Synthesis of Alkali-metal Diaquafluoro-oxoperoxovanadate(IV) Complexes $[VO(O_2)F(H_2O)_2]^-$

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Orange-red alkali metal diaquafluoro-oxoperoxovanadates(IV), $A[VO(O_2)F(H_2O)_2]$ ($A = NH_4$, K, Rb, or Cs), have been synthesised by the reaction of $A[VOF_4]$ with H_2O_2 in the molar ratio 1 : 12 followed by precipitation with ethanol. Characterisation of the compounds was made from the results of chemical analyses, chemical determination of oxidation state of vanadium, i.r. and electronic spectroscopic studies, and magnetic susceptibility measurements. I.r. spectra suggest that the peroxo-ligand is bonded to the V^{4+} centre in a triangular bidentate fashion.

Various aspects of peroxovanadium chemistry have attracted considerable current interest [1–6] probably because of the biochemical significance of peroxovanadium compounds.[7] While most of the recent papers on the topic deal with the solution chemistry of peroxovanadium complexes, synthesis and structural assessment of peroxo- and hetero-ligand peroxo-compounds of vanadium have received much less attention. In a continuation of our studies on the synthesis and structural assessment of hetero-ligand peroxo-compounds of vanadium(V) [8,9] we thought it would be worthwhile to synthesise hetero-ligand peroxovanadate(IV) compounds. Accordingly, we have now performed the reaction of alkali metal tetrafluoro-oxovanadates(V), $A[VOF_4]$ ($A = NH_4$, K, Rb, or Cs), with 6% hydrogen peroxide under weak acidic conditions (pH *ca.* 4) which enabled us to synthesise a series of alkali metal diaquafluoro-oxoperoxovanadates(IV), $A[VO(O_2)F(H_2O)_2]$; these peroxovanadate(IV) compounds were obtained, for the first time, in the solid state.

Experimental

The chemicals used were all reagent grade products. Alkali metal difluorides, AHF_2,[10] required for the preparation of the alkali metal tetrafluoro-oxovanadates(V), $A[VOF_4]$,[11] were synthesised by the methods developed in this laboratory. I.r. spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. Electronic spectral measurements were made on a Beckman model UV-26 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method, using $Hg[Co(NCS)_4]$ as the calibrant. Molar conductance measurements were made using a Philips PR 9500 conductivity bridge. 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 Alkali Metal Diaquafluoro-oxoperoxovanadate(IV) Complexes, $A[VO(O_2)F(H_2O)_2]$ ($A = NH_4$, K, Rb, *or* Cs).—As the methods of synthesis of these complexes are similar, only a representative method is described.

Freshly prepared $A[VOF_4]$ was dissolved in 6% hydrogen peroxide, maintaining the molar ratio $A[VOF_4]$: H_2O_2 at 1 : 12 (pH *ca.* 4), with gentle stirring. The red solution thus obtained was cooled in an ice-bath for *ca.* 20 min. Ethanol was added, in excess, with constant stirring and orange-red microcrystalline $A[VO(O_2)F(H_2O)_2]$ was obtained. The compound was separated by centrifugation and washed several times with ethanol and finally dried *in vacuo* over diphosphorus pentaoxide.

The amounts of reagents and the yields of the compounds $A[VO(O_2)F(H_2O)_2]$ are given in Table 1.

Table 1. Amounts of reagents used and yields of alkali metal diaquafluoro-oxoperoxovanadates(IV)

Compound	Yield/g (%)	Amount of $A[VOF_4]$/g (mmol)	Amount of 6% H_2O_2/cm^3 (mmol)
$[NH_4][VO(O_2)F(H_2O)_2]$	0.4	0.5	22.0
	(75)	(3.1)	(38.5)
$K[VO(O_2)F(H_2O)_2]$	0.3	0.5	19.0
	(57)	(2.8)	(33.5)
$Rb[VO(O_2)F(H_2O)_2]$	0.5	0.7	22.0
	(68)	(3.1)	(38.5)
$Cs[VO(O_2)F(H_2O)_2]$	0.5	0.7	17.0
	(69)	(2.5)	(30)

Elemental Analysis.—Vanadium estimation was done volumetrically. A solution of the peroxovanadate(IV) compounds, made slightly alkaline with a dilute sodium hydroxide solution, was boiled in order to completely expel the peroxo-oxygen and to convert vanadium(IV) to vanadium(V). The solution was cooled and neutralised with dilute sulphuric acid. A near-boiling solution of vanadium(V) was treated with a stream of sulphur dioxide for 10—15 min and then with a rapid stream of carbon dioxide to expel any excess of sulphur dioxide. The vanadium(IV) solution thus obtained was then cooled to *ca.* 80 °C, and titrated with a standard potassium permanganate solution.[12] The peroxide content in each of the compounds was determined by iodometry,[13] and also by titration with a standard Ce^{4+} solution.[14] Fluoride, potassium, and nitrogen were estimated by the methods described in our earlier paper.[9]

The analytical data, i.r. band positions and the electronic spectral data are set out in Table 2.

Results and Discussion

In the course of our studies involving the synthesis of peroxofluoro-compounds of vanadium(V),[8,9] we obtained a red solution containing V^{5+}, AF, and H_2O_2 at a pH *ca.* 4, and presumed that the species responsible for such a colour must be different from those previously isolated by us.[8,9] Further, it was expected that the number of peroxo-groups bonded to vanadium in acidic medium [5,12] would be less than that in alkaline medium, and that H_2O_2 would probably be able to reduce V^{5+} to V^{4+} in acidic medium. In view of the above considerations the reaction between $A[VOF_4]$ and 6% H_2O_2 was carried out and a red solution was obtained. The pH of the solution was found to be *ca.* 4. The peroxovanadium complex species was isolated in the solid state as its alkali metal salts, $A[VO(O_2)F(H_2O)_2]$, by addition of ethanol which

Table 2. Analytical data, magnetic moments, and structurally significant i.r. and electronic spectral bands of $A[VO(O_2)F(H_2O)_2]$ (A = NH_4, K, Rb, or Cs)

Compound	$\mu_{eff.}$ [a]/B.M.	Analysis [b] (%)				I.r. (cm^{-1})	Assignment	Electronic absorption (cm^{-1})	Transition
		A	V	O [c]	F				
$[NH_4][VO(O_2)F(H_2O)_2]$	1.73	8.3 [d]	30.2	19.3	10.8	955s	$\nu(V{-}O)$	11 628	$e \leftarrow b_2$
		(8.15) [d]	(29.6)	(18.6)	(11.05)	890s	$\nu(O{-}O)$		
						610s	$\nu(V{-}O_2)$		
						475s	$\nu(V{-}F \cdots V)$	17 699	$b_1 \leftarrow b_2$
						3 150m,br	$\nu(O{-}H)$		
						1 625w,br	$\delta(H{-}O{-}H)$		
						3 040s	$\nu(N{-}H)$ ν_1		
						1 440s	$\nu(N{-}H)$ ν_4		
$K[VO(O_2)F(H_2O)_2]$	1.75	20.8	25.9	17.1	10.4	950s	$\nu(V{-}O)$	11 905	$e \leftarrow b_2$
		(20.25)	(26.4)	(16.55)	(9.85)	880s	$\nu(O{-}O)$		
						620s	$\nu(V{-}O_2)$		
						470s	$\nu(V{-}F \cdots V)$	17 699	$b_1 \leftarrow b_2$
						3 165m,br	$\nu(O{-}H)$		
						1 620w,br	$\delta(H{-}O{-}H)$		
$Rb[VO(O_2)F(H_2O)_2]$	1.70		21.7	13.9	7.6	970s	$\nu(V{-}O)$		
			(21.25)	(13.35)	(7.95)	880s	$\nu(O{-}O)$		
						610s	$\nu(V{-}O_2)$		
						475s	$\nu(V{-}F \cdots V)$		
						3 160m,br	$\nu(O{-}H)$		
						1 635w,br	$\delta(H{-}O{-}H)$		
$Cs[VO(O_2)F(H_2O)_2]$	1.73		18.3	11.8	6.8	965s	$\nu(V{-}O)$		
			(17.75)	(11.15)	(6.6)	895s	$\nu(O{-}O)$		
						610s	$\nu(V{-}O_2)$		
						480s	$\nu(V{-}F \cdots V)$		
						3 150m,br	$\nu(O{-}H)$		
						1 620w,br	$\delta(H{-}O{-}H)$		

[a] Measured at 295 K. [b] Calculated values are in parentheses. [c] Peroxo-oxygen. [d] Analysis for N.

possibly facilitated the reduction of V^{5+} to V^{4+} and precipitation of the complex. The occurrence of reaction between $A[VOF_4]$ and H_2O_2 was ascertained by the appearance of a new band at *ca.* 890 cm^{-1}, due to the $\nu(O{-}O)$ mode of a co-ordinated O_2^{2-}, from a small amount of the sample isolated from the solution. It was previously reported [15] that $K_2[V_2O_3(O_2)_2F_2]$ was isolated from the reaction of V_2O_5, 40% HF, and H_2O_2 at high acidity and $K_2[VO(O_2)_2F]$ was isolated at pH 4. In the present case, however, the reaction of $A[VOF_4]$ with H_2O_2 at pH 4 followed by addition of ethanol afforded compounds of the type $A[VO(O_2)F(H_2O)_2]$.

Characterisation and Assessment of Structure.—The compounds $A[VO(O_2)F(H_2O)_2]$ are all orange-red, microcrystalline and insoluble in common organic solvents. They decompose in water thus precluding their molar conductance measurements. In fact, owing to their instability, most of the peroxovanadium compounds do not permit molar conductance measurements.[8,9,16] The compounds $A[VO(O_2)F(H_2O)_2]$ can, however, be stored in sealed containers and their stability can be ascertained by periodic estimation of the peroxide content. The estimation of peroxide is crucial in order to determine the number of O_2^{2-} ligands bonded to the metal centre. The peroxide content was estimated by cerimetry (Ce^{4+}) and also by iodometry, the results of which conclusively suggest the presence of one O_2^{2-} group co-ordinated to vanadium(IV). The direct titration with a standard $K[MnO_4]$ solution showed the involvement of three electron equivalents, two of which originated from O_2^{2-} and the third was due to the process $V^{4+} \longrightarrow V^{5+} + e$. The magnetic moment values of the compounds (295 K), lying between 1.70 and 1.75 B.M. (1 B.M. $\simeq 9.27 \times 10^{-24}$ J T^{-1}), are consistent with the presence of vanadium(IV) and are in excellent agreement with those reported in the literature for V^{4+} systems.[17]

The optical spectra of $A[VO(O_2)F(H_2O)_2]$ (A = NH_4 or K), recorded immediately after preparing solutions in cold dilute H_2O_2, showed three absorptions at *ca.* 11 700, *ca.* 17 699, and >21 400 cm^{-1}, with the last being obscured by strong charge-transfer transitions. The first two bands have been assigned to $e \leftarrow b_2$ and $b_1 \leftarrow b_2$ transitions respectively and agree very well with the reported spectra of oxovanadium(IV) complexes,[18] giving strong evidence for the presence of vanadium(IV) in the orange-red peroxovanadium compounds. Our observations also support the very recent report [6] concerning the existence of peroxovanadium(IV) in solutions.

The i.r. spectra (Table 2) of the series of four salts are similar, showing absorptions at *ca.* 3 160m, br, *ca.* 1 630w, br, *ca.* 960s, *ca.* 890s, *ca.* 615s, and *ca.* 475s cm^{-1}. The band at *ca.* 960 cm^{-1} has been assigned to the $\nu(V{-}O)$ mode of the terminally bonded V=O group,[18] while those at *ca.* 890 and *ca.* 615 cm^{-1} have been assigned to $\nu(O{-}O)$ and $\nu(V{-}O_2)$ respectively of the co-ordinated peroxide.[8,9,19,20] The absorptions at *ca.* 3 160m, br and *ca.* 1 630w, br cm^{-1} have been attributed to $\nu(O{-}H)$ and $\delta(H{-}O{-}H)$ modes of co-ordinated water. The lowering of the $\nu(O{-}H)$ frequencies and broadening of $\delta(H{-}O{-}H)$ bands relative to those of free water suggest the possibility of intramolecular hydrogen bonding.[21,22] The band at *ca.* 475 cm^{-1} is attributed to a V–F stretching mode; its position suggests the presence of bridging rather than terminal F. Since the $\nu(O{-}O)$ and the complementary $\nu(V{-}O_2)$ fall in the regions expected for the triangularly bonded O_2^{2-} ligands,[8,9,19,20] we infer that the peroxide group is bonded to the V^{4+} centre in a triangular bidentate manner. Two extra vibrations at 3 040 and 1 440 cm^{-1} in the case of the ammonium salt have been attributed to the ν_1 and ν_4 modes of NH_4^+. The ν_3 mode of NH_4^+ could not be identified due to its overlap with the broad $\nu(O{-}H)$ mode of water.

It thus appears that the complex ion has the formula $[VO(O_2)F(H_2O)_2]^-$, containing a triangularly bonded peroxide ligand. The complex species may have a polymeric structure through V–F–V bridging; however, the possibility of a weak V–O–V interaction can not be ruled out completely.

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