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STUDIES ON OXOPEROXOFLUOROVANADATES (V)

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SUMMARY

Two oxoperoxofluoro complexes of vanadium, viz., $(NH_4)_2[VO(O_2)(OH)F_2]$ and $K_4[V_2O_3(O_2)_2F_4]$ have been prepared by crystallising solutions of vanadium pentoxide in aqueous hydrofluoric acid with ammonium or potassium fluoride solutions containing hydrogen peroxide at $5^{\circ}C$. The orange crystalline substances are quite stable. They are very weakly paramagnetic and display strong $\nu(V{=}O)$ and $\nu(O{-}O)$ bands in their i.r. spectra. The TGA curves of the complexes show horizontals corresponding to the formation of $(NH_4)_4[V_2O_5F_4]$ and $K_4[V_2O_5F_4]$ respectively which have actually been isolated. These appear to be oxobridged complexes. The x-ray patterns of the two peroxo complexes are distinctly different.

INTRODUCTION

Quinquevalent vanadium has very great affinity towards oxide, peroxide and fluoride. Thus, oxofluorovanadates(V) of different types, e.g. $[VOF_4]^-$, $[VOF_5]^{2-}$, $[VO_2F_4]^{3-}$, $[VO_2F_3]^{2-}$, $[VO_2F_2]^-$ easily crystallise out from dilute hydrofluoric acid solutions of vanadates(V) or vanadium pentoxide containing alkali fluorides [1-8]. The peroxovanadium(V) compounds which are generally unstable, belong to different types [9,10], viz., $[V(O_2)_4]^{3-}$, $[VO(O_2)_3]^{3-}$, $[VO(O_2)_2]^-$, $[VO_2(O_2)_2]^{3-}$ and $[VO(O_2)]^+$. These may be considered to be derived from $[VO_4]^{3-}$, $[VO_3]^-$ or $[VO_2]^+$ by the replacement of one or more oxo groups by the peroxo ones. Only very few salts of the above ions have been isolated till now and few of their structures are known for certain. No compound of vanadium containing all these three ligands (O^{2-}, O_2^{2-} and F^-) is definitely known, although for its heavier congeners and also for molybdenum mixed complexes, e.g., $K_2[Nb(O_2)F_5]\cdot H_2O$, $K_2[TaO_2F_5]\cdot H_2O$ and $K_2[MoO(O_2)F_4]\cdot H_2O$ have been well characterised [9,11]. The formation of mixed complexes containing oxide, peroxide and fluoride is apparently due to their ability to undergo isomorphous replacement without causing a large structural distortion. In fact the compound $K_2[MoO(O_2)F_4]\cdot H_2O$ has been shown [11] to be isomorphous with $K_2[MoO_2F_4]\cdot H_2O$. The isolation and characterisation of two fairly stable oxoperoxofluorovanadates(V) have been presented in this communication. During the course of our investigation a paper [12] describing the preparation of peroxofluoro complexes, $(NH_4)_3[M(O_2)_2F_4]$, where M = V, Nb and Ta has appeared The vanadium complex, however, has been reported to be unstable and difficult to isolate without decomposition.

EXPERIMENTAL

Vanadium pentoxide used was of Riedel de Haën, West Germany. All the other chemicals were B.D.H. or E.Merck's A.R. or G.R. quality.

Vanadium was estimated [13] by titration with Fe^{2+} solution in the presence of sulphonated diphenylamine as indicator, after prolonged boiling of the sample solution with sodium peroxide. Fluorine was estimated [13] by titration with thorium nitrate using sodium alizarin sulphonate as indicator, after steam distillation of fluosilicic acid. Nitrogen was estimated by Kjeldahl's method. The peroxo content was determined by titration of freshly prepared solution with potassium permanganate in 2N sulphuric acid medium. At the initial stages of titration the colour of the solution intensified, but then gradually disappeared and there was no difficulty in the detection of the equivalence point. Potassium was estimated gravimetrically as potassium sulphate after removal of vanadate(V) with silver nitrate and then of excess of Ag(I) as chloride.

Conductance and magnetic susceptibility measurements and the recording of i.r. spectra were made by methods described previously [14]. Thermogravimetric analysis was carried out with a Derivatograph (System: F. PAULIK J. PAULIK L.ERDEY, MOM, BUDAPEST). About 100 mg of the finely powdered substances were heated at a rate of 2°/minute. X-ray powder pattern was obtained with a Philips' diffractometer (PW 1061) employing CuK_α radiation.

Preparation of the salts

$(NH_4)_2[VO(O_2)(OH)F_2]$. 2 g of ammonium fluoride dissolved in 6% H_2O_2(12 ml) was added to a saturated solution of vanadium pentoxide (1 g) in hydrofluoric acid (40%), both the solutions being previously cooled at 5°C. Orange crystals separated out on stirring the solution for 15 minutes, while the temperature was maintained at 5°C. These were separated by filtration and scrupulously dried by pressing between filter papers. The salt was then kept in a desiccator over sulphuric acid and caustic soda. The yield was 0.5 g.

$K_4[V_2O_3(O_2)_2F_4]$. This was prepared by the method similar to the above one except that 5.1 g of potassium fluoride was taken instead of ammonium fluoride.

$(NH_4)_4[V_2O_5F_4]$ and $K_4[V_2O_5F_4]$. These were obtained by heating the salts $(NH_4)_2[VO(O_2)(OH)F_2]$ and $K_4[V_2O_3(O_2)_2F_4]$ respectively in a platinum crucible at 85°C till constant weight (about 3 hours). The salts were coloured light yellow.

RESULTS AND DISCUSSION

The peroxofluoro complexes are orange crystalline substances which are stable when dry. All the salts (including the oxofluoro ones) are highly soluble in water but insoluble in common organic solvents. The peroxo salts decolourise adidified potassium permanganate solution with the evolution of oxygen. Aqueous solutions of the peroxofluoro complexes are stable for a few hours and do not liberate oxygen in contact with platinum electrodes.

The molecular conductances of the peroxo complexes at different dilutions indicate that the complex ions are highly dissociated in dilute solutions (Table 1).

The peroxofluoro complexes are very weakly paramagnetic (Table 2) which agrees with the very weak temperature independent paramagnetism observed with many vanadium(V) complexes.

The TGA curve of $(NH_4)_2[VO(O_2)(OH)F_2]$ indicates that it begins to decompose above room temperature. A good horizontal with 13.2% loss extends between 90-150°C. This can be accounted for the loss of half a molecule of oxygen and water each (calcd. 13.2%). Isothermal heating of the complex at 85°C till constant weight gave a loss of 12.8%. The yellow residue did not contain any peroxide. From the analysis and the mode of decomposition, the product may be formulated as $(NH_4)_4[V_2O_5F_4]$.

The potassium salt, $K_4[V_2O_3(O_2)_2F_4]$ also begins to decompose above room temperature. The TGA curve gave a good horizontal with 7.0% loss extending between 120-200°C which corresponds to the loss of half a molecule of oxygen (calcd. 7.2% on the basis of empirical formula with one vanadium). Isothermal heating of the complex at 85

TABLE 1

Analytical data* and conductance of the complexes

Compound	% V	% F	% O_2^{2-}	% K or N	Molecular conductance at 30°C, $ohm^{-1}mole^{-1}cm$.	
					M/512 solution	M/1024 solution
$(NH_4)_2[VO(O_2)(OH)F_2]$	27.1 (26.8)	20.4 (20.0)	16.7 (16.8)	15.0 (14.7)	558	636
$K_4[V_2O_3(O_2)_2F_4]$	22.6 (22.8)	17.2 (17.0)	14.5 (14.3)	35.8 (34.9)	512**	588**
$(NH_4)_4[V_2O_5F_4]$	31.2 (30.8)	23.0 (23.0)		17.5 (17.0)		
$K_4[V_2O_5F_4]$	24.4 (24.6)	18.6 (18.3)		38.1 (37.6)		

* The values in parenthesis are the calculated ones.
** Using empirical formula with one vanadium atom.

till constant weight gave a loss of 6.9%. The yellow residue did not contain any peroxide. The analysis agrees with the formula $K_4[V_2O_5F_4]$.

The band positions in the i.r. spectra of the salts are given in Table 2. The remarkable features in the spectra of the peroxofluoro complexes lie in the region 1000-800 cm^{-1}. The strong bands at 970 cm^{-1} in the spectrum of both the potassium and ammonium salts are assigned as $\nu(V{=}O)$ indicating the presence of terminal V=O groups in both the salts. The very strong bands at 895 cm^{-1} in both the spectra are assigned as $\nu(O{-}O)$. All peroxo complexes which have been studied [9] through i.r. spectra give strong or very strong bands between 860-900 cm^{-1}. The medium to strong intensity bands around 860 cm^{-1} may be due to further modes of $\nu(O{-}O)$ or $\delta(V{-}O{-}V)$. It is difficult to assign the $\delta(V{-}O{-}V)$ band in the spectra of the potassium peroxo salt which has been formulated as one containing both terminal and bridging V=O group.

TABLE 2

Magnetic moment and i.r. spectral bands* of the complexes

Compound	Magnetic moment μ_{eff}, BM at 30°C	ν, cm^{-1}
$(NH_4)_2[VO(O_2)(OH)F_2]$	0.40	3570(w), 3180(vs,b), 1610(vw), 1400(vs) (overlapped with mujol band), 1150(vw), 970(s), 895(vs), 860(s), 610(m), 590(s), 550(s), 500(m)
$K_4[V_2O_3(O_2)_2F_4]$	0.40**	3400(vw,b), 1610(vw), 1110(w), 970(s), 920(vs), 895(s), 890(s), 855(m), 605(m), 575(s), 520(s), 410(m)
$(NH_4)_4[V_2O_5F_4]$		3200(vs,b), 1670(w), 1035(w), 1010(w), 910(vs,b), 860(s), 700(m,b) (along with mujol band), 555(vs), 510(s), 410(m)
$K_4[V_2O_5F_4]$		3250(w), 1850(vw), 1110(vw), 930(vs,b), 740(m) (along with mujol band), 565(vs,b), 510(s), 410(m)

* In mujol.

** Using empirical formula with one vanadium.

However, compared with the spectrum of the ammonium salt, the spectrum of the potassium salt gives two additional bands in the region of 920-850 cm^{-1} (at 920 vs and 890 s) which suggests that the potassium salt contains bridging V-O-V groups.

The spectrum of the potassium salt obtained by the pyrolysis of the peroxo complex does not give any band assignable to $\nu(O-O)$. The spectrum of the corresponding ammonium salt, however gives a strong band at 860 cm^{-1} which may be assigned as $\delta(V-O-V)$. The corresponding band in the spectrum of $K_4[V_2O_5F_4]$ may be overlapped with either the very strong and broad $\nu(V=O)$ band around 930 cm^{-1}, or the nujol band around 740 cm^{-1}. The spectra of all the complexes show weak O-H bands around 3400 cm^{-1} caused by the absorption of slight water.

The potassium and the ammonium peroxo complexes give totally different, but well defined, diffraction patterns. The d values with their relative intensities are given in Table 3.

TABLE 3

X-Ray powder pattern of the peroxofluoro complexes

$(NH_4)_2[VO(O_2)(OH)F_2]$		$K_4[V_2O_3(O_2)_2F_4]$	
d(Å)	Intensity	d(Å)	Intensity
5.88	4	6.20	5
5.37	2	5.72	4
5.18	10	5.19	5
4.22	1	5.10	5
4.12	1	5.00	5
3.94	1	4.19	4
3.62	1	3.49	4
3.52	1	3.42	4
3.30	1	3.30	8
3.22	1	3.15	9
3.15	1	3.10	10
2.97	3	3.00	3
2.86	1	2.89	4
2.29	4	2.86	3
2.13	2	2.82	5
1.77	1	2.26	6
		2.09	7

The potassium and ammonium peroxo complexes which were obtained by the same method, have been formulated differently. The difference between the two empirical formulae of the two anions lies in half a molecule of water which is difficult to distinguish by chemical analysis. The losses in weight suffered by the two salts on heating were however, much different and these can be accounted for on the basis of the formulae suggested. The ammonium salt did not lose ammonia or hydrogen fluoride on heating at 85°C. The presence of larger number of bands in the i.r. spectrum of the potassium salt between 920-850 cm^{-1} (V-O-V and O-O regions) further indicates the polynuclear nature of the anion in it with V-O-V groups. However, as noted earlier, the assignment of δ(V-O-V) in the presence of peroxo group is difficult.

Attempts to prepare rubidium and caesium salts by the method analogous to that employed for the other two salts were unsuccessful. In both the cases the orange crystals deposited were too unstable to be dried. Similar observation that the stability of the peroxo complexes decreases with increasing size of the alkali metal ion was also made by previous workers [9].

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