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Synthesis, characterization and crystal structure of a stable aqua-dioxo-tetraperoxodivanadate(V) with a cation of macrocyclic tetraamine

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Abstract—The peroxo complex of vanadium(V) of composition $CymH_2[V_2O_2(O_2)_4H_2O] \cdot 2H_2O$, where Cym is 5,5,7,12,12,14-hexa-methyl,1,4,8,11-tetraazacyclotetradecane, was prepared by crystallization from a water–ethanol solution of vanadium pentoxide, hydrogen peroxide and Cym. The X-ray structure analysis revealed a dinuclear structure of the complex anion with two coordinatively non-equivalent vanadium atoms bridged by a tridentate η^2-peroxo ligand. The compound is the thermally most stable peroxo complex of vanadium(V) of this type. After simultaneous release of active oxygen and three water molecules at temperatures up to 90°C, the anhydrous metavanadate $CymH_2(VO_3)_2$ is formed. © 1997 Elsevier Science Ltd

Keywords: aqua-dioxo-tetraperoxo-divanadate(V); crystal structure, hexamethyl-tetraazacyclotetradecane; peroxo complex; thermal decomposition; metavanadate.

The majority of the known peroxo complexes of vanadium(V) represent anionic mononuclear mono-, di- or tetraperoxo complexes with inorganic, or in some cases with organic, e.g. alkylammonium cations. Besides some dinuclear heteroligand peroxo complexes with hydroxycarboxylates as bridging ligands [1,2], a number of di- and tetranuclear peroxo complexes with aqua [3–5], fluoro [6] or phosphato [7,8] heteroligands have been prepared in our laboratory and recently structurally characterized.

The thermal stability of the peroxo complexes from the viewpoint of the release of active oxygen [9,10], as well as the stability in aqueous solution [9–11] and the reactivity towards organic or inorganic substrates [12–14] depend on the nature of the heteroligand coordinated to vanadium. Moreover, our experiences in syntheses of the peroxo complexes of vanadium(V) indicate that the nature of the cation, especially that of organic ones, may also have a significant influence on the stability in solid state.

We report here the synthesis, spectral and thermal properties, and the crystal structure of the thermally stable complex $CymH_2[V_2O_2(O_2)_4H_2O] \cdot 2H_2O$.

EXPERIMENTAL

Reagents and apparatus

V_2O_5 was prepared by thermal decomposition of NH_4VO_3. KVO_3 was prepared by thermal decomposition of the crystallohydrate obtained by reaction of V_2O_5 with KOH at pH 8. $Cym \cdot 2H_2O$ was synthesized according to ref. [15] and $CymH_2Cl_2 \cdot 2H_2O$ by crystallization from a 5:2 ethanol–water solution of $Cym \cdot 2H_2O$ with pH adjusted with 1:3 HCl to 3.5. All other chemicals used were of analytical grade and supplied from Lachema.

Vanadium was estimated by titration with $FeSO_4$ and diphenylamine as indicator. Peroxo oxygen was

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determined by manganometry. Carbon, hydrogen and nitrogen were estimated on a Carlo Erba 1106 CHN analyzer.

The IR spectra in Nujol mulls were recorded on a Nicolet Magna 750 FTIR spectrophotometer. The UV–vis spectra were recorded on a Hewlett Packard 8452 spectrometer, with a $d = 0.1$ cm cell. The thermal analysis was performed on a Q-1500 Derivatograph (MOM Budapest), conditions: sample weight 80 mg, air atmosphere, heating rate 0.6°C min^{-1} up to 150°C and 2.5°C min^{-1} at temperatures 150–500°C. The given pH values of water–ethanol solutions are readings on a TTT-2 pH-meter (Radiometer Copenhagen) equipped with a GK 2401 C electrode.

Preparation of $\mathrm{CymH_2[V_2O_2(O_2)_4H_2O]\cdot 2H_2O}$

A solution of $\mathrm{Cym\cdot 2H_2O}$ (0.32 g, 1 mmol) in 70 cm^3 ethanol (95%) was mixed with a solution of V_2O_5 (0.18 g, 1 mmol) in 15 cm^3 H_2O_2 (30%) and 15 cm^3 water. From the resulting solution (pH 5.4), a pale yellow complex crystallized out at room temperature. The complex is stable for 2 years when stored in dark. It is weakly soluble in water (approx. 5×10^{-3} M) and insoluble in ethanol.

The complex can also be prepared by mixing the ethanolic solution of $\mathrm{Cym\cdot 2H_2O}$ with a solution of KVO_3 (0.28 g, 2 mmol) in 10 cm^3 H_2O_2 (30%). A pure product can be isolated within the pH range 2.2–7.5, the pH being adjusted either by addition of $\mathrm{Cym\cdot 2H_2O}$ or 1 : 2 HCl. Found: V, 16.9; C, 31.8; N, 9.3; H, 7.4; O_2^{2-}, 21.1. Calc. for $V_2C_{16}H_{44}N_4O_{13}$: V, 16.9; C, 31.9; N, 9.3; H, 7.3; O_2^{2-}, 21.1%.

X-ray structure determination

Low-temperature X-ray measurements were made on a KUMA KM4 diffractometer with graphite monochromated Mo-K_α radiation using the ω–2θ scan technique. Cell parameters and an oriented matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $10.78 < \theta < 11.64°$. No significant decay of the intensity of the three standard reflections recorded after every 90 reflections was observed. The data were not corrected for absorption effects. The crystal data and refinement results are given in Table 1.

The structure was solved by a combination of Patterson and difference-Fourier methods, and refined by a full-matrix least-squares procedure (SHELXL-93) [16] on $|F|^2$. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were obtained from a difference-Fourier map and refined isotropically. The final refinement was carried out with a weighting scheme of $w = 1/[\sigma^2(F_o^2)+(0.06570P)^2+7.10P]$, where $P = (F_o^2+2F_c^2)/3$ and 3932 reflections. The largest positive and negative peaks in the difference map were 0.73 and -0.74 e A^{-3}, respectively.

Additional material comprising the final coordinates of atoms, anisotropic displacement parameters and a list of observed and calculated structure factors is available from the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

In contrast to the $\mathrm{M_2^I[V_2O_2(O_2)_4H_2O]\cdot xH_2O}$ salts $[\mathrm{M^I = K^+,\ N(CH_3)_4^+}]$ [4,5] prepared by crystallization at -25°C and decomposing even at temperatures 0–5°C, the complex prepared is the thermally most stable compound of this type.

On the thermoanalytical curves of $\mathrm{CymH_2[V_2O_2(O_2)_4H_2O]\cdot 2H_2O}$ (Fig. 1), no significant decomposition was observed up to 60°C. In the temperature interval 20–170°C, only an exothermic process with maximum at 85°C occurred. The corresponding mass loss on the TG curve, 30.75%, is in good agreement with mass loss 30.22% calculated for water and active oxygen release, i.e. both processes proceed simultaneously. The products obtained by interrupting the dynamic heating at 95 or 150°C were identified by IR spectroscopy as the anhydrous metavanadate $\mathrm{CymH_2(VO_3)_2}$. The spectrum exhibits in the 400–1000 cm^{-1} region all bands characteristic for the metavanadates with a pyroxene-like polymeric chain structure of the polyanion [17]: 930 and 900 cm^{-1} [ν_s(V=O)]; 812 cm^{-1} [ν_{as}(V=O)]; 640 and 515 cm^{-1} [$\nu_{as}+\nu_s$(V—O—V)].

In aqueous solution (pH 6.5), the UV–vis spectrum of $\mathrm{CymH_2[V_2O_2(O_2)_4H_2O]\cdot 2H_2O}$ exhibits the LMCT ($\mathrm{L} = O_2^{2-}$) band with λ_{max} and ε values (326 nm, 1320 mol^{-1} dm^3 cm^{-1}) almost identical with those generally observed for aqua-diperoxo or some diperoxo-heteroligand complexes containing the $\mathrm{VO(O_2)_2}$ moiety [11,18,19], 330 nm and 660 mol^{-1} dm^3 cm^{-1}. The electron spectroscopy is obviously not able to distinguish whether the $\mathrm{[V_2O_2(O_2)_4H_2O]^{2-}}$ anion is preserved in solution or it is rapidly decomposed to the monomeric $\mathrm{[VO(O_2)_2(H_2O)_x]^-}$ ions. This decomposition was recently observed in diluted aqueous solutions by ^{51}V NMR spectroscopy [20]. In strongly acidic aqueous solutions with the predominant formation of the monoperoxo species, the electronic spectra of $\mathrm{KVO_3}$–Cym–$\mathrm{H_2O_2}$–HCl and $\mathrm{KVO_3}$–$\mathrm{H_2O_2}$–HCl solutions [with pH 0.7, $c(\mathrm{KVO_3}) = c(\mathrm{Cym}) = 10^{-2}$ M and sixfold excess of H_2O_2], both exhibit the same LMCT band with λ_{max} and ε values (456 nm, 267 mol^{-1} dm^3 cm^{-1}) characteristic for the aqua-monoperoxo species $\mathrm{[VO(O_2)(H_2O)_x]^+}$. The rate of self-decomposition of the aqua-monoperoxo complex in water is not influenced by the presence of Cym, i.e. the cyclic amine is not involved in any reaction with the vanadium peroxo complex.

Based on comparison of the bands in the IR spectra of the complex prepared and $\mathrm{CymH_2Cl_2\cdot 2H_2O}$ (Fig. 2), we have assigned the characteristic vibrations in the 400–1000 cm^{-1} region. The comparison of the

Table 1. Crystal data and structure refinement for $CymH_2[V_2O_2(O_2)_4H_2O] \cdot 2H_2O$

Formula	$C_{16}H_{44}N_4O_{13}V_2$
Formula weight	602.43
Crystal system	Triclinic
Space group	$P\bar{1}$
T (°C)	−150(2)
a (Å)	8.501(3)
b (Å)	9.939(3)
c (Å)	15.416(4)
α (°)	87.63(2)
β (°)	81.12(2)
γ (°)	83.90(3)
V (Å^3)	1279.2(7)
Z	2
D_c (g cm^{-3})	1.564
μ (mm^{-1})	0.799
F(000)	636
Crystal size (mm)	0.40 × 0.30 × 0.30
θ range (°)	2.06 to 25.08
Index ranges	$-10 <= h <= 10$, $-11 <= k <= 11$, $0 <= l <= 18$
No. of total data	4088
No. of unique data	3932 (R_{int} = 0.0493)
No. of observed data/parameters	2699/368
Goodness-of-fit on F^2	1.086
R indices (obs. data)	$R_1 = 0.0604$,[a] $wR_2 = 0.1608$[b]
R indices (all data)	$R_1 = 0.1039$,[a] $wR_2 = 0.1778$[b]

[a] $R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

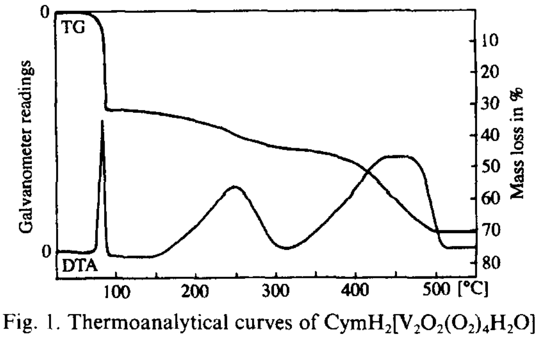

Fig. 1. Thermoanalytical curves of $CymH_2[V_2O_2(O_2)_4H_2O] \cdot 2H_2O$.

data published for caesium and tetramethylammonium compounds which were supported by normal coordinate analysis for the $[V_2O_2(O_2)_4H_2O]^{2-}$ anion [3] with the spectrum of $CymH_2[V_2O_2(O_2)_4H_2O] \cdot 2H_2O$ (Table 2) allowed us to propose in the complex prepared the same anion structure as found by X-ray analysis in K^+ and $N(CH_3)_4^+$ salts [4,5]. The relatively great thermal stability observed in the presence of the voluminous $CymH_2^{2+}$ cation was the reason for establishing the

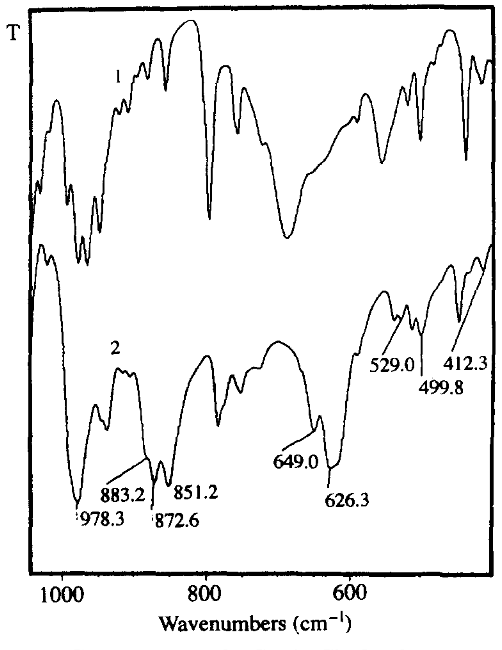

Fig. 2. IR spectra of $CymH_2Cl_2 \cdot 2H_2O$ (1) and $CymH_2[V_2O_2(O_2)_4H_2O] \cdot 2H_2O$ (2) in the 400–1000 cm^{-1} region.

Table 2. Characteristic IR bands for the $[V_2O_2(O_2)_4H_2O]^{2-}$ ion in the complex prepared and in the caesium and tetramethylammonium salts

$CymH_2^{2+}$	Cs^+ [3]	$N(CH_3)_4^+$ [3]	Assignment
	993 m		
978.3 vs	978 vs	978 vs	$\nu(V{=}O)$
	893 s		
883.2 sh	885 m	885 s	
872.6 vs	875 w	867 vs	$\nu(O_p—O_p)$
851.2 vs	855 vs	859 sh	
649.0 m	645 s	642 s	$\nu(V—O_p)$
626.3 vs	619 m	619 s	
529.0 w	520 m	533 w	$\nu(V—O_p)$
499.8 m		495 w	
412.3 w	401 w	403 w	$\nu(V—OH_2)$

Table 3. Bond lengths (Å) for $CymH_2[V_2O_2(O_2)_4H_2O] \cdot 2H_2O$

Vanadium environment			
V(1)—O(1)	1.870(5)	V(2)—O(6)	1.943(4)
V(1)—O(2)	1.887(5)	V(2)—O(7)	1.873(4)
V(1)—O(3)	1.879(5)	V(2)—O(8)	1.877(4)
V(1)—O(4)	1.885(4)	V(2)—O(9)	1.868(4)
V(1)—O(5)	1.596(5)	V(2)—O(10)	1.596(5)
V(1)—O(6)	2.035(4)	V(2)—O(21)	2.005(5)
O(1)—O(2)	1.467(6)	O(6)—O(7)	1.477(6)
O(3)—O(4)	1.479(6)	O(8)—O(9)	1.462(6)
Two nonequivalent cations			
N(1)—C(1)	1.450(8)	N(11)—C(11)	1.462(8)
N(1)—C(2)	1.471(8)	N(11)—C(12)	1.490(7)
N(2)—C(5)	1.475(8)	N(12)—C(15)	1.496(8)
N(2)—C(4)	1.526(9)	N(12)—C(14)	1.536(8)
C(1)—C(5)^i	1.509(10)	C(11)—C(15)^{ii}	1.505(9)
C(2)—C(3)	1.514(9)	C(12)—C(16)	1.520(9)
C(2)—C(6)	1.532(9)	C(12)—C(13)	1.525(9)
C(3)—C(4)	1.548(9)	C(13)—C(14)	1.530(9)
C(4)—C(8)	1.469(11)	C(14)—C(17)	1.492(9)
C(4)—C(7)	1.542(10)	C(14)—C(18)	1.540(9)
C(5)—C(1)^i	1.509(10)	C(15)—C(11)^{ii}	1.505(9)

Symmetry transformations used to generate equivalent atoms: (i) $-x+2,\ -y,\ -z+1$; (ii) $-x+1,\ -y-1,\ -z$.

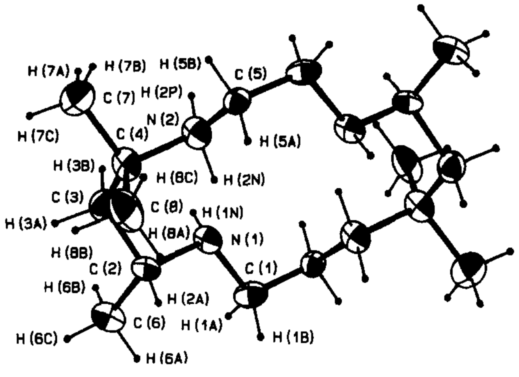

Fig. 3. Perspective view of one of two non-equivalent $CymH_2^{2+}$ cations. ORTEP drawing shows 50% probability for the thermal ellipsoids.

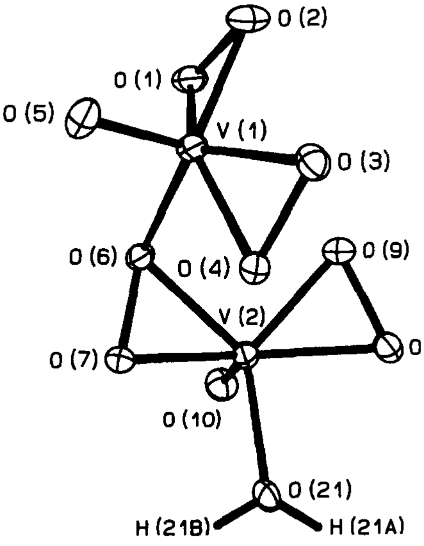

Fig. 4. ORTEP representation at the 50% probability of the $[V_2O_2(O_2)_4H_2O]^{2-}$ anion.

crystal structure by X-ray analysis, which revealed the structure proposed.

The crystal structure is built up from two structurally nonequivalent $CymH_2^{2+}$ cations, $[V_2O_2(O_2)_4H_2O]^{2-}$ anions and crystal water molecules. The bond lengths and the bond and torsion angles for $CymH_2^{2+}$ and for the complex anion are given in Tables 3 and 4. The ORTEP drawings of one of two cations and of the complex anion are shown in Figs 3 and 4. The complex anion has a dinuclear structure with coordinatively nonequivalent vanadium atoms with pentagonal pyramidal arrangement of oxygen atoms. The basal planes of the pentagonal pyramids around V(1) and V(2) atoms consist of O(1), O(2), O(3), O(4) and O(6) atoms (the maximum deviation from the planarity being 0.051 Å), and O(6), O(7), O(8), O(9) and O(21) atoms (maximum deviation 0.069 Å), respectively. Both the V(1) and V(2) atoms are moved from the basal plane by 0.522(2), respectively, 0.469(2) Å towards the double-bonded apical oxygen atoms O(5) and O(10), respectively. No significant differences in V(1)—O_p (O_p is peroxo oxygen) and V(2)—O_p distances, when compared with values for the less stable potassium and tetramethylammonium salts (Table 5), were observed. Even the range of $d[O_p—O_p]$ values and the vanadium-bridging peroxo oxygen distance, V(1)—O_p(b), in the complex prepared are comparable to the values for the very unstable potassium salt. The only rather significant difference in the structure of the complex anion is the markedly greater dihedral angle between the basal planes of the connected pyramids,

Table 4. Bond angles (°) and torsion angles (°) for $\mathrm{CymH_2[V_2O_2(O_2)_4H_2O]\cdot 2H_2O}$

O(5)—V(1)—O(1)	109.0(2)	O(10)—V(2)—O(9)	105.4(2)
O(5)—V(1)—O(3)	108.3(2)	O(10)—V(2)—O(7)	106.9(2)
O(1)—V(1)—O(3)	128.4(2)	O(9)—V(2)—O(7)	129.0(2)
O(5)—V(1)—O(4)	104.8(2)	O(10)—V(2)—O(8)	107.0(2)
O(1)—V(1)—O(4)	144.2(2)	O(9)—V(2)—O(8)	45.9(2)
O(3)—V(1)—O(4)	46.3(2)	O(7)—V(2)—O(8)	145.2(2)
O(5)—V(1)—O(2)	105.7(2)	O(10)—V(2)—O(6)	103.0(2)
O(1)—V(1)—O(2)	46.0(2)	O(9)—V(2)—O(6)	89.3(2)
O(3)—V(1)—O(2)	90.2(2)	O(7)—V(2)—O(6)	45.5(2)
O(4)—V(1)—O(2)	133.0(2)	O(8)—V(2)—O(6)	131.1(2)
O(5)—V(1)—O(6)	102.1(2)	O(10)—V(2)—O(21)	99.5(2)
O(1)—V(1)—O(6)	78.3(2)	O(9)—V(2)—O(21)	128.4(2)
O(3)—V(1)—O(6)	126.0(2)	O(7)—V(2)—O(21)	83.2(2)
O(4)—V(1)—O(6)	83.5(2)	O(8)—V(2)—O(21)	83.8(2)
O(2)—V(1)—O(6)	123.1(2)	O(6)—V(2)—O(21)	128.0(2)
O(2)—O(1)—V(1)	67.6(3)	O(7)—O(6)—V(2)	64.8(2)
O(1)—O(2)—V(1)	66.4(2)	O(6)—O(7)—V(2)	69.7(2)
O(4)—O(3)—V(1)	67.1(2)	O(9)—O(8)—V(2)	66.7(2)
O(3)—O(4)—V(1)	66.7(2)	O(8)—O(9)—V(2)	67.3(2)
O(7)—O(6)—V(1)	113.0(3)	V(2)—O(6)—V(1)	109.0(2)
C(1)—N(1)—C(2)	114.1(5)	C(11)—N(11)—C(12)	112.0(5)
C(5)—N(2)—C(4)	117.2(5)	C(15)—N(12)—C(14)	115.6(5)
N(1)—C(1)—C(5)^{i}	111.8(6)	N(11)—C(11)—C(15)^{ii}	112.0(5)
N(1)—C(2)—C(3)	109.0(5)	N(11)—C(12)—C(16)	112.5(5)
N(1)—C(2)—C(6)	114.5(6)	N(11)—C(12)—C(13)	111.0(5)
C(3)—C(2)—C(6)	111.2(6)	C(16)—C(12)—C(13)	110.6(5)
C(2)—C(3)—C(4)	115.4(6)	C(12)—C(13)—C(14)	117.7(5)
C(8)—C(4)—N(2)	110.7(6)	C(17)—C(14)—C(13)	110.5(6)
C(8)—C(4)—C(7)	108.3(6)	C(17)—C(14)—N(12)	107.9(5)
N(2)—C(4)—C(7)	107.3(6)	C(13)—C(14)—N(12)	105.7(5)
C(8)—C(4)—C(3)	114.9(6)	C(17)—C(14)—C(18)	112.6(6)
N(2)—C(4)—C(3)	108.2(5)	C(13)—C(14)—C(18)	111.5(5)
C(7)—C(4)—C(3)	107.1(6)	N(12)—C(14)—C(18)	108.4(5)
N(2)—C(5)—C(1)	112.7(5)	N(12)—C(15)—C(11)	110.8(5)

Symmetry transformations used to generate equivalent atoms: (i) $-x+2$, $-y$, $-z+1$; (ii) $-x+1$, $-y-1$, $-z$.

Table 5. Vanadium-peroxo oxygen and peroxo oxygen-peroxo oxygen bond lengths (Å) in structures with the $\mathrm{[V_2O_2(O_2)_4H_2O]^{2-}}$ anion

	Bond lengths in $\mathrm{M_n[V_2O_2(O_2)_4H_2O]\cdot xH_2O}$		
Bond[a]	M = $\mathrm{CymH_2^{2+}}$	M = $\mathrm{K^+}$ [5]	M = $\mathrm{N(CH_3)_4^+}$ [4]
V(1)—$\mathrm{O_p}$	1.870(5)-1.885(4)	1.869(4)-1.914(4)	1.865(3)-1.883(4)
V(2)—$\mathrm{O_p}$	1.868(4), 1.877(4)	1.878(3), 1.881(3)	1.868(3), 1.880(4)
V(2)—$\mathrm{O_p}$(b)	1.873(4), 1.943(4)	1.894(4), 1.947(4)	1.863(4), 1.919(4)
V(1)—$\mathrm{O_p}$(b)	2.035(4)	2.032(3)	2.045(3)
$\mathrm{O_p}$—$\mathrm{O_p}$	1.462(6)-1.479(6)	1.457(5)-1.470(5)	1.458(5)-1.468(5)

[a] $\mathrm{O_p}$ = peroxo oxygen; $\mathrm{O_p}$(b) = bridging peroxo oxygen.

64.89(0.10)°, than found in structures of $\mathrm{N(CH_3)_4^+}$ (60.8°) and $\mathrm{K^+}$ (57.1°) salts [4,5]. This is why the shortest nonbonded V—O distances, which were considered to indicate the tendency for both vanadium atoms to attain the pentagonal bipyramidal coordination [4,5], *d*[V(1)—O(9)] = 2.980 Å and *d*[V(2)—O(4)] = 2.764 Å, are very long.

As no structural data for the complex anion were found to give an explanation for the relatively high thermal stability of $\mathrm{CymH_2[V_2O_2(O_2)_4H_4O]\cdot 2H_2O}$, this is obviously caused by the $CymH_2^{2+}$ cation and its interactions with the peroxovanadate ion.

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