Tetraalkylammonium Oxalatooxoperoxovanadates

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The oxalatooxoperoxo complexes of vanadium(V) $[N(CH_3)_4]_3[VO(O_2)(C_2O_4)_2] \cdot 1.8H_2O \cdot 0.2H_2O_2$, $[N(CH_3)_4]_3[VO(O_2)_2(C_2O_4)] \cdot 3H_2O$, and $[N(C_2H_5)_4][VO(O_2)(C_2O_4)] \cdot 0.5H_2O$ were prepared. While the first two complexes are analogous to the corresponding monomeric complexes with alkali metal cations, the third one differs from all the known oxalatooxoperoxovanadates in the stoichiometry and properties and has probably a polymeric structure. Tetrabutylammonium complexes, the existence of which in solution can be supposed based on spectrophotometric measurements, were not obtained in the solid state.

Vanadium(V) peroxo complexes play an important role as oxygen transfer reagents in catalytic oxidations of organic compounds with hydrogen peroxide. To use such complexes in oxidation reactions, it is necessary to have substances soluble in organic solvents. For anionic complexes, this solubility can be achieved by the exchange of an inorganic for organic cation, usually of the NR_4^+ (R-alkyl) type.

Substances, potentially efficient in oxygen transfer reactions, are the oxalato complexes. The first syntheses of vanadium(V) oxalatooxoperoxo complexes $M_3[VO(O_2)_2(C_2O_4)] \cdot 2H_2O$ (M = K^+, NH_4^+) were reported by *Vuletić* and *Djordjević* [1], the crystal structure of potassium salt was solved later by *Begin et al.* [2]. The preparation of the first bis-(oxalato) complex of the approximate composition $K_3[VO(O_2)(C_2O_4)_2] \cdot H_2O$ was published by us [3]. The crystal structure determination of this complex by *Stomberg* [4] showed that the peroxide is bound partly as a ligand in the complex anion and partly as peroxohydrate, so the formula revealed by structural analysis is $K_3[VO_{1+x}(O_2)_{1-x}(C_2O_4)_2] \cdot (0.5 - y)H_2O \cdot yH_2O_2$ (x = 0.2, y = 0.1). Both the monooxalato and bis(oxalato) salts contain monomeric anions with a pentagonal bipyramidal structure. Besides the usual coordination to the central atom as bidentate ligands, the peroxide and oxalate ions can form also various types of bridges between vanadium atoms:
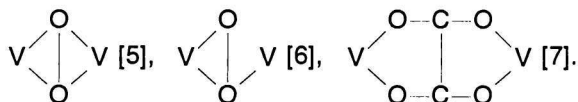
The formation of different structural types is often dependent on the cation properties.

This paper deals with the synthesis and characterization of tetraalkylammonium oxalatooxoperoxo-vanadates. In order to address the problem of relation between the cation properties and the structure of complexes, NR_4^+ cations with various alkyl chain length were used.

EXPERIMENTAL

Elemental analyses were carried out on a CHN analyzer (Erba). Vanadium was determined as V_2O_5 after annealing the sample in a Pt crucible. Titration of complexes with potassium permanganate yielded the sum of O_2^{2-} and $C_2O_4^-$. The peroxide content was calculated from the oxalate content which was derived from carbon analysis or determined after separation of CaC_2O_4.

The infrared spectra were measured with a spectrophotometer Specord M-80 by the nujol method. The electron spectra were recorded on a Hewlett—Packard 84-52A apparatus. The thermoanalytical curves were registered on a derivatograph Q 1500 D (MOM, Budapest).

$[N(CH_3)_4]_3[VO(O_2)(C_2O_4)_2] \cdot 1.8H_2O \cdot 0.2H_2O_2$ (*I*)*

V_2O_5 (0.182 g; 1 mmol) was dissolved in 5.4 cm^3 of 10 % aqueous solution of $N(CH_3)_4OH$. After filtration and evaporation of the solvent in a water bath, the solid vanadate was cooled to -25 °C and solution of $H_2C_2O_4 \cdot 2H_2O$ (0.504 g; 4 mmol) in 4 cm^3 of ethanol and 0.5 cm^3 of 30 % H_2O_2 were added. The obtained red solution was allowed to crystallize at 5 °C. Dark red crystals were isolated after two days and washed with ethanol.

For compound *I* w_i(calc.): 7.83 % N, 35.81 % C, 7.51 % H, 9.49 % V, 7.16 % O_2^{2-}; w_i(found): 7.48 % N, 36.25 % C, 7.90 % H, 9.16 % V, 7.05 % O_2^{2-}.

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*Composition in mass fractions.

$[N(CH_3)_4]_3[VO(O_2)_2(C_2O_4)] \cdot 3H_2O$ (*II*)

V_2O_5 (0.182 g; 1 mmol) was dissolved in 5.4 cm^3 of solution of $N(CH_3)_4OH$ (10 %). After filtration and evaporation the residue was cooled (− 25 °C) and solution of $H_2C_2O_4 \cdot 2H_2O$ (0.252 g; 2 mmol) in 4 cm^3 of 8 % H_2O_2 was added. The obtained orange solution was allowed to stand at 5 °C. The yellow microcrystalline compound isolated after several days was washed with ethanol and dried in a desiccator over silica gel.

For compound *II* w_i(calc.): 8.48 % N, 33.93 % C, 8.55 % H, 10.28 % V, 12.92 % O_2^{2-}; w_i(found): 8.55 % N, 33.96 % C, 8.58 % H, 9.87 % V, 12.00 % O_2^{2-}.

Both the tetramethylammonium complexes are very soluble in water. The electron spectra of their aqueous solutions exhibit bands characteristic of vanadium(V) monoperoxo and diperoxo complexes (λ_{max} = 440 nm for *I* and 330 nm for *II*).

$[N(C_2H_5)_4][VO(O_2)(C_2O_4)] \cdot 0.5H_2O$ (*III*)

V_2O_5 (0.91 g; 5 mmol) was dissolved in 10 cm^3 of $N(C_2H_5)_4OH$ solution (c = 1 mol dm^{-3}). The solution was filtered and $H_2C_2O_4 \cdot 2H_2O$ (1.26 g; 10 mmol) and 4 cm^3 of H_2O_2 (30 %) were added. After several days' standing at 5 °C a red microcrystalline product was isolated.

For compound *III* w_i(calc.): 4.29 % N, 36.82 % C, 6.49 % H, 15.61 % V, 9.81 % O_2^{2-}; w_i(found): 4.12 % N, 36.71 % C, 6.28 % H, 15.13 % V, 9.80 % O_2^{2-}.

In contrast to *I* and *II*, *III* is not hygroscopic, it is little soluble in water and practically insoluble in other solvents. The electron spectrum of saturated aqueous solution of *III* exhibits a band characteristic of monoperoxo complexes of vanadium (λ_{max} = 430 nm). During the thermal decomposition of the solid complex *III* under dynamic conditions (DTA), the peroxo oxygen is released at temperatures above 100 °C (for sample mass 70 mg and heating rate 2.5 °C min^{-1} the corresponding exothermic peak is at 135 °C). This indicates a considerable stability of *III*.

Solutions of complexes with tetrabutylammonium cation were prepared in the following way:

$[N(C_4H_9)_4]_3[VO(O_2)(C_2O_4)_2]$ (*IV*)

$H_2C_2O_4 \cdot 2H_2O$ (0.214 g) was dissolved in 2.3 cm^3 of $N(C_4H_9)_4OH$ solution (c = 0.75 mol dm^{-3}) and cooled to 0 °C (solution A).

V_2O_5 (0.0773 g) was dissolved in 1.15 cm^3 of the same solution of $N(C_4H_9)_4OH$. The obtained solution was evaporated on a water bath and 1 cm^3 of H_2O and 0.5 cm^3 of H_2O_2 (30 %) were added at 0 °C to the residue (solution B). The solutions A and B were mixed at 0 °C and the resulting yellow solution was filtered.

$[N(C_4H_9)_4]_3[VO(O_2)_2(C_2O_4)]$ (*V*)

The similar procedure was used as for the preparation of *IV* but 0.107 g of $H_2C_2O_4 \cdot 2H_2O$ was used for preparation of A and 0.5 cm^3 of H_2O and 1 cm^3 of H_2O_2 (30 %) for preparation of B.

At the electron spectra measurements the solution of *IV* or *V* (0.1 cm^3) was added to the solvent (1.9 cm^3) thus forming either a one-phase (H_2O, H_2O—CH_3CN) or a two-phase (H_2O—CH_2Cl_2) system in which the complex was transferred into the organic solvent.

RESULTS AND DISCUSSION

The red complex *I* contains, like $K_3[VO_{1+x}(O_2)_{1-x}(C_2O_4)_2] \cdot (0.5-y)H_2O \cdot yH_2O_2$ (x = 0.2, y = 0.1), a part of the peroxo oxygen in the form of peroxohydrate. The characteristic infrared bands of the $VO(O_2)$ group (Table 1) are in the region typical of monoperoxo complexes [8]: $\nu(V=O)$ and $\nu(O_p—O_p)$ (O_p is a peroxo oxygen) at $\tilde{\nu}$ = 935 cm^{-1} and 925 cm^{-1} and $\nu(V—O_p)$ at $\tilde{\nu}$ = 564 cm^{-1}. The infrared spectrum of *II* exhibits characteristic bands of the diperoxo group $VO(O_2)_2$ [9]: $\nu(V=O)$ at $\tilde{\nu}$ = 925 cm^{-1}, $\nu(O_p—O_p)$ at $\tilde{\nu}$ = 884 cm^{-1} and 870 cm^{-1}, and $\nu(V—O_p)$ at $\tilde{\nu}$ = 632 cm^{-1}, 592 cm^{-1}, and 483 cm^{-1}. Based on the position and intensity of bands corresponding to vibrations of the $VO(O_2)$ and $VO(O_2)_2$ groups, the usual monomeric pentagonal bipyramidal structure for anions in *I* and *II* can be proposed.

The situation is quite different with the complex *III*. The infrared spectrum (Table 1, Fig. 1) has features of the spectrum of a monoperoxo complex

Table 1. Characteristic Infrared Bands of the Prepared Compounds

$\tilde{\nu}/cm^{-1}$			Assignment[a]
I	*II*	*III*	
1680 vs	1667 vs	1702 s	$\nu_a(C=O)$
		1640 s	
		1606 s	
1407 s		1403 m	$\nu_s(CO) + \nu(CC)$
1277 s	1294 s	1352 s	$\nu_s(CO) + \sigma(O—C=O)$
		1310 s	
935 s	925 s	965 s	$\nu(V=O)$
925 m	885 m	946 s	$\nu(O_p—O_p)$
	870 s		
787 s	797 m	816 m	$\sigma(O—C=O) + \nu(VO_{ox})$[b]
564 m	632 m	555 m	$\nu(V—O_p)$
	592 m		
	483 m		

a) Assignment of bands of the coordinated oxalato group according to [10]. b) O_{ox} – oxygen from the oxalato group.
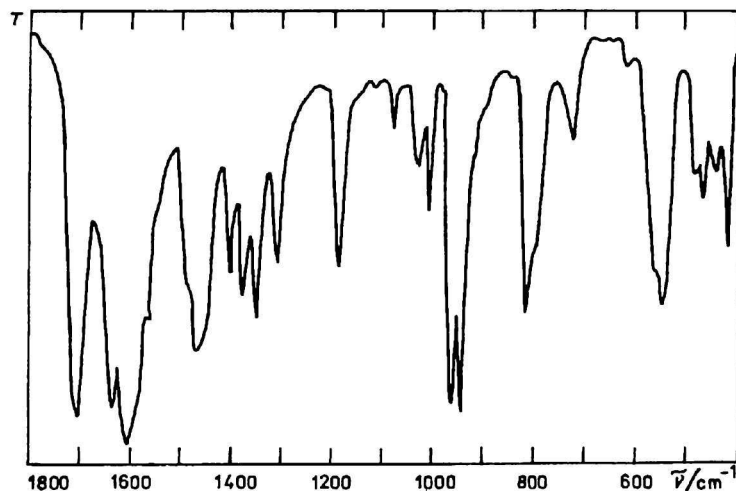
Fig. 1. Infrared spectrum of $[N(C_2H_5)_4][VO(O_2)(C_2O_4)] \cdot 0.5H_2O$.

but a greater number of bands corresponding to C—O stretching vibrations indicates a lower bonding symmetry of the oxalato group [10]. The stoichiometry of *III* does not allow to make a rational proposal of a monomeric structure based on coordination numbers six or seven observed for vanadium(V) peroxo complexes. Nevertheless, several polymeric structures with pentagonal pyramidal or pentagonal bipyramidal geometry around vanadium, *e.g.* a dimeric structure with a bridging water molecule, a tetrameric cyclic structure with bridging oxalato groups or a polymeric structure with η_2, η_2 peroxo groups, can be considered. All these structures are unusual and without X-ray analysis none of them can be preferred. In spite of considerable effort, we were not successful in isolating crystals suitable for X-ray measurements. The low solubility in water and the relatively high stability of the solid complex indicates its polymeric character.

The complexes with tetrabutylammonium cation were prepared only in solution. The electron spectrum of *IV* displays the typical CT band at $\lambda = 440$ nm. The shift of this band in comparison with the maximum for $[VO(O_2)(H_2O)_4]^+$ ($\lambda = 460$ nm) gives evidence for bonding of the oxalato group to vanadium. In addition to that, unlike $[VO(O_2)(H_2O)_4]^+$, the $[VO(O_2)(C_2O_4)_2]^{3-}$ ion has a negative charge and

so it can be transferred by means of NR_4^+ cation into organic phase. The stability of *IV* is solvent-dependent. In aqueous solution at 20 °C *IV* is stable for several hours while in CH_3CN and CH_2Cl_2 it is gradually decomposed (Table 2).

The characteristic CT band in the spectrum of *V* is in agreement with the published data for diperoxo complexes [11]. The stability of *V* in aqueous solution is considerable, but in CH_3CN at 50 °C it is decomposed in 30 min (Table 2, Fig. 2). An attempt to transfer *V* into CH_2Cl_2 failed – the corresponding electron spectrum displayed only a band of a monoperoxo complex. There is no satisfactory explanation for this phenomenon. *Di Furia et al.* [12] studying the monoperoxo-diperoxo complex equilibria in ethanol and dioxane did not observe the formation of a diperoxo complex in dioxane. They were able to rationalize this observation on the basis of depression of the acid dissociation constant of a diperoxo complex in the solvent with a low dielectric constant, but the complexes investigated were quite different from those presented here. The position of CT band for vanadium(V) diperoxo complexes is very little affected by substitution of ligands in the coordination sphere [12], therefore, the bonding of oxalato group to vanadium cannot be evidenced by a shift of this band. The large stability of

Table 2. Position of CT Bands and Stability of Complexes (Expressed as Absorbance Decrease)

Complex	Solvent	λ_{max}/nm	Stability
IV	H_2O	440	several hours without decrease of A^a (20 °C)
	CH_3CN	440	$A_{90} = 0.7\ A_0$ (20 °C)
	CH_2Cl_2	440	$A_{90} = 0.4\ A_0$ (30 °C)
V	H_2O	330	several days without change of A (5 °C)
			$A_{60} = A_0$ (80 °C)
	CH_3CN	330	$A_{60} = A_0$ (5 °C)
			full decomposition in 30 min (50 °C)
	CH_2Cl_2	440^b	

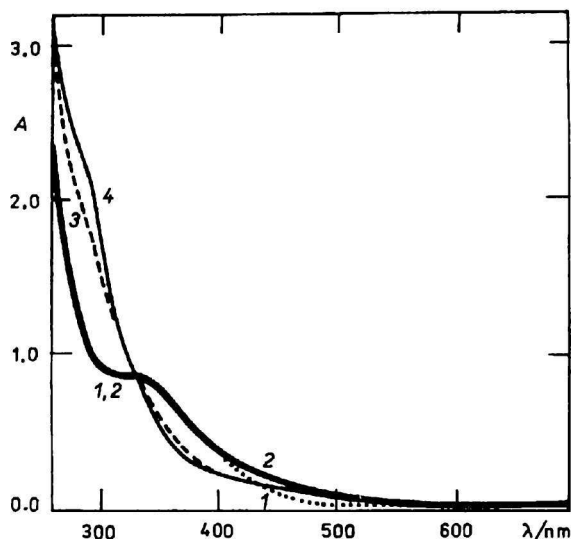*a) A – Absorption at λ_{max} with time in minutes in subscript. b) See the text.*

Fig. 2. Electron spectra of $[N(C_4H_9)_4]_3[VO(O_2)_2(C_2O_4)]$ in CH_3CN at 50 °C. *1.* Immediately after preparation of solution; *2.* after 15 min; *3.* after 30 min; *4.* after 45 min.

V in aqueous solution considerably exceeding the stability of $[VO(O_2)_2(H_2O)]^-$ can be, however, regarded as an indirect evidence for such bonding.

The formation of oxalatooxoperoxo complexes of vanadium(V) with tetraalkylammonium cations is strongly dependent on the alkyl chain length. While solid tetramethylammonium complexes are analogous to the known alkali metal complexes, with tetraethylammonium cation the formation of this type of complexes was not observed. Tetraethylammonium

complex has unusual stoichiometry and properties. The syntheses of solid tetrabutylammonium complexes were not successful.

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