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Tetraalkylammonium Fluorooxoperoxovanadates

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Summary. Compounds crystallizing from the MOH-HF-V_2O_5-H_2O_2-H_2O (M=$N(CH_3)_4$, $N(C_2H_5)_4$, $N(C_4H_9)_4$) system have been characterized by elemental analysis, vibrational spectra, and X-ray powder patterns. Besides $[N(CH_3)_4]_2[VO(O_2)_2F]\cdot 2H_2O$ (**1**) and $[N(CH_3)_4]_3[V_2O_2(O_2)_4F]$ (**2**) which correspond to the known compounds $M_2[VO(O_2)_2F]$ (M = K, NH_4, Cs) and $(NH_4)_3[V_2O_2(O_2)_4F]\cdot 2H_2O$, respectively, complexes of two new types have been obtained: $[N(C_2H_5)_4]_2[V_2O_{5-x}(O_2)_xF_2]\cdot H_2O$($x \sim 0.25$, **3**) and the first trinuclear peroxo complex of vanadium(V), $[N(C_4H_9)_4]_2[V_3O_3(O_2)_4F_3]\cdot 6H_2O$(**4**).

Keywords. Fluorooxoperoxovanadates; Tetraalkylammonium.

Tetraalkylammonium-Fluorooxoperoxovanadate

Zusammenfassung. Aus dem System MOH-HF-V_2O_5-H_2O_2-H_2O (M=$N(CH_3)_4$, $N(C_2H_5)_4$, $N(C_4H_9)_4$) kristallisierende Verbindungen wurden mittels Elementaranalyse, Schwingungsspektroskopie und Röntgendiffraktion charakterisiert. Neben $[N(CH_3)_4]_2[VO(O_2)_2F]\cdot 2H_2O$ (**1**) und $[N(CH_3)_4]_3][V_2O_2(O_2)_4F]$ (**2**), welche den bekannten Verbindungen $M_2[VO(O_2)_2F]$ (M = K, NH_4, Cs) und $(NH_4)_3[V_2O_2(O_2)_4)F]\cdot 2H_2O$ entsprechen, wurden zwei neue Typen von Komplexen erhalten: $[N(C_2H_5)_4]_2[V_2O_{5-x}(O_2)_xF_2]\cdot H_2O$ ($x \sim 0.25$, **3**) und der erste dreikernige Peroxokomplex von Vanadium(V), $[N(C_4H_9)_4]_2[V_3O_3(O_2)_4F_3]\cdot 6H_2O$ (**4**).

Introduction

Since 1980, when the preparation of the first well characterized fluorooxoperoxo complex of vanadium(V), $K_2[VO(O_2)_2F]$, was published [1], a series of complexes of this type has been reported [2–5]. The crystal structures have been solved for the mononuclear complexes $M_2[VO(O_2)_2F]$ (M = K[6], NH_4[7], Cs[8]), $(NH_4)_3$-$[VO(O_2)_2F_2]$ [9], $(NH_4)_2(V(O_2)_3F]\cdot H_2O$ [10][1], and for the dinuclear complex $K_3[V_2O_2(O_2)_3F_3]\cdot 2H_2O\cdot HF$ [12]. With respect to the ability of oxo, peroxo, and fluoro ligands to form bridges between two vanadium atoms, a greater variety of di- or polynuclear complexes can be expected.

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[1] The structure of this compound has been determined only with $R = 0.25$. Our attempts to reproduce the synthesis were unsuccessful. *Thompson et al.* [11] were unable to repeat the synthesis of a similar complex ($Na_2[V(O_2)_3F]$, [11]). The existence of this type of complexes is questionable.

This paper deals with the products crystallizing from the *M*OH-HF-V_2O_5-H_2O_2-H_2O ($M = NR_4^+$, R = alkyl) system. In order to address the question of influence of the cation properties on the formation of complexes, NR_4^+ cations with various alkyl chain length were used.

Results and discussion

The yellow complex **1** can be obtained from approximately neutral solutions of the composition $N(CH_3)_4OH$-HF-V_2O_5-H_2O_2-H_2O containing an excess of fluoride ions. Crystallization from the same system at *pH* 5–6 under addition of ethanol results in fomation of **2**.

The infrared spectra of **1** and **2** (Table 1) exhibit characteristic bands of the $VO(O_2)_2$ group. The positions of these bands are in agreement with a pentagonal pyramidal arrangement around the vanadium atom [13]. This is supported by the Raman spectrum of **2** (Fig. 1), where the position of 530 cm^{-1} for the very strong, characteristic *Raman* band assigned to $\nu(V–O_p)$ (O_p: peroxo oxygen) is typical for a pentagonal pyramidal geometry [14]. Hence, complex **1** is analogous to $K_2[VO(O_2)_2F]$ [6]. The $[V_2O_2(O_2)_4F]^{3-}$ ion in **2** probably consists of two pentagonal pyramidal groups of $VO(O_2)_2F$ which are connected *via* the shared fluorine atom similarly to the proposed structure of the anion in $(NH_4)_3[V_2O_2(O_2)_4F]$ [3]. In contrast to the latter compound, **2** is much more stable and can be stored at 5°C for a long time.

The IR spectrum of **3** (Table 1, Fig. 2a) exhibits bands which can be assigned to the vibrations of the VOV bridge. Especially, the strong and broad band at 785 cm^{-1} ($\nu_{as}(V–O–V)$), which lacks in the spectra of peroxo complexes of vanadium and which is present in divanadates with tetrahedral geometry around vanadium, is very characteristic. The complex contains only a small amount of peroxidic oxygen which is released at temperature above 120°C (for a sample mass of 150 mg and a heating rate of 2.5°C/min, the corresponding exothermic peak on the DTA curve is

Table 1. Characteristic infrared bands of **1**–**4**

1	2	3	4	Assignment
962vs	958 vs		996 s	$\nu(V{=}O)$
	949 vs		973 vs	
		925 vs		$\nu_s+\nu_{as}(VO_2)$
888 sh	880 s	870 vw	910 vs	$\nu(O_p–O_p)$
873 vs	868 vs		880 s	
		785 vs		$\nu_{as}(VOV)$
635 sh	645 sh	618 m	617 vs	$\nu(V–O_p)$
613 s	626 s	598 s	590 s	v(V–F)
540 w	598 m	578 sh	558 s	
457 m	527 w		485 m	
	465 m		459 w	
			424 vw	
			393 w	
		510 w		$\nu_s(VOV)$

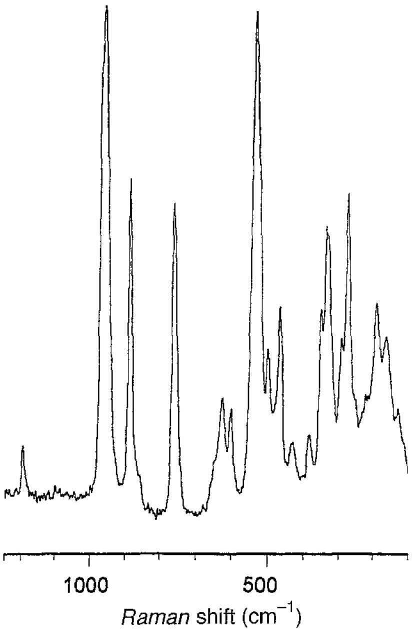


Fig. 1. *Raman* spectrum of $[N(CH_3)_4]_3[V_2O_2(O_2)_4F]$

located at 135°C). This indicates a considerable stability of the bound peroxo group; therefore, the presence of peroxidic oxygen as peroxohydrate is less probable. As can be seen from Fig. 2, the release of peroxidic oxygen causes only small changes in the infrared spectrum. On the basis of these results and chemical analysis as well, we formulate complex **3** as $[N(C_2H_5)_4]_2[V_2O_{5-x}(O_2)_xF_2]\cdot H_2O$ with a dimeric anion FO_2V-O-VO_2F in which partial substitution of oxygen by peroxo groups occurred.

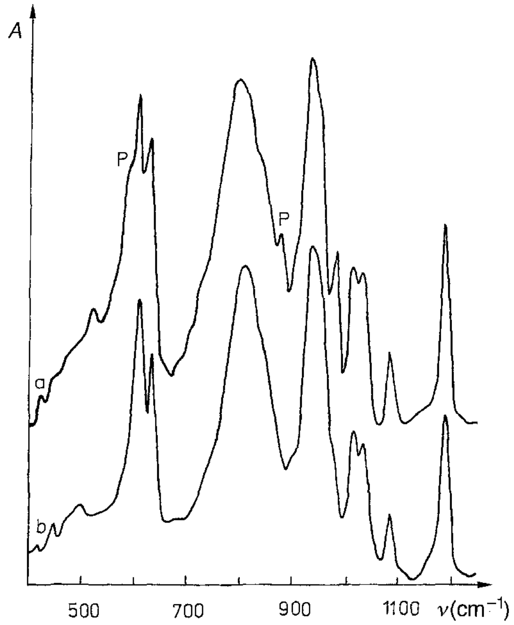
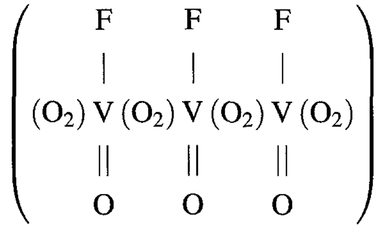


Fig. 2. IR spectrum of $[N(C_2H_5)_4]_2[V_2O_{5-x}(O_2)_xF_2]\cdot H_2O$($x \sim 0.25$, a) and the same complex after DTA up to 250°C(b); P indicates bands due to the peroxo oxygen

The red complex **4** [15] is the first example of a 3:4 ($V:O_2^{2-}$) stoichiometry for a vanadium peroxo complex. The IR spectrum of **4** (Table 1) exhibits bands of the $V=O$, $V\!<\!\overset{O}{\underset{O}{|}}$, and V-F groups and, in agreement with the expected oligonuclear structure, is rather complicated in the region of $V–O_p$ and V–F stretchings. Although **4** crystallizes in form of regular octahedral crystals, the compound decomposes under X-ray radiation. Therefore, no X-ray structure analysis could be performed. The structure proposal is not straightforward, but a trinuclear structure with $\mu-\eta_2,\eta_2$ peroxo groups



$$\left(\begin{array}{ccccccc} & F & & F & & F & \\ & | & & | & & | & \\ (O_2) & V & (O_2) & V & (O_2) & V & (O_2) \\ & \| & & \| & & \| & \\ & O & & O & & O & \end{array}\right)$$

seems to be the most probable.

Similarly to oxalatooxoperoxovanadates [16], the formation of fluorooxoperoxo complexes of vanadium is strongly dependent on the size of the NR_4^+ cation. Whereas solid tetramethylammonium complexes are analogous to the known alkali metal and ammonium complexes, the complexes with tetraethylammonium and tetrabutylammonium cations are completely different. Using the tetraethyl ammonium cation, only a slightly peroxidated compound was obtained. The complex with tetrabutylammonium cation has a unique stoichiometry and probably a trinuclear structure.

Experimental

Elemental analyses were performed according to Ref. [3]. C, H, N were determined on a Carlo Erba CHN analyzer. IR spectra were recorded with Specord M-80 (Zeiss) and Nicolet 750 Magna FTIR spectrometers as Nujol mulls. The *Raman* spectrum of (**2**) was measured with a Nicolet Raman 950 spectrometer. The thermoanalytical curves were registered on a Derivatograph Q 1500 D (MOM Budapest). We could not obtain suitable single crystals for X-ray analyses. However, powder diffraction patterns were obtained on a Philips diffractograph equipped with a PW 1050 goniometer. For the strongly hygroscopic compounds **3** and **4**, the measurements were performed in silicon oil.

$[N(CH_3)_4]_2[VO(O_2)_2F]\cdot 2H_2O$ (**1**)

V_2O_5 (0.91 g, 5 mmol) was dissolved in an aqueous solution of $N(CH_3)_4OH$ (25%, 11 cm^3, 30 mmol). After filtration and evaporation of the solvent on a water bath, the solid residue was cooled (0°C) and dissolved in cold H_2O_2 (30%, 2.5 cm^3). To the yellow solution HF (40%, 0.9 cm^3) was added ($pH \sim 7$). After several days, yellow crystals were isolated from the solution standing at 0°C.

Calcd.: C 28.75%, H 7.24%, N 8.38%, F 5.95%, V 15.24%, O_2^{2-} 19.15%; found: C 28.86%, H 8.29%, N 8.34%, F 5.82%, V 15.77%, O_2^{2-} 18.91%. The hygroscopic complex is stable for several days when stored at 0°C above silica gel. Interplanar distances and relative intensities (nm (I_{rel})) for ten most intensive diffractions: 0.785(75), 0.677(32), 0.626(33), 0.609(43), 0.536(100), 0.411(56), 0.388(29), 0.379(35), 0.361(46), 0.346(27).

$[N(CH_3)_4]_3[V_2O_2(O_2)_4F]$ (**2**)

V_2O_5 (0.91 g, 5 mmol) was dissolved in an aqueous solution of $N(CH_3)_4OH$ (25%, 14.6 cm^3, 40 mmol). To the cooled solution (0°C), cold H_2O_2 (30%, 4 cm^3) and HF (40%, 1.75 cm^3) were added (*pH* 5–6). Ethanol (200 cm^3) was then added under continous stirring. The yellow precipitate formed was filtered off and dried at 5°C. Yellow crystals in form of hexagonal plates were obtained from the filtrate after 12 h of standing in dessiccator over P_2O_5 at 5°C. Both products were identical according to elemental analyses and IR spectra.

Calcd.: C 28.63%, H 7.20%, N 8.35%, F 3.77%, V 20.24%, O_2^{2-} 25.43%; found: C 28.70%, H 7.38%, N 8.23%, F 3.78%, V 20.02%, O_2^{2-} 25.34% **2** is stable at 5°C. Interplanar distances and relative intensities (nm(I_{rel})) for ten most intensive diffractions: 0.958(37), 0.721(61), 0.675(100), 0.479(16), 0.417(82), 0.400(20), 0.383(7), 0.355(5), 0.339(25), 0.315(6).

$[N(C_2H_5)_4]_2[V_2O_{5-x}(O_2)_xF_2]\cdot H_2O$ ($x \sim 0.25$, **3**)

V_2O_5 (0.7585 g, 4.25 mmol) was dissolved in an aqueous solution of $N(C_2H_5)_4OH$ (35%, 8.2 cm^3, 57 mmol). After filtration and evaporation of the solvent (water bath), the solid residue was cooled and dissolved in cold H_2O_2 (30%, 4 cm^3). To the solution, HF (40%, 0.4 cm^3) was added. Light violet crystals were obtained after 5 days of standing at 5°C. The hygroscopic products is stable for a long time when stored in desiccator over silica gel at 5°C.

Calcd. for $N(C_2H_5)_4]_2[V_2O_{4.75}(O_2)_{0.25}F_2]\cdot H_2O$: C 38.25%, H 8.43%, N 5.58%, F 7.56%, V 20.28%, O_2^{2-} 1.59%; found: C 39.66%, H 8.73%, N 5.64%, F 7.28%, V 20.16%, O_2^{2-} 1.57%. Interplanar distances and relative intesities (nm (I_{rel})) for ten most intensive diffractions: 0.842(44), 0.776(100), 0.686(87), 0.446(59), 0.442(41), 0.419(55), 0.411(19), 0.374(58), 0.368(29), 0.331(28).

$[N(C_4H_9)_4]_2[V_3O_3(O_2)_4F_3]\cdot 6H_2O$ (**4**)

V_2O_5 (0.6068 g, 3 mmol) was dissolved in an aqueous solution of $N(C_4H_9)_4OH$ (0.88 *M*, 7 cm^3, 125 mmol). After evaporation of the solvent (water bath), the solid residue was cooled to 0°C and dissolved in cold H_2O_2 (3%,17.3 cm^3). After addition of HF (40%, 0.7 cm^3) to this solution, an orange substance was precipitated and filtered off. The red crystals of **4** were isolated from the filtrate after standing for several hours at 0°C. Calcd.: C 39.23%, H 8.65%, N 2.86%, F 5.82%, V 15.61%, O_2^{2-} 13.08%; found: C 39.77%, H 8.25%, N 2.98%, F 6.20%, V 15.80%, O_2^{2-} 13.70%. The compound decomposes under X-ray radiation.

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