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Oxo Peroxo Glycolato Complexes of Vanadium(V). Crystal Structure of $(NBu_4)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot H_2O$

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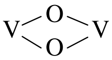
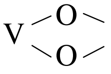
Summary. Oxo peroxo glycolato complexes of vanadium(V) ($M_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot nH_2O$ ($n = 0, 1$; $M = NBu_4^+$ (**1**), K^+ (**2**), NH_4^+ (**3**), Cs^+ (**4**), NPr_4^+ (**5**)) as well as $(NBu_4)_2[V_2O_4(C_2H_2O_3)_2] \cdot H_2O$ (**6**) have been prepared and characterized by spectroscopic methods. X-Ray structure analysis of **1** revealed the presence of dinuclear $[V_2O_2(O_2)_2(C_2H_2O_3)_2]^{2-}$ anions with a  $\mathrm{V}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{V}$ bridging core and six coordinated vanadium(V) atoms in a distorted pentagonal pyramidal array.

Keywords. Glycolatooxoperoxovanadates; IR spectra; ^{51}V NMR spectra.

Introduction

Transition metal peroxo complexes can play an important role in the catalytic oxidation of organic substrates by hydrogen peroxide [1, 2]. The versatility of their oxidative potential is impressive; thus, vanadium(V) peroxo complexes are able to oxidize alkenes, alcohols, ketones, sulfur and phosphorus derivatives, and even aromatic and aliphatic hydrocarbons [3, 4]. The reactivity of vanadium(V) peroxo complexes in oxidations depends strongly on the character of their heteroligands; nevertheless the relation between composition of the coordination sphere and reactivity is still poorly understood. For further reactivity studies, the synthesis of novel, structurally different complexes soluble in organic solvents is highly desiderable. Whereas the bonding of most heteroligands leads to the formation of mononuclear vanadium(V) peroxo complexes, α-hydroxycarboxylato ligands seem to enforce a dinuclear structure with the  $\mathrm{V}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{V}$ core. Such structures have been found in all three complexes of this type structurally characterized to date, *i.e.* citrato [5], malato [6], and *L*-tartrato [7] peroxo complexes of vanadium. The

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reactivity of α-hydroxycarboxylato peroxo complexes of vanadium(V) has not been studied so far, evidently because of the insolubility of the complexes in organic media.

This paper describes the synthesis and characterization of dinuclear oxo peroxo glycolato complexes of vanadium and the crystal structure of the first α-hydroxycarboxylato peroxo complex of vanadium soluble in organic solvents, $(NBu_4)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot H_2O$.

Results and Discussion

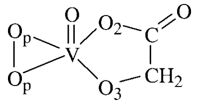
Synthesis and characterization

The orange-red or red glycolato complexes $M_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot nH_2O$ ($M = K^+, NH_4^+, Cs^+, NPr_4^+, NBu_4^+$; $n = 0, 1$) were obtained by crystallization from the system MVO$_3$–glycolic acid–H_2O_2–H_2O–(EtOH). Whereas the solid complexes are quite stable, their solutions in water or acetonitrile turned yellow at room temperature and then slowly to green due to the loss of peroxidic oxygen and reduction of vanadium(V) to vanadium(IV). The IR spectra of the prepared glycolato complexes (Table 1) allowed to draw some conclusions concerning the coordination mode of ligands. The alcoholic groups of the glycolato ligands are presumably deprotonated, as no IR bands occur in the region of ν(OH) vibrations for the anhydrous complexes $M_2[V_2O_2(O_2)_2(C_2H_2O_3)_2]$ ($M = Cs^+, NPr_4^+$). A monodentate coordination of the deprotonated carboxylate groups is apparent from

Table 1. Characteristic IR bands (cm^{-1}) for $M_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot nH_2O$($M = K^+, NH_4^+, Cs^+, NPr_4^+, NBu_4^+$; $n = 0, 1$)

K^+	NH_4^+	Cs^+	NPr_4^+	NBu_4^+	Assignment
3554 m 3308 w 3179 m	3250 sh			3532 m 3458 m	$\nu(H_2O)$
1628 vs	1653 vs	1665 vs	1665 vs 1653 vs	1667 vs 1651 vs	ν(C=O)
1366 vs	1351 vs	1350 vs	1345 s	1365 s 1351 s	$\nu(C{-}O_2)^a$
1090 s	1083 s	1089 s	1081 s	1076 s	$\nu(C{-}O_3)^a$
939 s	942 vs	941 vs	989 s? 973 m	978 s	ν(V=O)
923 s 916 m	914 vs	923 vs	919 s	929 vs 922 s	$\nu(O_p{-}O_p)^a$
591 m 551 w	572 m 554 m	573 m 549 m	579 m	584 m	$\nu(V{-}O_p)^a$

[a] Designation of atoms:



the positions of symmetric (*ca.* 1350 $\mathrm{cm^{-1}}$) and antisymmetric (*ca.* 1650 $\mathrm{cm^{-1}}$) stretching modes and from the Δ value of about 300 $\mathrm{cm^{-1}}$ ($\Delta = \nu_{as}(\mathrm{COO^-}) - \nu_{s}(\mathrm{COO^-})$), which is typical for this type of bonding [8]. The characteristic bands of the oxo monoperoxo vanadium moiety with an η^2-bonded peroxo group were observed in the expected regions [3, 9] (*ca.* 930–980 $\mathrm{cm^{-1}}$ for V=O stretchings, *ca.* 920 $\mathrm{cm^{-1}}$ for O–O stretchings, 550–590 $\mathrm{cm^{-1}}$ for V–O (peroxo) stretchings). The relatively low V=O stretching wavenumbers of potassium, ammonium, and cesium salts can arise from the V=O···V=O interactions in the crystal structure.

Crystal and molecular structure

The crystallographic data and the data collection parameters of $(\mathrm{NBu_4})_2[\mathrm{V_2O_2(O_2)_2(C_2H_2O_3)_2}]\cdot\mathrm{H_2O}$ are summarized in Table 2. In the dinuclear anion (Fig. 1), the vanadium atoms are bridged by the O(5) and O(5a) hydroxyl oxygens from both glycolato ligands. The coordination about each vanadium atom is that of distorted pentagonal pyramid and differs from the pentagonal bipyramidal coordination found so far in α-hydroxycarboxylato peroxo complexes of vanadium [5–7]. The equatorial positions are occupied by peroxo groups (O(2), O(3), O(2a), O(3a)), both bridging hydroxyl oxygens (O(5), O(5a)), and oxygen atoms O(4) and

Table 2. Crystal data and structure refinement for $(\mathrm{NBu_4})_2[\mathrm{V_2O_2(O_2)_2(C_2H_2O_3)_2}]\cdot\mathrm{H_2O}$

Empirical formula	$\mathrm{C_{36}H_{78}N_2O_{13}V_2}$
Formula weight	848.92
Temperature	163(2)K
Crystal system	Monoclinic
Space group	*P*2(1)/n
Unit cell dimensions	$a = 12.800(3)$ Å $\alpha = 90°$
	$b = 13.787(5)$ Å $\beta = 101.59(3)°$
	$c = 12.855(6)$ Å $\gamma = 90°$
Volume	2222.3(14) $\mathrm{Å^3}$
Z	2
Density (calculated)	1.289 $\mathrm{g/cm^3}$
Absorption coefficient	0.482 $\mathrm{mm^{-1}}$
Wavelength	0.71073 Å
F(000)	928
Crystal size	0.80×0.80×0.50 mm
Theta range for data collection	2.05 to 25.05°
Index ranges	$-15 \le h \le 0$, $-15 \le k \le 0$, $-14 \le l \le 14$
Reflections collected	3660
Independent reflections	3490 ($R_{\mathrm{int}} = 0.0452$)
Goodness-of-fit on F^2	1.007
Final *R* indices ($I > 2\sigma_I$)	$R_1 = 0.0809$, $w_{R2} = 0.2153$
R indices (all data)	$R_1 = 0.1240$, $w_{R2} = 0.2543$
Largest diff. peak and hole	0.421 and −0.432 $\mathrm{e\cdot Å^{-3}}$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3490/0/258

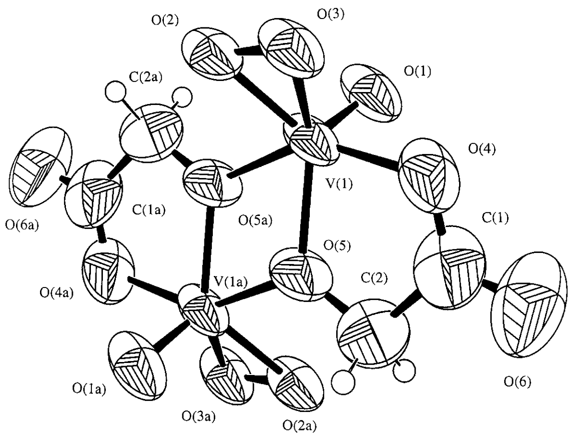


Fig. 1. ORTEP presentation of $[V_2O_2(O_2)_2(C_2H_2O_3)_2]_2^{2-}$ (50% probability level)

Table 3. Selected bond lengths (Å) and angles (°) for $(NBu_4)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot H_2O$

V1-O1′	1.53(4)	O1′-V1-O4	94(2)
V1-O1	1.541(8)	O1-V1-O4	93.9(4)
V1-O2	1.848(6)	O2-V1-O4	125.2(3)
V1-O3	1.864(6)	O3-V1-O4	80.1(4)
V1-O3′	1.89(3)	O3′-V1-O4	121.4(8)
V1-O2′	1.90(3)	O2′-V1-O4	79.8(11)
V1-O5	1.923(4)	O5-V1-O4	77.8(2)
V1-O4	1.991(6)	O1-V1-O5[a]	111(2)
V1-O5′	2.011(4)	O1-V1-O5[a]	97.1(3)
O2-O3	1.436(12)	O2-V1-O5[a]	80.2(2)
O2′-O3′	1.36(5)	O3-V1-O5[a]	124.3(3)
O4-C1	1.265(11)	O3′-V1-O5	71.8(7)
O5-C2	1.401(9)	O2′-V1-O5[a]	110.4(10)
O5-V1[a]	2.011(4)	O5-V1-O5[a]	69.7(2)
O6-C1	1.228(10)	O4-V1-O5[a]	146.9(2)
C1-C2	1.505(11)	O3-O2-V1	67.8(5)
O1-V1-O2	108.9(4)	O2-O3-V1	66.6(3)
O1-V1-O3	109.9(3)	O3′-O2′-V1	68(2)
O2-V1-O3	45.5(4)	O2′-O3′-V1	70(2)
O1′-V1-O3′	109(2)	C1-O4-V1	120.2(5)
O1′-V1-O2′	108(2)	C2-O5-V1	120.0(4)
O3′-V1-O2′	42.0(14)	C2-O5-V1[a]	128.8(4)
O1′-V1-O5	129(2)	V1-O5-V1[a]	110.3(2)
O1-V1-O5	120.9(3)	O6-C1-O4	125.6(9)
O2-V1-O5	123.6(2)	O6-C1-C2	120.7(10)
O3-V1-O5	125.4(3)	O4-C1-C2	113.7(9)
O3′-V1-O5	119.1(7)	O5-C2-C1	108.3(7)
O2′-V1-O5	119.5(9)		

[a] Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y+1$, $-z$

O(4a) from the monodentate carboxylic groups. The double bonded oxygen atoms O(1) and O(1a) are in the apical positions. The V=O bonds are mutually approximately *anti*. Selected distances and angles, which are in the expected intervals, are given in Table 3.

Solution stability

A solution of **1** in organic solvents exhibits a LMCT (peroxo → vanadium) band at *ca.* 420 nm, the position of which is solvent dependent (420 nm for MeCN, 412 nm for CH_2Cl_2) and which is characteristic for vanadium(V) monoperoxo complexes [10, 11]. This band was not observed for aqueous solutions due to the slow dissolution of the complex in water and its rapid decomposition to $[VO(O_2)_2H_2O]^-$, the nonperoxidic glycolato complex, and several minor species as proved by ^{51}V NMR measurements. The peroxo oxygen release from the complex in solution can be monitored on the basis of the decreasing intensity of the corresponding band in the UV/Vis spectra (Fig. 2) or, for more concentrated solutions ($c \geq 10^{-2}\,mol \cdot dm^{-3}$), by manganometric titration. As follows from the results of titrations, **1** in MeCN can be considered to be stable for several hours. On the other hand, **1** in H_2O losses more than a half of the peroxide oxygen in 30 min.

More information on solution structures and stabilities was obtained from ^{51}V NMR measurements. Whereas only one ^{51}V NMR signal was observed for **1** in CH_2Cl_2 (Fig. 3c), **1** dissolved in MeCN exhibited two different ^{51}V NMR signals as shown in Fig. 3b. The intensity ratio of these peaks is not influenced by an excess of glycolic acid, and therefore the 1:1 vanadium-to-ligand ratio is presumably preserved in the complex. The intensity ratio is in the $5 \cdot 10^3$–$10^{-1}\,mol \cdot dm^{-3}$ range independent of the concentration of the complex. An equilibrium between the mononuclear and dinuclear species is, therefore, improbable. Summarizing the interpretation of the ^{51}V NMR data we can surmise that no significant changes in

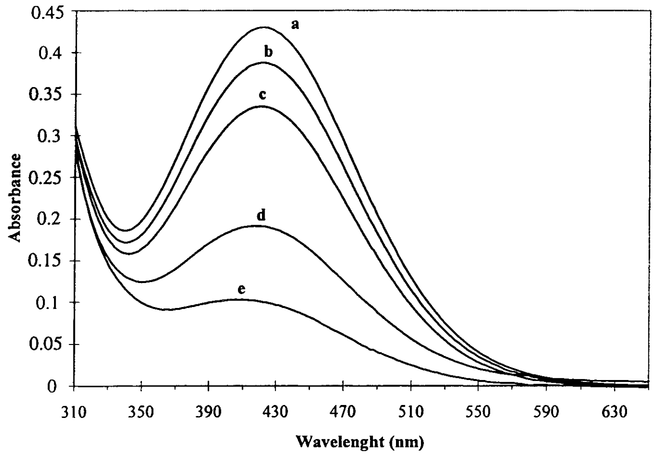


Fig. 2. Electron spectra of **1** in MeCN ($5 \cdot 10^{-3}\,mol \cdot dm^{-3}$): a: 5 h, b: 24 h, c: 2 d, d: 9 d, e: 16 d after dissolving of the complex

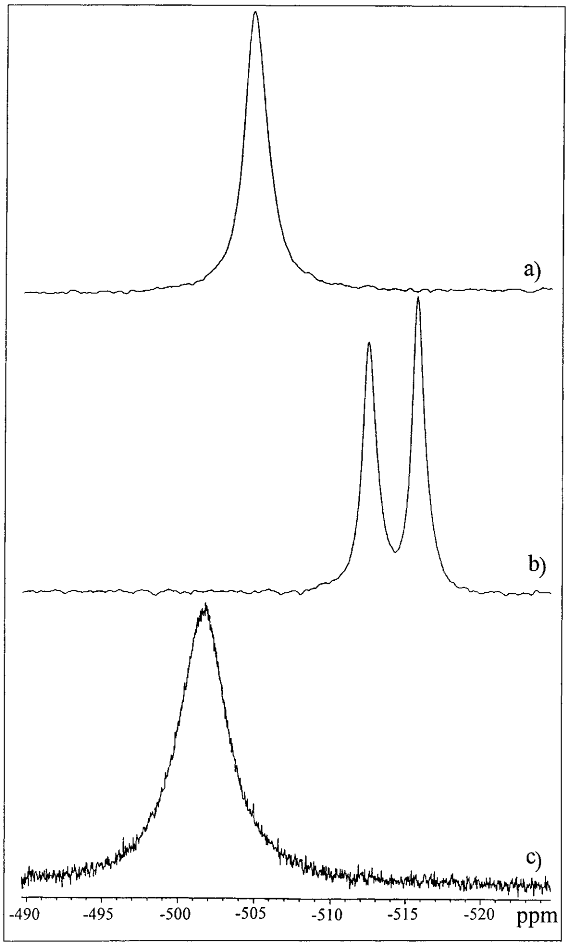


Fig. 3. Selected ^{51}V NMR spectra; a) complex **6** in MeCN, b) complex **1** in MeCN, c) complex **1** in CH_2Cl_2; $c = 10^{-2}\,\mathrm{mol \cdot dm^{-3}}$, $T = 25°C$

the composition of the complex anion in MeCN and CH_2Cl_2 solution occured. This is supported also by the fact that **1** can be recrystallized from the MeCN and CH_2Cl_2 solutions. Nevertheless, the problem of two signals in the ^{51}V NMR spectrum of **1** in MeCN, unlike the one-signal spectra of **1** in CH_2Cl_2 and of the non-peroxidic complex **6** in MeCN (Fig. 3a), cannot be resolved satisfactorily. It is possible that the observed doublet is due to an equilibrium between the *anti* and *syn*, or *anti* and orthogonal arrangements of the complex.

The decomposition of **1** in MeCN proceeds through intermediate(s) **A** characterized by two signals at −491 and −527 ppm (Fig. 4). As the integrals of both signals are always approximately the same, we assume that these signals correspond to an asymmetric dinuclear species $[V_2O_3(O_2)(C_2H_2O_3)_2]^{2-}$ with non-equivalent vanadium atoms which is formed by the release of oxygen from one of the peroxo groups in **1**. The release of the second atom of active oxygen from the

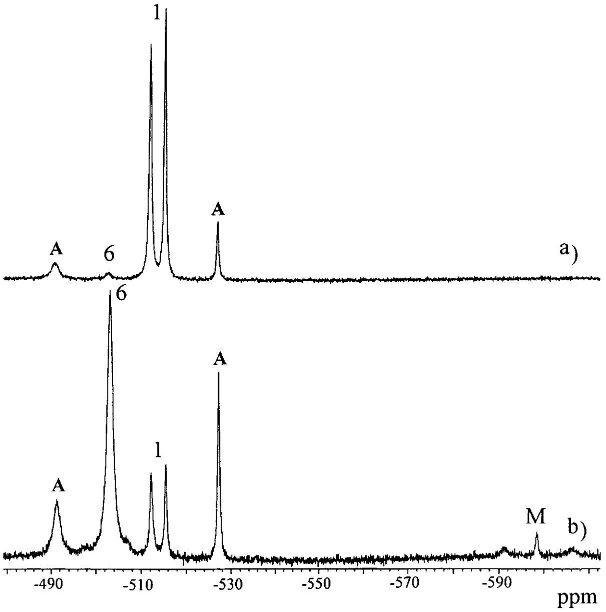


Fig. 4. ^{51}V NMR spectra of **1** in MeCN ($c = 10^{-2}\,\mathrm{mol \cdot dm^{-3}}$, solutions kept at 25°C); a) 150 min after dissolution, b) 3 days after dissolution; **1**: $(NBu_4)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot H_2O$, **6**: $(NBu_4)_2[V_2O_4(C_2H_2O_3)_2] \cdot H_2O$, **A**: intermediates, **M**: minor unidentified species

intermediate results in formation of the nonperoxidic complex **6**. The sequence of decompositions is shown in Scheme 1.

$$\underset{\mathbf{1}}{[V_2O_2(O_2)_2(C_2H_2O_3)_2]^{2-}} \underset{H_2O_2}{\overset{-1/2O_2}{\rightleftarrows}} \underset{\mathbf{A}}{[V_2O_3(O_2)(C_2H_2O_3)_2]^{2-}} \underset{H_2O_2}{\overset{-1/2O_2}{\rightleftarrows}}$$

$$\underset{\mathbf{6}}{[V_2O_4(C_2H_2O_3)_2]^{2-}} \rightarrow \text{Further decomposition products } \mathbf{M} \text{ and reduction of vanadium(V)}$$

Scheme 1

Addition of H_2O_2 to the solution of 6 leads to the formation of first **A** and then **1**.

Preliminary reactivity studies showed that **1** is able to hydroxylate benzene to give phenol under mild conditions, although the yield of phenol was not very high (*ca.* 12% based on the peroxo oxygen content).

Experimental

Materials, instruments, and analytical methods

KVO_3 was prepared according to Ref. [12]. All other chemicals were used as supplied (Lachema, Loba Chemie, Aldrich). The electronic spectra were measured on a Hewlett-Packard 84–52A spectrophotometer. The IR spectra were scanned on a Nicolet Magna 750 spectrophotometer as nujol mulls or as KBr pellets. ^{51}V NMR spectra were recorded on a Varian 300 spectrometer operating at 78.94 MHz. Chemical shifts were referenced to external $VOCl_3$. C, H, N were estimated on a CHN-analyzer (Carlo Erba). Vanadium(V) was reduced 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 $ZnCl_2$ [13]. Peroxidic oxygen was determined by titration with $KMnO_4$.

All peroxo complexes prepared are stable at 5°C for at least three months.

$(NBu_4)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot H_2O$ (**1**)

NH_4VO_3 (0.585 g, 5 mmol) was dissolved in a stirred H_2O (5 cm^3) and NBu_4OH (3.28 cm^3 of a 40% solution, 5 mmol) mixture, and NH_3 was removed from the solution by brief boiling. The resulting solution was cooled and added to a solution of glycolic acid (0.38 g, 5 mmol) in H_2O (10 cm^3). A solution of H_2O_2 (30%, 1.5 cm^3) was then addded with vigorous stirring. The red solution obtained was filtered and allowed to crystallize at 5°C. The dark red crystals were collected over 24 h. $C_{36}H_{78}N_2O_{13}V_2$; (found: C 50.4, H 9.3, N 2.6, V 11.0, O_2^{2-} 7.8; calcd.: C 50.9, H 9.3, N 3.3, V 12.0, O_2^{2-} 7.6.

$K_2[V_2O_2(O_2)_2(C_2H_2O_3)_2 \cdot H_2O$ (**2**)

KVO_3 (0.69 g, 5 mmol) and glycolic acid (0.38 g, 5 mmol) were dissolved in H_2O (10 cm^3) with stirring and slow addition of H_2O_2 (30%, 1.5 cm^3). The resulting orange-red solution was filtered and allowed to crystallize at 5°C. Light red crystals were formed over several days. $C_4H_6K_2O_{13}V_2$; (found: C 10.0, H 1.7, O_2^{2-} 14.3, V 23.0; calcd.: C 10.9, H 1.4, O_2^{2-} 14.5, V 23.4.

$(NH_4)_2[V_2O_2(O_2)_2)(C_2H_2O_3)_2] \cdot H_2O$ (**3**)

NH_4VO_3(0.585 g, 5 mmol) and glycolic acid (0.38 g, 5 mmol) were dissolved in H_2O (5 cm^3), and H_2O_2 (30%, 1.5 cm^3) was added with continues stirring. EtOH (96%) was then added until a precipitate formed. The red compound was isolated after 3 days' standing at 5°C. $C_4H_{14}N_2O_{13}V_2$; (found: C 12.1, H 3.0, N 6.6, O_2^{2-} 16.1, V 25.1; calcd.: C 12.0, H 3.5, N 7.0, O_2^{2-} 16.0, V 25.5.

$Cs_2[V_2O_2(O_2)_2(C_2H_2O_3)_2]$ (**4**)

NH_4VO_3 (0.2925 g, 2.5 mmol) was dissolved in a solution of CsOH (4.05 cm^3, 0.62 $mol \cdot dm^{-3}$, 2.5 mmol), and NH_3 was removed from the solution by warming to the boiling point. After cooling, glycolic acid (0.19 g, 2.5 mmol) and H_2O_2 (30%, 1 cm^3) were added with stirring. The resulting orange-red complex was filtered off after 4 days' standing at 5°C. $C_4H_4Cs_2O_{12}V_2$; (found: C 7.7, H 0.7, O_2^{2-} 10.2, V 15.7; calcd.: C 7.9, H 0.7, O_2^{2-} 10.5, V 16.6.

$(NPr_4)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2]$ (**5**)

To a solution of NH_4VO_3 (0.292 g, 2.5 mmol) in H_2O (5 cm^3) a solution of NPr_4OH (2.5 cm^3, 1 $mol \cdot dm^{-3}$, 2.5 mmol) was added, and NH_3 was removed from the solution by brief boiling. After cooling, glycolic acid (0.19 g, 2.5 mmol) dissolved in H_2O (5 cm^3) and H_2O_2 (30%, 1 cm^3) were added with continuous stirring. The dark red crystals were isolated after 4 days' standing at 5°C. $C_{28}H_{60}N_2O_{12}V_2$; (found; C 46.1, H 8.4, N 3.7, O_2^{2-} 8.5, V 13.9; calcd.: C 46.8, H 8.4, N 3.9, O_2^{2-} 8.9, V 14.2.

$(NBu_4)_2[V_2O_4(C_2H_2O_3)_2] \cdot H_2O$ (**6**)

NH_4VO_3 (0.234 g, 2 mmol) was dissolved in NBu_4OH (40% aqueous solution, 2 mmol) and H_2O ($3\,cm^3$) at 100°C. After total release of NH_3, the solution was cooled (0°C), and glycolic acid (0.152 g, 2 mmol) was added. A white-yellow compound precipitated during *ca.* 10 min. The complex is stable at 5°C for several months. $C_{36}H_{78}N_2O_{11}V_2$; (found: C 52.9, H 9.7, N 3.3, V 12.6; calcd.: C 52.9, H 9.6, N 3.4, V 12.5.

Stoichiometric oxidation of benzene by $(NBu_4)_2[V_2O_2(O_2)_2(C_2H_2O_3)_2] \cdot H_2O$ (**1**)

The oxidation reaction was carried out in a small closed flask under continuous stirring. Solvent: MeCN, concentration of the complex: $0.04\,mol \cdot dm^{-3}$, concentration of benzene: $2\,mol \cdot dm^{-3}$, *T*: 20°C, reaction time: 120 min. The yield of phenol was determined with a GC apparatus (Chrom4, LP Praha) using a glass column (120 cm) filled with Carbowax 1500 (10%) on Chromatone N-AW-HMDS.

Crystal structure determination

The X-ray structure determination was performed on a four circle diffractometer KUMA KM-4 equipped with a nitrogen gas OXFORD CRYOSTREAM cooler at −110°C. A lower temperature was avoided because the crystals undergo a phase transition resulting in destruction of the crystals at temperatures below −120°C.

The dimensions of the crystal used for data collection were $0.8 \times 0.8 \times 0.5$ mm. The final values of the lattice parameters were determined by the least-squares method from 30 reflections in the $17.7° < 2\theta < 24.3°$range. The diffraction intensities were measured within the $4° < 2\theta < 50°$region with the ω-2θ scan technique using graphite monochromatized Mo*Kα* radiation. No significant decay of the intensity of three standard reflections after every 200 reflections was observed. Data were not corrected for absorpition effects.

The structure was solved by direct methods [14]. All atoms, except hydrogen atoms, were refined anisotropically by a full-matrix least squares procedure [15] with $w = 1/(\sigma^2(F_o)^2 + (0.12P)^2 + 5.0P)$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms bonded to carbon atoms were placed in calculated positions and refined with a riding model. The O(3) atom and the peroxo group O(1)-O(2) are disordered in the sense that ligands have two orientations about the central atoms with mutually interchanged positions of oxo and peroxo groups and fixed positions of glycolato groups. This type of disorder has been described in details by *Stomberg* [16]. The probabilities of occurrence in one of two possible orientations (O(1)-O(2)-O(3) or O(1′)-O(2′)-O(3′)) are 0.66 and 0.34. Components of U_{ij} tensor of corresponding O(1)-O(2)-O(3) and O(1′)-O(2′)-O(3′) atoms were fixed at the same values. The maximum and minimum electron densities in the final differential Fourier map were 0.428 and $-0.437\ e \cdot Å^{-3}$. The CCDC deposition code is 113891.

Acknowledgements

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