Synthesis and Structural Assessment of Ammonium and Caesium Difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs), and Alkali-metal Difluorodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb)

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The product obtained by treating an aqueous solution of $UO_2(NO_3)_2\cdot6H_2O$ with NH_4OH or KOH reacts with AF (A = NH_4, Rb, or Cs) or KF, 30% H_2O_2, and a very small amount of 40% HF, in the mol ratio $UO_2(NO_3)_2\cdot6H_2O$: AF : H_2O_2 of 1 : 4 : 110.8, at pH 6.5—7 to afford ammonium and caesium difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs), and potassium and rubidium difluorodioxoperoxouranate(VI) monohydrates, $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb). The i.r. spectra suggest that the peroxo-ligand is bonded to the UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner.

Peroxouranate chemistry is highly complicated[1,2] owing to the formation of a host of different species with a slight variation of pH of the reaction medium. Peroxouranates containing O_2^{2-}:U ratios of 1:1, 1:2, 2:1, 3:1, 3:2, and 5:2 have been described in the literature,[1] of which $UO_2(O_2)_2\cdot nH_2O$ (n = 2 or 4) is the best characterised example. Reports on heteroligand peroxouranates are few, except for some on carbonato- and oxalato-peroxouranates.[1] The only fluoroperoxouranate known,[1] to our knowledge, is $Na[UO_2(O_2)F(OH_2)]\cdot4H_2O$. Our interest in the area of peroxo-metal chemistry[3] has now led us to synthesise a series of novel compounds $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb), the first full series of fluoroperoxouranate compounds. The present paper reports the synthesis, characterisation, and assessment of the structure of the title compounds.

Experimental

All chemicals were of reagent grade. I.r. spectra were recorded on a Perkin-Elmer model 683 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method; $Hg[Co(NCS)_4]$ was used as calibrant. The pH of the reaction solutions was measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of $A_2[UO_2(O_2)F_2]$ (A = NH_4 *or* Cs) *and* $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K *or* Rb).—$UO_2(NO_3)_2\cdot6H_2O$ (1.0 g, 1.99 mmol) was dissolved in water (10—15 cm^3) followed by addition of 25% ammonium hydroxide solution, or a concentrated solution of potassium hydroxide only in the case of the K^+ salt, with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off, washed free from alkali and nitrate, and then mixed with alkali-metal or ammonium fluoride, AF (A = NH_4, Rb, Cs, or K) and 30% H_2O_2 (25 cm^3, 220.5 mmol) while maintaining the U : F^- : H_2O_2 ratio at 1:4:110.8. Dropwise addition of 40% HF (1 cm^3) with constant stirring afforded a clear yellow solution (pH ~ 2), the pH of which was raised to 6.5—7 by carefully adding a 10% solution of ammonium or potassium hydroxide in the cases of the NH_4^+ and K^+ salts respectively and solid A_2CO_3 (A = Rb or Cs) for the Rb^+ or Cs^+ salts. An equal volume of ethanol was added with occasional stirring to obtain yellow microcrystalline $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) or $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb). Each compound was allowed to settle for *ca.* 30 min, separated by centrifugation, purified by washing with ethanol, and finally dried *in vacuo* over diphosphorus pentaoxide.

The amounts of reagents used and the yields of the compounds are set out in Table 1.

Elemental Analysis.—Uranium was estimated gravimetrically as U_3O_8.[4] The peroxide content was determined by redox titration with standard solutions of $KMnO_4$[5] or Ce^{4+}.[6] Fluoride was estimated gravimetrically as lead chloride fluoride, PbClF.[7] Nitrogen and potassium were estimated by methods described in previous papers.[3]

The analytical data and structurally significant i.r. bands and their assignments are summarised in Table 2.

Results and Discussion

Both fluoride[8] and peroxide[1] can, under the appropriate conditions, co-ordinate to UO_2^{2+}. Accordingly we carried out the reaction of UO_2^{2+} with alkali-metal or ammonium fluoride, AF, and H_2O_2 at pH 6.5—7 which enabled us to synthesise the difluorodioxoperoxouranate(VI) compounds, $[UO_2(O_2)F_2]^{2-}$, in aqueous medium. The complex ion was isolated as its alkali-metal and ammonium salts, $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb) by the addition of ethanol which facilitated precipitation. It must be emphasised that maintenance of the pH at 6.5—7 is vital for the formation and thence successful isolation of the compounds in the solid state. It has been observed by carrying out similar reactions at pH 2—4 that the products obtained under these conditions either do not contain peroxide at all or do to a practically negligible extent, suggesting thereby that acidic conditions are not conducive to the desired synthesis. The compounds isolated under such conditions were found to be oxofluoro- rather than fluoroperoxo-uranates(VI). Thus we believe that the course of reaction involves the formation of oxofluorouranate(VI) first followed by uptake of peroxide with the increase in pH of the medium to produce ultimately the complex ion $[UO_2(O_2)F_2]^{2-}$. In the cases of the Rb^+ and Cs^+ salts, the pH of the reaction medium was raised to 6.5—7 by the addition of the respective carbonates, exploiting the reaction $CO_3^{2-} + 2H^+ \longrightarrow CO_2\uparrow + H_2O$, instead of NH_4OH which was otherwise thought to be suitable. Attempts to use ammonia solution to raise the pH to 6.5—7 resulted in the isolation of $[NH_4]_2[UO_2(O_2)F_2]$ even though the stipulated amount of RbF or CsF was used. This could be due to the relatively lower solubility of $[NH_4]_2[UO_2(O_2)F_2]$.

Table 1. Amounts of reagents used and yields of alkali-metal and ammonium difluorodioxoperoxouranates(VI)

Compound	Yield/g (%)	Amount of $UO_2(NO_3)_2\cdot6H_2O$/g (mmol)	Amount of AF/g (mmol)	Amount of H_2O_2/cm^3 (mmol)
$[NH_4]_2[UO_2(O_2)F_2]$	0.5	1	0.3	25
	(67)	(1.99)	(8.1)	(220.5)
$K_2[UO_2(O_2)F_2]\cdot H_2O$	0.6	1	0.47	25
	(69)	(1.99)	(8.1)	(220.5)
$Rb_2[UO_2(O_2)F_2]\cdot H_2O$	0.8	1	0.84	25
	(73)	(1.99)	(8.0)	(220.5)
$Cs_2[UO_2(O_2)F_2]$	0.9	1	1.23	25
	(75)	(1.99)	(8.1)	(220.5)

Table 2. Analytical data and structurally significant i.r. bands of alkali-metal and ammonium difluorodioxoperoxouranates(VI)

	Analysis[a] (%)					
Compound	A	U	O[b]	F	I.r. (cm^{-1})	Assignments
$[NH_4]_2[UO_2(O_2)F_2]$	7.55[c]	63.8	8.70	9.80	885s	ν(U=O)
	(7.45)[c]	(63.3)	(8.50)	(10.1)	900s	
					855s	ν(O–O)
					350s,br	ν(U–F–U)
					3 160m	ν_3
					3 040s	ν_1 N–H
					1 400s	ν_4
$K_2[UO_2(O_2)F_2]\cdot H_2O$	18.4[d]	54.9	7.80	9.10	890s	ν(U=O)
	(17.95)[d]	(54.55)	(7.35)	(8.70)	860s	ν(O–O)
					370s,br	ν(U–F–U)
					3 440s	ν(O–H)
					1 640m	δ(H–O–H)
$Rb_2[UO_2(O_2)F_2]\cdot H_2O$		45.4	6.40	7.50	905s	ν(U=O)
		(45.0)	(6.05)	(7.20)	860s	ν(O–O)
					360s,br	ν(U–F–U)
					3 450s	ν(O–H)
					1 640m	δ(H–O–H)
$Cs_2[UO_2(O_2)F_2]$		39.8	5.50	6.10	900s	ν(U=O)
		(39.3)	(5.30)	(6.25)	860s	ν(O–O)
					360s,br	ν(U–F–U)

[a] Calculated values are in parentheses. [b] Peroxo-oxygen. [c] Analysis for N. [d] Analysis for K.

Characterisation and Assessment of Structure.—The newly synthesised compounds are insoluble in common organic solvents, and very sparingly soluble in water. They dissolve completely in a slightly acidified (H_2SO_4) solution from which uranium can be quantitatively precipitated by the addition of ammonium hydroxide. The determination of peroxide content, considered to be extremely important, was accomplished by redox titrations with a standard Ce^{4+} solution, and also with a standard $KMnO_4$ solution, in the presence of boric acid to prevent any loss of active oxygen; results conspicuously suggested the presence of one O_2^{2-} group co-ordinated to the UO_2^{2+} centre in each of the compounds. The occurrence of hexavalent uranium has been confirmed by the diamagnetic nature of the compounds. It may be noted that while the ammonium and caesium salts of the $[UO_2(O_2)F_2]^{2-}$ ion are anhydrous, those of the potassium and rubidium are monohydrates.

The principal features of the i.r. spectra are the absorptions at 910—880, 870—850, and 370—350 cm^{-1}, which have been assigned to ν(U=O) (*trans*-linked O=U=O group),[8] ν(–O–O–),[3,9] and ν(U–F)[10] modes respectively. The strong and sharp ν(–O–O–) band at *ca.* 860 cm^{-1} supports the view that the O_2^{2-} is co-ordinated to the UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner.[3,9] The somewhat lower value of ν(U–F), compared to those of binary fluorouranates(VI),[10] and slightly broad nature of the band indicate the distinct possibility of fluoride acting as a bridging group. The two bands at *ca.* 3 440 and at *ca.* 1 640 cm^{-1} in the spectra of both the K^+ and Rb^+ salts resemble in their shapes and positions those from the ν(O–H) and δ(H–O–H) modes of unco-ordinated water.[11]

Conclusions

It is evident that fluoroperoxouranates, $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb), can be synthesised under the appropriate conditions. The pH of 6.5—7 is very crucial for the formation of the $[UO_2(O_2)F_2]^{2-}$ ion. The peroxide is bonded to the UO_2^{2+} in a triangular bidentate manner. The complex $[UO_2(O_2)F_2]^{2-}$ may have a polymeric structure through –U–F–U– chains.

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