

Composition of the fluorooxoperoxo complexes of vanadium(V) crystallizing from acid medium

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Some problems involved in the determination of composition of the fluoro-oxoperoxo complexes of vanadium(V) obtained from acid medium are discussed in this paper. Owing to low stability of these complexes, the prepared substances may contain decomposition products, which results in a decrease in content of the peroxidic oxygen and formulation of the obtained substances as complexes with the ratio $n(\text{O}_2^-)/n(\text{V}) = 1$. The existence of the fluorooxoperoxo complexes of this type has not been hitherto confirmed.

В работе обсуждаются вопросы, связанные с определением состава фтор-оксо-пероксокомплексов ванадия(V), полученных из кислой среды. Вследствие малой устойчивости комплексов, полученные вещества могут содержать продукты разложения, что ведет к снижению содержания перекисного кислорода и к возможному описанию полученных соединений как комплексов с отношением $n(\text{O}_2^-)/n(\text{V}) = 1$. Существование фтор-оксо-пероксокомплексов этого типа не было до сих пор подтверждено.

Since 1974, when the first paper dealing with the preparation of the fluorooxoperoxo complexes of vanadium(V) was published [1], the preparation of several complexes of this type [2—10] has been described (Table 1). The composition of the complexes listed in Table 1 is different though the conditions of syntheses are, to a great degree, analogous. In this paper, we are going to point out the problems accompanying the determination of composition of the fluorooxoperoxo complexes of vanadium(V) and to elucidate some inconsistency of the published data.

The composition of ions in aqueous solutions of the oxoperoxo complexes of vanadium(V) has been quite reliably examined by the use of UV, VIS, Raman, and ^{51}V NMR spectroscopy [11]. On the other hand, the data about the ions present in the solutions containing vanadium(V), hydrogen peroxide, fluoride of an alkaline metal or hydrofluoric acid are, for the time being, missing and the composition of

Table 1

Summary of syntheses of fluorooxoperoxo complexes of vanadium(V) prepared from acid medium

Complex	Starting solution	$\theta/^\circ\text{C}^a$	Method of isolation	Published data ^b	Ref.
$(\text{NH}_4)_2[\text{VO}(\text{O}_2)\text{OHF}_2]$ orange	To saturated solution of V_2O_5 (1 g) in 40 % HF 12 cm ³ of solution of NH_4F (2 g NH_4F in 12 cm ³ 6 % H_2O_2) were added.	5	Crystallization	IR X-Ray PTD	[2]
$\text{K}_4[\text{V}_2\text{O}_3(\text{O}_2)_2\text{F}_4]$ orange	To saturated solution of V_2O_5 (1 g) in 40 % HF 12 cm ³ of solution of KF (5.1 g KF in 12 cm ³ 6 % H_2O_2) were added.	5	Crystallization	IR X-Ray PTD	[2]
$\text{K}_2[\text{V}_2\text{O}_3(\text{O}_2)_2\text{F}_2]$ dark-yellow	To 10 cm ³ of solution of V_2O_5 (1 g in 10 cm ³ HF) 10 cm ³ of solution of H_2O_2 and solution of KOH (1.2 g KOH in 5 cm ³ H_2O) were added.	0	Solution poured into methanol	IR R	[3]
$\text{K}_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot 2\text{H}_2\text{O}$ orange	To 20 cm ³ of solution of KVO_3 (1.38 g KVO_3 in 20 cm ³ H_2O) 4 cm ³ 20 % H_2O_2 and 1.56 g KHF_2 were added.	5	Crystallization	IR R X-Ray PTD	[4, 5]
$(\text{NH}_4)_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot 2\text{H}_2\text{O}$ dark-orange	1.17 g NH_4VO_3 was dissolved at $\theta \approx -25^\circ\text{C}$ in 3 cm ³ 30 % H_2O_2 ; 5 cm ³ 40 % HF and 12 cm ³ of ethanol were added into the solution.	-25	Crystallization (separation after 3 h)	IR X-Ray	[4]; this paper

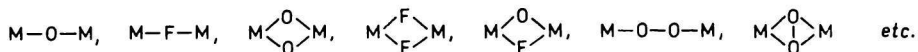
Table 1 (Continued)

Complex	Starting solution	$\theta/^\circ\text{C}^a$	Method of isolation	Published data ^b	Ref.
$(\text{NH}_4)_3[\text{V}(\text{O}_2)_2\text{F}_4]$ red-brown	To the solution of V_2O_5 in 30 % HF H_2O_2 was added. pH of solution was adjusted to 4—6.	—	—	—	[1]
$\text{K}_2[\text{VO}(\text{O}_2)_2\text{F}]$ yellow	0.91 g V_2O_5 and 5.81 g KF were heated in 100 cm^3 H_2O , till a yellow solution was formed. To the solution 10 cm^3 30 % H_2O_2 were added.	10	Crystallization after addition of ethanol	IR PTD CS	[6—8]
$(\text{NH}_4)_2[\text{VO}(\text{O}_2)_2\text{F}]$ orange	1.17 g NH_4VO_3 was dissolved in 14 cm^3 18 % H_2O_2 . 4.44 g NH_4F were added into the solution.	0	Crystallization	IR CS	[4, 9]
$(\text{NH}_4)_3[\text{V}_2\text{O}_2(\text{O}_2)_4\text{F}] \cdot n\text{H}_2\text{O}$ yellow	A. 1.17 g NH_4VO_3 was dissolved in 20 cm^3 15 % H_2O_2 . B. 1.11 g NH_4F was dissolved in 20 cm^3 15 % H_2O_2 . Solutions A and B were cooled and joined.	0	By means of ethanol (-25°C) Precipitate immediately separated	IR	[4]
$(\text{NH}_4)_3[\text{VO}(\text{O}_2)_2\text{F}_2]$ dark-yellow	0.585 g NH_4VO_3 was dissolved in 20 cm^3 30 % H_2O_2 . 11.1 g NH_4F was added into the solution.	0	Crystallization	CS	[10]; this paper

a) Temperature of solution during crystallization (before precipitation).

b) IR — infrared spectrum, R — Raman spectrum, X-Ray — X-ray diffraction pattern, PTD — products of thermal decomposition, CS — crystal structure.

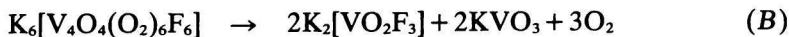
the solid complexes cannot be compared with the composition of the ions present in a solution. Moreover, the variability of hypothetical coordination polyhedrons containing oxo, peroxy, and fluoro ligands bonded to the vanadium atom is considerable even for the assumed coordination number 6 or 7. This variability results from the fact that all three ligands may be bonded either as terminal or bridged ligands while the bridges may be of different type, e.g.



A fairly thorough study of the products crystallizing from the systems $MVO_3-MF(HF)-H_2O_2-H_2O$ ($M = K, NH_4$) has revealed that the main products are complexes $M_2[VO(O_2)_2F]$ which crystallize from slightly acid solutions ($pH \approx 5$) and complexes $M_3[HV_2O_2(O_2)_3F_4] \cdot 2H_2O$ which crystallize from more acid solutions ($pH \approx 3$). Under certain conditions, we can obtain an unstable complex $(NH_4)_3[V_2O_2(O_2)_4F]$ from these systems. A formation of complexes with the ratio $n(O_2^{2-})/n(V) = 1$ was not observed [4]. *Stomberg* has found that a long standing of the crystals $(NH_4)_2[VO(O_2)_2F]$ in the crystallization solution brings about their transformation in a new complex $(NH_4)_3[VO(O_2)_2F_2]$ in some cases [10]. The reproducible preparation of this substance is described in Table 1.

An important factor which may affect the obtained experimental results is instability of these complexes. Most fluorooxoperoxy complexes of vanadium(V) decompose in the course of measurements of Raman spectra (especially if argon laser is used) and in the case of $(NH_4)_3[V_2O_2(O_2)_4F]$ the decomposition was observed during measurement of the infrared spectrum. A decomposition of the complexes during the record of X-ray diffraction patterns is also not out of the question. If we want to characterize the complexes by using these methods, we have to know the spectra and X-ray diffraction patterns of the decomposition products which come into consideration, i.e. fluorooxy complexes of vanadium(V) and corresponding vanadates*.

The complexes $M_2[VO(O_2)_2F]$ are relatively stable, $K_2[VO(O_2)_2F]$ decomposes at temperatures over $100^\circ C$ [8]. The complexes $M_3[HV_2O_2(O_2)_3F_4] \cdot 2H_2O$ are less stable. $K_3[HV_2O_2(O_2)_3F_4] \cdot 2H_2O$ slowly decomposes at temperatures under $50^\circ C$ and the proceeding decomposition reactions may be expressed by the following equations [5]



* According to our results, the fluorooxoperoxy complexes of vanadium(V) decompose especially in the course of crystallization from solutions which have been considerably acidified with hydrofluoric acid. The products isolated from these solutions are less stable and frequently decompose, e.g. during drying.

The decomposition of $(\text{NH}_4)_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot 2\text{H}_2\text{O}$ is more complicated and only the complex $(\text{NH}_4)_3[\text{V}_2\text{O}_4\text{F}_5]$ has been identified as reaction intermediate so far [12].

Tables 2—4 contain some published data about the complexes $(\text{NH}_4)_2[\text{VO}(\text{O}_2)\text{OHF}]$, $\text{K}_4[\text{V}_2\text{O}_3(\text{O}_2)_2\text{F}_4]$, and $\text{K}_2[\text{V}_2\text{O}_3(\text{O}_2)_2\text{F}_2]$ as well as about the substances

Table 2

X-Ray diffraction patterns of $(\text{NH}_4)_2[\text{VO}(\text{O}_2)\text{OHF}_2]$, $(\text{NH}_4)_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot 2\text{H}_2\text{O}$, and $(\text{NH}_4)_3[\text{V}_2\text{O}_4\text{F}_5]$

$(\text{NH}_4)_2[\text{VO}(\text{O}_2)\text{OHF}_2]$ [2]		$(\text{NH}_4)_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot 2\text{H}_2\text{O}^a$ This paper		$(\text{NH}_4)_3[\text{V}_2\text{O}_4\text{F}_5]^b$ [13]	
<i>d</i> /nm	<i>I_r</i> /%	<i>d</i> /nm	<i>I_r</i> /%	<i>d</i> /nm	<i>I_r</i> /%
0.588	40	0.584	74	—	—
0.537	20	0.535	14	—	—
0.518	100	0.523	15	0.518	100
0.422	10	—	—	0.423	5
0.412	10	—	—	—	—
0.394	10	0.394	49	—	—
0.362	10	—	—	0.364	16
0.352	10	0.353	27	—	—
0.330	10	0.331	25	—	—
0.322	10	0.322	14	—	—
0.315	10	—	—	0.313	4
0.297	30	—	—	0.299	19
0.286	10	—	—	—	—
0.229	40	—	—	0.229	4
0.213	20	—	—	0.212	2
0.177	10	—	—	0.1775	5

a) Other diffractions for $(\text{NH}_4)_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot 2\text{H}_2\text{O}$ ($I_r > 10\%$): 0.306, 0.255, 0.246, 0.205. The most intensive line for $d = 0.610$ is outside the investigated region.

b) Other diffractions for $(\text{NH}_4)_3[\text{V}_2\text{O}_4\text{F}_5]$ ($I_r > 5\%$): 0.243.

arising in decomposition of fluoroxyperoxo complexes of vanadium(V). It is obvious from Tables 2 and 3 that the diffraction patterns of $(\text{NH}_4)_2[\text{VO}(\text{O}_2)\text{OHF}_2]$ and $\text{K}_4[\text{V}_2\text{O}_3(\text{O}_2)_2\text{F}_4]$ may be almost fully made up from the diffraction patterns of $(\text{NH}_4)_3[\text{HV}_2\text{O}_2(\text{O}_2)_3\text{F}_4] \cdot 2\text{H}_2\text{O}$, and $(\text{NH}_4)_3[\text{V}_2\text{O}_4\text{F}_5]$ or $\text{K}_6[\text{V}_4\text{O}_4(\text{O}_2)_6\text{F}_6]$, $\text{K}_2[\text{VO}_2\text{F}_3]$, and KVO_3 . An analogous result may be obtained by comparing the infrared spectra of these substances [2, 4, 13] or [2, 5, 13, 15]. The vibrational spectra of $\text{K}_2[\text{V}_2\text{O}_3(\text{O}_2)_2\text{F}_2]$ (Table 4) are difficult to be distinguished from the

Table 3

X-Ray diffraction patterns of $K_4[V_2O_3(O_2)_2F_4]$,
 $K_6[V_4O_4(O_2)_6F_6]$, $K_2[VO_2F_3]$, and KVO_3

$K_4[V_2O_3(O_2)_2F_4]$ [2]		$K_6[V_4O_4(O_2)_6F_6]^a$ [5]		$K_2[VO_2F_3]^b$ [13]		KVO_3 [14]	
<i>d</i> /nm	<i>I_r</i> /%	<i>d</i> /nm	<i>I_r</i> /%	<i>d</i> /nm	<i>I_r</i> /%	<i>d</i> /nm	<i>I_r</i> /%
0.620	50	0.614	25	0.618	29	—	
0.572	40	—		0.568	61	—	
0.519	50	0.524	15	—		—	
0.510	50	—		0.506	7	—	
0.500	50	0.501	100	—		—	
0.419	40	0.418	11	0.418	33	—	
0.349	40	0.348	28	—		—	
0.342	40	0.341	15	—		—	
0.330	80	0.329	64	—		—	
0.315	90	0.318	26	0.316	74	—	
0.310	100	0.310	59	0.310	100	0.311	100
0.300	30	—		0.299	25	—	
0.289	40	0.289	21	—		—	
0.286	30	—		0.286	16	—	
0.282	50	—		—		0.283	98
0.226	60	—		0.226	47	—	
0.209	70	0.208	22	—		—	

a) Other diffractions for $K_6[V_4O_4(O_2)_6F_6]$ ($I_r > 20\%$): 0.411, 0.322.

b) Other diffractions for $K_2[VO_2F_3]$ ($I_r > 20\%$): 0.218.

Table 4

Infrared and Raman spectra of $K_2[V_2O_3(O_2)_2F_2]$,
 KVO_3 , $K_2[VO_2F_3]$, and $K_6[V_4O_4(O_2)_6F_6]$

$K_2[V_2O_3(O_2)_2F_2]$ [3]		KVO_3 [15]		$K_2[VO_2F_3]$ [13]	$K_6[V_4O_4(O_2)_6F_6]^a$ [5]
IR $\tilde{\nu}/\text{cm}^{-1}$	R $\tilde{\nu}/\text{cm}^{-1}$	IR $\tilde{\nu}/\text{cm}^{-1}$	R $\tilde{\nu}/\text{cm}^{-1}$	IR $\tilde{\nu}/\text{cm}^{-1}$	IR $\tilde{\nu}/\text{cm}^{-1}$
	995 vw				
980 s	985 vw				979 vs
970 s	960 vw	960 w	950 w		
930 s	935 vs	935 vs	940 s	930 s	920 s
	925 vs				
	905 w		910 m		
890 s	890 w	890 w		895 s	900 s

Table 4 (Continued)

$K_2[V_2O_5(O_2)_2F_2]$ [3]		KVO_3 [15]		$K_2[VO_2F_3]$ [13]	$K_6[V_4O_4(O_2)_6F_6]^{4-}$ [5]
IR $\tilde{\nu}/\text{cm}^{-1}$	R $\tilde{\nu}/\text{cm}^{-1}$	IR $\tilde{\nu}/\text{cm}^{-1}$	R $\tilde{\nu}/\text{cm}^{-1}$	IR $\tilde{\nu}/\text{cm}^{-1}$	IR $\tilde{\nu}/\text{cm}^{-1}$
860 s		850 s			856 m
690 s, b		693 s, b			
	645 s		648 m		
	630 s				
570 s				575 m	580 s
550 s				544 s	
530 s	525 s		520 w	522 s	520 m
510 s	500 s	495 w	498 s		500 m
430 m	430 m			434 w	
390 w	380 w	385 m	383 w		
350 s	355 w	352 w	362 m		360 s
320 s	325 vs	318 s	322 m		332 s
280 w	290 s	262 w			275 w
220 w	240 vs	219 w	230 s		232 m

a) Other bands for $K_6[V_4O_4(O_2)_6F_6]^{4-}$: 610 s.

spectra of a mixture of decomposition products of the complex $K_3[HV_2O_2(O_2)_3F_4] \cdot 2H_2O$. From this view-point, the intensive and broad band of the stretching vibration $\nu_{as}(V-O-V)$ is especially characteristic (at about 690 cm^{-1} in infrared spectrum). It does not appear in the spectrum of any known peroxo complex of vanadium(V) [16]. With respect to these facts, it may be that the fluoroperoxo complexes of vanadium(V) with the ratio $n(O_2^{2-})/n(V) = 1$ given in Table 1 are not pure substances.

As for other complexes listed in Table 1, the existence of the complex $(NH_4)_3[V(O_2)_2F_4]$ has not been confirmed. This complex is not sufficiently characterized in paper [1] and the attempts to prepare it have not been successful.

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