

Oxalatooxoperoxo Complexes of Vanadium(V) with Organic Cations

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The oxalatooxoperoxovanadates(V) (H₃dien)[VO(O₂)(C₂O₄)₂]·H₂O (*I*), (H₃tren)[VO(O₂)(C₂O₄)₂]·3H₂O (*II*), (Hampic)₃[VO(O₂)(C₂O₄)₂]·2H₂O (*III*), and (Hampic)₃[VO(O₂)₂(C₂O₄)₂]·4H₂O (*IV*) (dien = diethylenetriamine, tren = tris(2-aminoethyl)amine, ampic = 2-amino-3-methylpyridine) have been prepared and characterized by elemental analyses and IR spectroscopy. Based on the position and intensity of the characteristic infrared bands, the usual monomeric pentagonal bipyramidal structure for anions in *I*–*IV* can be proposed. The proposed structure was confirmed for *II* by X-ray diffraction study. *II* crystallizes with triclinic cell $a = 895.8(2)$ pm, $b = 899.3(3)$ pm, $c = 1207.6(3)$ pm, $\alpha = 93.25(2)^\circ$, $\beta = 99.31(2)^\circ$, $\gamma = 90.86(2)^\circ$, space group *P*-1, $Z = 2$.

The first syntheses of oxalatooxoperoxovanadates M₃[VO(O₂)₂(C₂O₄)]·2H₂O (M = K, NH₄) were reported by Vuletić and Djordjević [1], the crystal structure of potassium salt was determined by Begín *et al.* [2]. The synthesis of the first bis(oxalato) complex was published by our group [3]. The structure determination of this complex showed [4] that the peroxide is bound partly as ligand and partly as peroxyhydrate. The formula revealed by structure analysis was K₃[VO_{1+x}(O₂)_{1-x}(C₂O₄)₂]·(0.5 – *y*)H₂O·*y*H₂O₂ ($x = 0.2$, $y = 0.1$). Both structurally characterized mono- and bis(oxalato)vanadates contain monomeric anions with approximate pentagonal bipyramidal structure. N(C₂H₅)₄[VO(O₂)(C₂O₄)]·0.5H₂O differs from other oxalatooxoperoxovanadates in stoichiometry and properties and has evidently polymeric structure [5].

Dien (diethylenetriamine), tren (tris(2-aminoethyl)amine), and ampic (2-amino-3-methylpyridine) can act either as ligands coordinating to central atom or, after protonation, as cations compensating the charge of the complex anions. The way in which they act is depending mainly on pH and concentration of other ligands present in solution.

This paper deals with the products obtained from the systems V₂O₅—oxalic acid—dien (tren, ampic)—H₂O₂—H₂O. All reactions lead to formation of oxalatooxoperoxovanadates with corresponding organic cation.

EXPERIMENTAL

Elemental analyses of C, H, N were carried out on a Carlo Erba 1106 CHN analyzer. Vanadium(V) was estimated after reduction to vanadium(IV) using ascorbic acid. An excess of standard EDTA solution was added to the obtained solution and the vanadium content was determined by a back titration with ZnCl₂ [6]. Peroxidic oxygen was determined by titration with KMnO₄.

Infrared spectra were measured on a Nicolet 750 Magna FTIR spectrometer with the samples as KBr pellets or nujol mulls.

Complexes *I*–*IV*

(H₃dien)[VO(O₂)(C₂O₄)₂]·H₂O (*I*)

V₂O₅ (0.091 g; 0.5 mmol) was dissolved in aqueous dien solution (5 cm³, $c = 0.2$ mol dm⁻³). Solution of oxalic acid (0.252 g; 2 mmol in 10 cm³ of H₂O and 1 cm³ of H₂O₂ (30 %)) was added under continuous stirring. The obtained red solution was allowed to crystallize at 5 °C. The light red crystals were isolated after 24 h.

For compound *I* w_i (calc.): 24.07 % C, 4.54 % H, 10.52 % N, 12.76 % V, 8.02 % O₂²⁻; w_i (found): 24.26 % C, 4.60 % H, 10.52 % N, 12.64 % V, 8.00 % O₂²⁻.

(H₃tren)[VO(O₂)(C₂O₄)₂]·3H₂O (*II*)

V₂O₅ (0.455 g; 2.5 mmol) was dissolved in aqueous

tren solution (20 cm³, $c = 0.25$ mol dm⁻³). Solution of oxalic acid (0.630 g; 5 mmol in 40 cm³ of H₂O and 3 cm³ of H₂O₂ (30 %)) was added under continuous stirring. The obtained solution was allowed to crystallize at 5 °C. Red crystals were isolated after 24 h.

For compound *II* w_i (calc.): 25.11 % C, 5.69 % H, 11.72 % N, 10.65 % V, 6.69 % O₂²⁻; w_i (found): 24.89 % C, 5.49 % H, 11.59 % N, 11.00 % V, 6.90 % O₂²⁻.

(Hampic)₃[VO(O₂)(C₂O₄)₂] · 2H₂O (*III*)

V₂O₅ (0.182 g; 1 mmol) was dissolved in aqueous ampic solution (50 cm³, $c = 0.12$ mol dm⁻³). Solution of oxalic acid (0.504 g; 4 mmol in 50 cm³ of H₂O and 1 cm³ of H₂O₂ (30 %)) was added under continuous stirring. The obtained solution was allowed to crystallize at 5 °C. Dark red crystals were isolated after 4 days.

For compound *III* w_i (calc.): 41.38 % C, 4.90 % H, 13.16 % N, 5.01 % O₂²⁻; w_i (found): 41.56 % C, 4.68 % H, 13.27 % N, 4.99 % O₂²⁻.

(Hampic)₃[VO(O₂)₂(C₂O₄)] · 4H₂O (*IV*)

V₂O₅ (0.182 g; 1 mmol) was dissolved in aqueous ampic solution (50 cm³, $c = 0.12$ mol dm⁻³). Solution of oxalic acid (0.252 g; 2 mmol in 50 cm³ of H₂O and 8 cm³ of H₂O₂ (30 %)) was added under continuous stirring. The obtained solution was allowed to crystallize at 5 °C. Yellow crystals were isolated after 4 days.

For compound *IV* w_i (calc.): 38.84 % C, 5.70 % H, 13.59 % N, 10.35 % O₂²⁻; w_i (found): 39.15 % C, 5.21 % H, 13.75 % N, 10.46 % O₂²⁻.

Crystal Structure Determination

The diffraction experiment was carried out on Kuma KM-4 four-circle kappa-axis diffractometer, equipped with Oxford Cryostream Cooler [7], fine focus sealed Mo tube, and a graphite monochromator. The diffractometer is controlled by Kuma KM-4 software that was also used for determination and refinement of cell parameters.

The phase problem was solved by direct methods using SHELXS [8]. SHELXL-97 (release 97-2) [8] was used to refine the structure. No correction for absorption was made. Refinements on F^2 for all reflections weighted R -factors wR and all goodnesses of fit S are based on F^2 , conventional R -factors are based on F , with F set to zero for negative F^2 . The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factor, etc. and is not relevant to the choice of reflections for refinement. All esd's are estimated using the full covariance matrix. The cell esd's are taken into account individually in the estimation of esd's in distances, angles. All atoms, other than hydrogens, were refined using anisotropic thermal parameters. There is a disorder involving alternate positions of peroxo (O1—O2) and "double bonded" oxygen (O3) groups (alternative groups are O1B—O2B and O3B). During

Table 1. Crystal Data and Structure Refinement for *II*

Empirical formula	C ₁₀ H ₂₇ N ₄ O ₁₄ V
M_r	478.30
Temperature	153(2) K
Wavelength	71.073 pm
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a = 895.8(2)$ pm $b = 899.3(3)$ pm $c = 1207.6(3)$ pm $\alpha = 93.25(2)^\circ$ $\beta = 99.31(2)^\circ$ $\gamma = 90.86(2)^\circ$
Z	2
Calculated density	1.658 g cm ⁻³
Absorption coefficient	0.598 mm ⁻¹
$F(000)$	500
Crystal size	0.60 × 0.60 × 0.30 mm
Θ range for data collection	1.71 to 25.06°
Limiting indices	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-14 \leq l \leq 0$
Reflections collected/unique	3252/3252
Completeness to $\Theta = 25.06^\circ$	95.5 %
Max. and min. transmission	0.8410 and 0.7155
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3252/10/380
Goodness-of-fit on F^2	0.848
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0391$, $wR2 = 0.1190$
R indices (all data)	$R1 = 0.0436$, $wR2 = 0.1251$

the refinement the sum of s.o.f.s was constrained to be unity. Bond lengths O—O and V—O were constrained to be similar in both major and minor groups. Refinement converged to occupation factor of 0.8(1).

Hydrogen atoms were refined isotropically, but temperature factors of H-atoms of water molecules were constrained. The results are given in Tables 1 and 2.

RESULTS AND DISCUSSION

All prepared compounds contain protonated organic amines as cations, bonding of nitrogen atoms to vanadium was not observed even in the case when pH was adjusted to neutral or slightly alkaline.

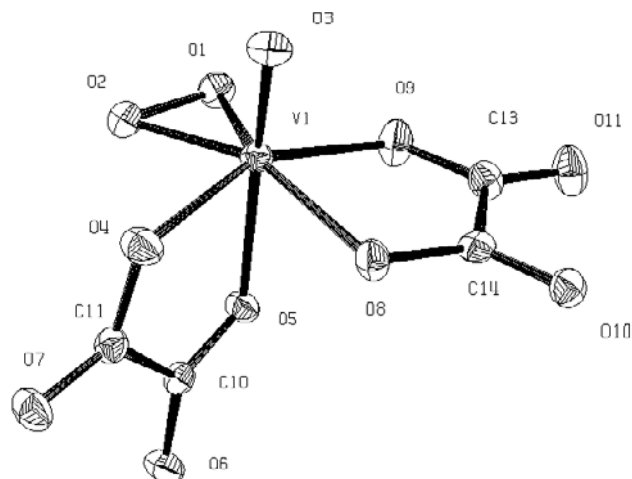
Infrared spectra of monoperoxo complexes *I*, *II*, and *III* (Table 3) exhibit characteristic bands of the VO(O₂) group [9, 10]. The bands near $\tilde{\nu} = 950$ cm⁻¹ are assigned to V=O stretches in agreement with a double-bond character of this bond. The O_p—O_p (O_p is peroxo oxygen) stretching modes, observed at $\tilde{\nu} \approx 930$ cm⁻¹, lie at higher wavenumbers than the corresponding bands in the spectra of diperoxo-vanadates which are near 880 cm⁻¹. This characteristic difference arises from the fact that the O_p—O_p bond lengths are significantly shorter for the monoperoxo complexes than for the diperoxo complexes of vanadium. The V—O_p stretching vibrations appear at about 550 cm⁻¹ what is the region characteristic of monoperoxo complexes and sub-

Table 2. Selected Bond Lengths/pm and Angles/° for *II*

V1—O1	187.5(4)
V1—O2	188.3(3)
V1—O3	162.4(3)
V1—O4	203.3(2)
V1—O5	214.5(2)
V1—O8	211.5(2)
V1—O9	201.8(2)
V1—O1B	186.4(6)
V1—O2B	187.3(6)
V1—O3B	162.3(6)
O1—O2	143.7(5)
O1B—O2B	144.3(7)
O3—V1—O1	102.62(15)
O3—V1—O2	99.10(14)
O1—V1—O1	44.96(14)
O3—V1—O9	99.81(16)
O1—V1—O9	77.63(14)
O2—V1—O9	122.16(11)
O3—V1—O4	93.28(16)
O1—V1—O4	123.02(14)
O2—V1—O4	78.84(12)
O9—V1—O4	152.49(10)
O2—V1—O8	156.23(11)
O9—V1—O8	76.74(9)
O4—V1—O8	79.02(9)
O1—V1—O5	89.60(11)
O2—V1—O5	87.13(10)
O9—V1—O5	85.93(9)
O4—V1—O5	77.02(8)
O8—V1—O5	79.57(8)
O2—O1—V1	67.80(2)
O1—O2—V1	67.23(17)

stantially different from the region of these vibrations for diperoxo complexes (see below). The profiles of the IR spectra of compounds *I*, *II*, and *III* in the region of the V=O, O_p—O_p, and V—O_p stretches are like those of K₃[VO(O₂)(Hedta)]·4H₂O (Hedta = ethylenediaminetetraacetato(3-)) [14], K₂[VO(O₂)(nta)]·2H₂O (nta = nitrilotriacetato(3-)) [15], and other seven coordinated vanadium(V) monoperoxo complexes with the known crystal structure. It is therefore likely that anions in *I*, *II*, and *III* possess pentagonal bipyramidal structure.

The IR spectrum of *IV* (Table 3) exhibits bands

**Fig. 1.** ORTEP drawing [16] of [VO(O₂)(C₂O₄)₂]³⁻.

typical for a diperoxo complex: at 918 cm⁻¹ (assigned to ν(V=O)), at 869 cm⁻¹ (due to the O_p—O_p stretch), and at 622 cm⁻¹, 590 cm⁻¹, and 484 cm⁻¹ (assigned to asymmetric and symmetric V—O_p stretching vibrations) [12]. The wavenumber span of the V—O_p stretching vibrations for vanadium diperoxo complexes is due to the interactions of two peroxo ligands in the equatorial plane more than 130 cm⁻¹ (138 cm⁻¹ for *IV*). Based on the positions of bands corresponding to V—O_p stretches [13] we propose a pentagonal bipyramidal structure for the anion in *IV*.

The structure proposal for *II* was confirmed by X-ray structure analysis. The crystals of *II* contain two formula units in the triclinic cell (Table 1). The H₃tren³⁺ cations, [VO(O₂)(C₂O₄)₂]³⁻ anions, and molecules of crystal water are held together by electrostatic forces and hydrogen bonds. The bond lengths and angles, which are in Table 2, are in the expected ranges. In the monomeric anion vanadium atom is coordinated by oxo group, η₂-peroxo group, and the two bidentate oxalato groups. The coordination about vanadium atom is that of distorted pentagonal bipyramide. The equatorial positions are occupied by a peroxo group (O1—O2) and three oxygen atoms of the oxalato groups (O4, O8, and O9). The axial positions

Table 3. Characteristic Infrared Bands ($\tilde{\nu}_1/\text{cm}^{-1}$) of the Prepared Compounds

<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	Assignment ^a
964 vs	943 vs	951 vs	918 s	ν(V=O)
940 vs	932 s	930 sh	869 vs	ν(O _p —O _p)
800 vs	797 s	796 vs	786 s	ν(C—O _{ox}) + δ(O=C—O _{ox}) + δ(C—C) ^b
780 m				
540 s	555 m	570 m	622 s	ν(V—O _p)
	535 s		590 s	
			484 m	

^a) Assignment of bands of the coordinated oxalato group according to [11].

^b) O_{ox} – oxygen atom from the oxalato group coordinated to central atom.

are taken by double-bonded oxygen atom (O3) and the last oxygen atom from the oxalato groups (Fig. 1).

The crystals of *II* are disordered in the sense that ligands have two orientations about the central atoms with mutually interchanged position of oxo and peroxo groups, similarly to the structure of potassium oxalatooxoperoxovanadate [4].

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