds decompose before melting. The thermogram of the zirconium compound showed that decomposition commenced at *c.* 225 °C with a major weight loss occurring at 365 °C; an endothermic peak and two further small endotherms indicate stepwise oxidation of zirconium fluoride to zirconium oxofluorides. A separate experiment showed that the initial decomposition (240 °C) corresponded to the loss pyridine and HF, as established from the gaseous IR spectra. The residual products as determined from XRD data were a mixture of $Zr(OF)_{2.7}$ [5a] and $Zr_7O_9F_{12}$ [5b] in a 2:1 ratio [wt. loss (%): theor.: 44.38; expt.: 44.65; based on $pyHZrF_5$ taken].

In the case of the niobium salt, $pyHNbOF_4$, the thermogram showed an initial decomposition at *c.* 216 °C with an endotherm peak occurring at 315 °C when a major weight loss occurred. At higher temperatures, a gradual weight loss due to oxidation occurred. In a separate experiment, it was observed that fumes were evolved at *c.* 320 °C and the compound turned black, and on further heating to 500 °C the colour of the material became less dark and at *c.* 680 °C was white. The white product was characterised as Nb_2O_5 [5c,d] [wt. loss (%): theor.: 49.85; expt.: 49.79; based on $pyHNbOF_4$ taken].

IR analysis

The infrared vibrational data of the compounds $pyHZrF_5$ and $pyHNbOF_4$ together with their assignments are listed in Table 1. The assignments for both the compounds have been made on the basis of other metal pyridinium salts [6,7].

XRD data

The X-ray diffraction data for $pyHZrF_5$ and $pyHNbOF_4$ are listed in Table 2.

Results and discussion

On the basis of the products formed, the reactions can be depicted as follows:

$$ZrOCl_2 \cdot 8H_2O + C_5H_5NH(HF)_xF \longrightarrow C_5H_5NHZrF_5 + 9H_2O + 2HCl$$

$$Nb_2O_5 + 2C_5H_5NH(HF)_xF \longrightarrow 2C_5H_5NHNbOF_4 + 3H_2O$$

In both cases the presence of a high value for the N−H stretching vibration at *c.* 3298 cm^{-1} in $pyHZrF_5$ and at *c.* 3265 cm^{-1} in $pyHNbOF_4$ indicates the presence of only very weak or the complete absence of hydrogen bonding in the solids [6, 8, 9]. The ν_{M-F} (M = metal) band in $pyHZrF_5$ is broad, possibly due to low site

TABLE 2. X-Ray diffraction data for pyridinium pentafluorozirconate and pyridinium oxotetrafluoroniobate

$pyHZrF_5$		$pyHNbOF_4$	
d (Å)	I/I_0	*d* (Å)	I/I_0
9.5429	100	6.9451	68
8.4598	32	5.6174	10
6.7116	17	4.9369	100
6.0115	10	3.9100	12
4.8180	40	3.7800	20
4.6121	34	3.5124	40
4.3224	6	3.4162	50
4.2497	7	3.3379	20
4.0460	8	3.2512	17
3.881	15	3.1352	24
3.6062	20	3.0069	15
3.4442	9	2.7049	7
3.3251	27	2.6645	4
3.1487	17	2.6178	6
3.0140	6	2.5083	6
2.7681	5	2.3402	16
2.5446	6	2.2211	9
2.4429	4	2.1538	5
2.3291	5	2.0059	5
2.2573	6	1.9521	25
2.1054	5	1.9128	9
2.0376	7	1.9090	4
1.9378	8	1.8501	5
		1.7533	8
		1.7378	4
		1.7107	4
		1.6621	4
		1.6116	4
		1.5791	2
		1.4067	13

symmetry [10] or to a polymeric structure. The complex $pyHNbOF_4$ shows ν_{Nb-O} at 797 cm^{-1} and ν_{Nb-F} at 580 cm^{-1}. These assignments were made on the basis of the general trend where the ν_{M-O} mode for oxofluorides appears at higher frequency than the ν_{M-F} modes. Another interesting feature is the splitting of δ_{M-F} at 319 and 252 cm^{-1} in $pyHZrF_5$ and at 316 and 246 cm^{-1} in $pyHNbOF_4$. This is perhaps due to interaction of the ions in the unit cell and/or a result of the low site symmetry of the ion in the crystal lattice [10] or because of their polymeric nature.

In the case of the zirconium salts, various fluorozirconate species have been separated from aqueous hydrogen fluoride solutions possessing different concentrations of ammonium and alkali metal cations [11]. In the present case, even in the presence of excess pyridinium ions, no variation occurred in the product formed with only one species, $C_5H_5NHZrF_5$, being present. A restriction on the number of pyridinium ions present might be due to the bulky size of the pyridinium ions as well as to the thermodynamic stability of the $pyHZrF_5$ salt formed.

In the case of niobium, partial fluorination to $pyHNbOF_4$ may be attributed to the avoidance of overcrowding by the fluoride ions around the metal and the higher bond order of the M—O bond due to π back-bonding providing it with a greater thermodynamic stability [12].

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