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Fluoroperoxouranates(VI). Synthesis and physico-chemical studies of $(NH_4)_2[UO_2(O_2)F_2]$ and $K_2[UO_2(O_2)F_2(H_2O)]$

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Abstract

Complex peroxouranates $(NH_4)_2[UO_2(O_2)F_2]$ (**1**) and $K_2[UO_2(O_2)F_2(H_2O)]$ (**2**) have been synthesized from the reaction of $UO_3 \cdot 4H_2O$ with AHF_2 ($A = NH_4$ or K) and hydrogen peroxide. The reaction of **1** with SO_2(g) in an aqueous medium afforded a fluoro(sulfato)dioxouranate(VI) complex $(NH_4)_2[UO_2F_2(SO_4)] \cdot H_2O$ (**3**). Infrared and laser Raman spectroscopic studies have been made.

Introduction

We have been studying recently the chemistry of fluoro and mixed fluoro complexes of UO_2^{2+} [1–3] and peroxometallates [4–7]. During the course of our investigation it became necessary to synthesize fluoro(peroxo)uranates(VI). Since the preparation of such complexes [3] is rather tedious, we sought to develop an easier route. A new synthesis for $(NH_4)_2[UO_2(O_2)F_2]$ (**1**) and an additional example of a fluoro(peroxo)uranate(VI), $K_2[UO_2(O_2)F_2(H_2O)]$ (**2**), from the reaction of $UO_3 \cdot 4H_2O$ with AHF_2 ($A = NH_4$ or K) and hydrogen peroxide and the subsequent reaction of **1** with SO_2(g) in an aqueous medium constitute the subject of the current report.

Experimental

Reagent grade chemicals were used for the syntheses. Fresh samples of NH_4HF_2 and KHF_2 were prepared by the method described earlier [8]. Reactivity grade water [4, 5, 7] was used in the studies. Infrared and laser Raman (LR) spectra were recorded using instruments detailed previously [7]. Uranium, peroxide, fluoride and sulfate were estimated as reported previously [3, 7, 9].

Starting material, $UO_3 \cdot 4H_2O$

To a solution consisting of 5 g of $UO_2(NO_3)_2 \cdot 6H_2O$ in 100 cm^3 water was added 10 cm^3 of pyridine whereupon a yellow precipitate appeared. The precipitate was washed three or four times with water, twice with acetone, and finally dried by heating on a steam bath to obtain $UO_3 \cdot 4H_2O$. Complete removal of pyridine was monitored by IR spectroscopy.

Synthesis of $(NH_4)_2[UO_2(O_2)F_2]$ (1) and $K_2[UO_2(O_2)F_2(H_2O)]$ (2)

General method

A 1.0 g (2.8 mmol) sample of $UO_3 \cdot 4H_2O$ and 2.0 g (35.1 mmol) of NH_4HF_2 or 2.73 g (35.05 mmol) of KHF_2 were mixed together and the mixture dissolved in 20 cm^3 water in a 250 cm^3 polyethylene beaker by warming on a steam bath. The solution was filtered to remove undissolved residue and then cooled to room temperature. To this was added 24 cm^3 (211.8 mmol) of 30% H_2O_2 with stirring and the pH of the solution was raised to 6 by dropwise addition of aqueous ammonia (sp. gr. 0.9) or a 25% solution of KOH whereupon a yellow solid began to appear. Complete precipitation of the product was achieved by adding 25 cm^3 of ethanol. The compound was separated by suction filtration. The yield of $(NH_4)_2[UO_2(O_2)F_2]$ (**1**) was 1 g (95%) whilst that of $K_2[UO_2(O_2)F_2(H_2O)]$ (**2**) was 1.1 g (88%).

Reaction of $(NH_4)_2[UO_2(O_2)F_2]$ (1) with SO_2(g)

Through a suspension of **1** (1 g, 2.7 mmol) in 20 cm^3 of deoxygenated water was passed SO_2(g) with constant stirring until a clear yellow solution was obtained at pH 2. The solution was concentrated to half of its original volume by heating on a steam bath. On addition of ethanol, a yellow crystalline product was obtained. This was separated by filtration, washed with ethanol and dried *in vacuo* over conc. H_2SO_4. The yield of $(NH_4)_2[UO_2F_2(SO_4)] \cdot H_2O$ (**3**) was 0.9 g (77%).

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TABLE 1. Analytical data and structurally significant IR and Raman bands for compounds **1**–**3**

Compound	Analysis[a] (%)				IR (cm^{-1})	Raman (cm^{-1})	Assignments	
	N or K	U	O_A[b] or SO_4[c]	F				
$(NH_4)_2[UO_2(O_2)F_2]$ (**1**)	7.55 (7.45)	63.8 (63.29)	8.38[b] (8.51)[b]	9.82 (10.10)	900(s) 885(s)		$\nu(U=O)$	
					850(s)		$\nu(O-O)$	
					350(m,br)		$\nu(U-F)$	
					1470(s) 1430(s)		$\nu_4(N-H)$	
					1715(w)		$\nu_4+\nu_6$	
					2845(w)		$2\nu_4$	
$K_2[UO_2(O_2)F_2(H_2O)]$ (**2**)	18.10 (17.92)	54.72 (54.56)	6.93[b] (7.34)[b]	8.22 (8.71)	895(s) 880(s)	860 835	$\nu(U=O)$	
					855(s)	815	$\nu(O-O)$	
					360(m)		$\nu(U-F)$	
					3545(s)		$\nu(O-H)$	
					1635(s)		$\delta(H-O-H)$	
					725(m)		$\rho_r(H-O-H)$	
$(NH_4)_2[UO_2F_2(SO_4)]\cdot H_2O$ (**3**)	5.82 (6.12)	52.16 (51.95)	20.14[c] (20.96)[c]	7.95 (8.29)	910(s)		$\nu(U=O)$	
					1165(s) 1120(s) 1075(s)		ν_3	$\nu(S-O)$ modes
					995(m)		ν_1	
					678(s) 625(s) 560(s)		ν_4	
					455(m)		ν_2	
					1405(s)		$\nu_4(N-H)$	
					3450(s,br)		$\nu(O-H)$	
					1640(s)		$\delta(H-O-H)$	
					370(m)		$\nu(U-F)$	

[a] Calculated values are given in parentheses.
[b] Active oxygen.
[c] Sulfate.

Results and discussion

Synthesis

Based upon the reaction of $UO_3\cdot 4H_2O$ with AHF_2 ($A = NH_4$ or K) and hydrogen peroxide, a new methodology has now been developed for the synthesis of fluoro(peroxo)uranates(VI), $(NH_4)_2[UO_2(O_2)F_2]$ (**1**) and $K_2[UO_2(O_2)F_2(H_2O)]$ (**2**), in very high yields. While a complex similar to **1** is known [3], species **2** is new. The sequence of addition of AHF_2 followed by H_2O_2 is important since the reverse order leads to the precipitation of $UO_2(O_2)\cdot 4H_2O$.

Properties and characterization

Compounds **1** and **2** are yellow, microcrystalline and sparingly soluble solids. They attack glass slowly in the presence of moisture and decompose in dilute acids producing H_2O_2.

The IR spectra of **1** and **2** and the laser Raman spectrum of **2** provide clear evidence for the occurrence of UO_2^{2+}, chelated O_2^{2-} and coordinated F^- (Table 1) with the corresponding absorptions being in the expected regions [3, 10, 11]. The observed splitting of the $\nu(U=O)$ mode indicates the possibility of bent $[O=U=O]^{2+}$ cores in the complexes. Apart from these, the IR spectrum of **2** exhibits features characteristic of the coordinated aqua ligand [12a]. Interestingly, as a result of hydrogen-bond formation between NH_4^+ and F^-, the ν_4 mode of NH_4^+ ion appeared in the IR spectrum of **1** at a frequency higher than 1400 cm^{-1}, the combination band ($\nu_4+\nu_6$) became IR-active [13] and the U–F stretching band was lowered and broadened in comparison to that of **2**.

Reactivity

The reaction of $SO_2(g)$ with **1** in an aqueous medium was facile and straighforward. The complete dissolution of **1** and the absence of the peroxo mode [ν(O=O) at *c.* 850 cm^{-1}] in the IR spectrum of the product isolated from the solution indicated that the reaction had been completed. The bonded peroxide interacted with the substrate gas giving rise to a ternary complex $(NH_4)_2[UO_2F_2(SO_4)]\cdot H_2O$ (**3**) at pH 2. Product **3** is new although many uranyl fluoride sulfato complexes, e.g. $K_2[UO_2F_2(SO_4)]\cdot H_2O$ [14], $NH_4[UO_2F(SO_4)]$ [15, 16], $(NH_4)_2[UO_2F_2(SO_4)]$ [16], $(NH_4)_7[(UO_2)_2F_9(SO_4)]$ [15] and $(NH_4)_2[(UO_2)_2F_4(SO_4)(H_2O)_2]$ [15], are known.

The yellow complex **3** is soluble in water with the electrical conductance of its solution (10^{-3} M) being 258 Ω^{-1} cm^2 mol^{-1} in conformity with its 2:1 electrolytic nature. The vibrational spectrum of **3** supports its formulation. In contrast to the spectra of **1** and **2**, the ν(U=O) band for **3** was not split, suggesting the presence of a linear O=U=O grouping. The evidence for bidentate sulfate was provided by the splitting of the ν_3 and ν_4 vibrations into three bands each (Table 1). Significantly, the occurrence of the split ν_3 modes at relatively lower wavenumbers (< 1200 cm^{-1}) relative to those of a chelated sulfate [12b] indicates the bridging nature of the bidentate ligand. Equally interesting was the broadening of the ν(U–F) band, implying the existence of fluoride bridges. Incidentally, this type of double bridging is encountered in mixed fluoro(sulfato)metallates [17] including $K_2[UO_2F_2(SO_4)]\cdot H_2O$ [14]. The IR spectrum of **3** is fully consistent with that of the crystallographically characterized $K_2[UO_2F_2(SO_4)]\cdot H_2O$ [14]. Given the similarity of the spectra, a similar structure for the former complex is likely.

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