

# Unveiling of a Trinuclear Cyclic Peroxidovanadate: A Potential Oxidant in Vanadium-Catalyzed Reactions

Lukáš Krivosudský,<sup>\*,†</sup> Peter Schwendt,<sup>†</sup> and Róbert Gyepes<sup>‡,§</sup>

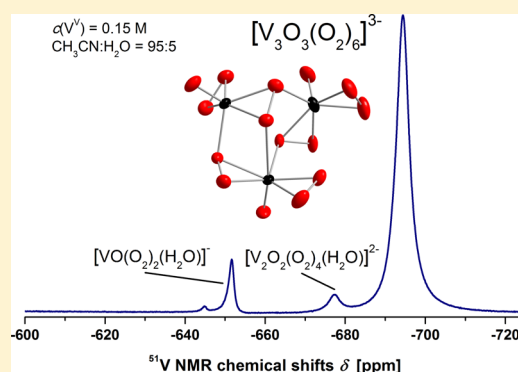
<sup>†</sup>Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, 84215 Bratislava, Slovakia

<sup>‡</sup>Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

<sup>§</sup>J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

## Supporting Information

**ABSTRACT:** The first peroxidovanadium trimer was prepared in the form of its tetrabutylammonium salt,  $(\text{NBu}_4)_3[\text{V}_3\text{O}_3(\text{O}_2)_6]\cdot 2\text{H}_2\text{O}$ . Its X-ray structure analysis revealed a unique cyclic structure of the  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  ion incorporating the yet unobserved  $\mu_3\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1$  coordination mode of one of its peroxido ligands. While relatively stable in nonaqueous solvents, the  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  ion quickly decomposes in diluted aqueous solutions. A higher vanadium concentration or a higher  $\text{CH}_3\text{CN}$  content in the mixed  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent facilitates the formation of oligomers  $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$  and  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ .  $^{51}\text{V}$  NMR investigations indicated that the trinuclear species is incorporated in vanadium-catalyzed oxidations in the presence of  $\text{H}_2\text{O}_2$ .



## INTRODUCTION

The importance of vanadium peroxido complexes in some biological systems (insulin mimetic properties,<sup>1,2</sup> vanadium-dependent haloperoxidases,<sup>3–5</sup> and antineoplastic properties<sup>6,7</sup>) as well as their activity as oxygen-transfer agents in organic reactions<sup>8,9</sup> stimulated great interest in their chemistry. The decomposition process of heteroligand peroxidovanadium complexes both in biological systems and in solutions can lead to the formation of simple peroxidovanadates carrying no organic ligands (except coordinated solvent molecules). This process can exert a significant influence on the activity of vanadium compounds available in the system; therefore, a detailed knowledge of simple peroxidovanadate species present in solutions is of utmost importance. Despite the seemingly uncomplicated structure of “simple” peroxidovanadates, their solution chemistry is actually not simple at all,<sup>10–18</sup> because in their aqueous solution with a pH range between 0 and 11, the very thorough and most complete study<sup>17</sup> proposed the existence of as much as 12 possible species. In addition, the formation of one ion ( $[\text{V}(\text{O}_2)_4]^{3-}$ ) in strongly alkaline solutions carrying a high excess of  $\text{H}_2\text{O}_2$  has been suggested.

The majority of recent speciation studies was performed in a medium representing physiological conditions (a relatively low vanadium concentration and 0.150 M NaCl). The low  $c(\text{V})$  (vanadium concentration) has been inevitable also for precise quantitative measurements and calculation of the formation constants.<sup>17</sup> On the other hand, there are some indications that the composition of concentrated solutions can be different. The composition of solid complexes crystallizing from solution does

not necessarily correspond to any proposed solution species.<sup>17</sup> This is the case of complexes  $\text{M}_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]$ ,<sup>19–21</sup> which crystallize from approximately neutral solutions, and the case of  $(\text{NH}_4)_4[\text{V}_2\text{O}_3(\text{O}_2)_4]$  crystallizing from alkaline solutions, which do not have analogues in solution. Moreover, we have found that concentrated peroxidovanadium solutions exhibit two  $^{51}\text{V}$  NMR signals in the  $-680$  to  $-700$  ppm range, where only one peak of  $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$  is usually observed.<sup>22</sup>

Such discrepancies inspired us to study peroxidovanadium species in their concentrated aqueous solutions and in nonaqueous solutions at various  $c(\text{V})$ . In spite of the generally accepted view that peroxidovanadium complexes are reluctant to oligomerize beyond the formation of dimers,<sup>10–18</sup> we have been able to augment a series of peroxidovanadates characterized heretofore by single-crystal diffraction— $\text{M}_3[\text{V}(\text{O}_2)_4]$ ,<sup>24</sup>  $\text{M}_4[\text{V}_2\text{O}_3(\text{O}_2)_4]$ ,<sup>25</sup>  $\text{M}_3[\text{V}_2\text{O}_2\text{OH}(\text{O}_2)_4]$ ,<sup>26</sup> and  $\text{M}_2[\text{V}_2\text{O}_2(\text{O}_2)_4\text{H}_2\text{O}]$ <sup>19–21</sup>—by an entirely new compound  $\text{M}_3[\text{V}_3\text{O}_3(\text{O}_2)_6]\cdot 2\text{H}_2\text{O}$  featuring a completely novel trinuclear cyclic anion.

## RESULTS AND DISCUSSION

**Structure.**  $(\text{NBu}_4)_3[\text{V}_3\text{O}_3(\text{O}_2)_6]\cdot 2\text{H}_2\text{O}$  (**1**) was prepared by facile synthesis from the reaction system  $\text{V}_2\text{O}_5\text{--NBu}_4\text{OH--L-glutamic acid--H}_2\text{O}_2$  (pH = 6.7) and the composition of the compound was confirmed by satisfactory results of elemental analyses (C, H, N, V, and  $\text{O}_2^{2-}$ ). Compound **1** exhibits in IR

Received: March 16, 2015

spectral bands of the  $\nu(\text{V}=\text{O})$ ,  $\nu(\text{O}_p-\text{O}_p)$ , and  $\nu(\text{V}-\text{O}_p)$  vibrations typical for diperoxidovanadium complexes (Table 1)

**Table 1.** Characteristic Bands in the Vibrational Spectra of **1**<sup>a</sup>

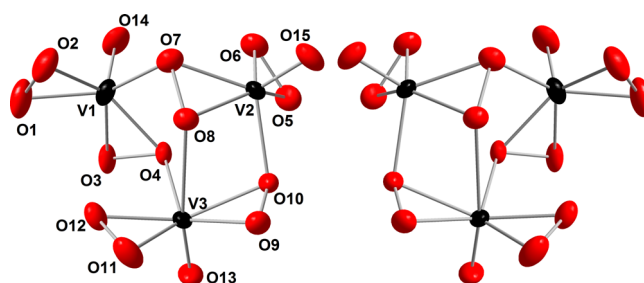
Nujol mull	CD <sub>3</sub> CN solution	assignment
984 vs	983 vs	$\nu(\text{V}=\text{O})$
968 vs	965 vs	
881 vs	883 vs	$\nu(\text{O}_p-\text{O}_p)$
860 s		
838 m		
642 m	650 m	$\nu(\text{V}-\text{O}_p)$
635 s		
618 m	625 w	
601 s	603 s	
588 m	592 sh	
492 w		
449 vw		

<sup>a</sup>s = strong, m = medium, w = weak, sh = shoulder, v = very, and O<sub>p</sub> = peroxido oxygen atom.

and Figure S1 in the Supporting Information, SI). The assignment of bands in a CD<sub>3</sub>CN solution was allowed by the stability of **1** in the solution and good agreement between the solid-state and solution IR spectra. The UV–vis spectrum of **1** in acetonitrile shows the characteristic broad band at 360–400 nm ( $\epsilon = 910 \text{ mol}^{-1}\cdot\text{dm}^3\cdot\text{cm}^{-1}$ ) corresponding to the ligand-to-metal charge-transfer (LMCT) transition in diperoxidovanadates (Figure S2 in the SI). X-ray structural analysis (Table 2) revealed that the cyclic anion  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  (Figure 1) is composed of three vanadium(V) atoms adopting

**Table 2.** Crystal Data and Structure Refinement

empirical formula	C <sub>48</sub> H <sub>112</sub> N <sub>3</sub> O <sub>17</sub> V <sub>3</sub>
fw	1156.23
T (K)	150
$\lambda$ (Å)	0.71073
cryst syst	monoclinic
space group	P2 <sub>1</sub> /c
unit cell dimens	
a (Å)	16.1241(8)
b (Å)	16.0913(8)
c (Å)	23.8767(13)
$\beta$ (deg)	93.145(2)
V (Å <sup>3</sup> )	6185.7(5)
Z	4
D <sub>calc</sub> (g·cm <sup>-3</sup> )	1.242
abs coeff (mm <sup>-1</sup> )	0.507
F(000)	2504
cryst size (mm)	0.41 × 0.28 × 0.18
$\theta$ range for data collection (deg)	2.60–11.90
limiting indices	–20 ≤ h ≤ 20 –20 ≤ k ≤ 20 –30 ≤ l ≤ 31
reflns collected/unique ( $R_{\text{int}} = 0.0998$ )	70499/14204
completeness to 2 $\theta$ (%)	99
data/restraints/parameters	14204/3/657
GOF on F <sup>2</sup>	1.019
final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0605, wR2 = 0.1142
R indices (all data)	R1 = 0.1289, wR2 = 0.1420
largest difference in the peak and hole (e·Å <sup>-3</sup> )	0.846 and –0.626



**Figure 1.** Two enantiomers of the  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  anion present in the solid-state structure of **1**. The thermal ellipsoids of both anions are displayed with 50% probability.

simultaneously a pentagonal-pyramidal (atoms V1 and V2) and a pentagonal bipyramidal (atom V3) coordination environment. Each vanadium(V) atom is coordinated by one double-bonded oxido ligand in the apical position and one nonbridging peroxido ligand in the pentagonal pseudoplane. The second peroxido ligand in the pentagonal pseudoplanes of the atoms V1 and V2 is coordinated in  $\mu\text{-}\eta^2\text{:}\eta^1$  mode, linking the pairs of atoms V1–V3 and V2–V3. The central peroxido ligand formed by atoms O7 and O8 is coordinated to all three atoms V1, V2, and V3 by adopting the so-far-unobserved  $\mu_3\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1$  coordination mode. The relatively short distance between the atom O8 of this peroxido ligand and the atom V3 [2.394(2) Å] compared to the distances V1...O12 and V2...O4 [2.944(2) and 2.847(2) Å, respectively] suggests the presence of some weak covalent attraction, which has been confirmed by a single-point density functional theory (DFT) computation reporting the respective Mayer bond order to be 0.134.

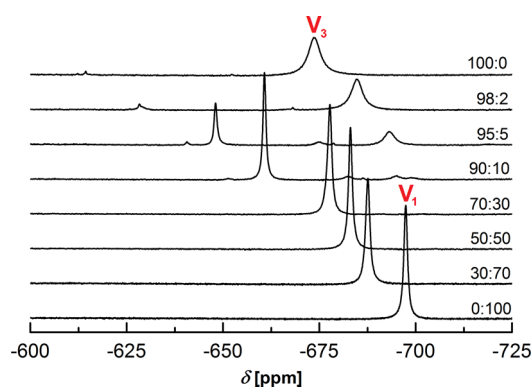
Brought together, the  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  anion consists of three  $[\text{VO}(\text{O}_2)_2]^-$  units and resembles a condensed trinuclear anhydride of  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ . It can be formally considered as a peroxidated derivative of  $(\text{V}_3\text{O}_9)^{3-}$ .<sup>27</sup> An undoubtedly impressive feature of the  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  anion is its chirality because both propeller enantiomers are present in the centrosymmetric lattice.

#### Speciation in the Mixed Acetonitrile/Water Solvent.

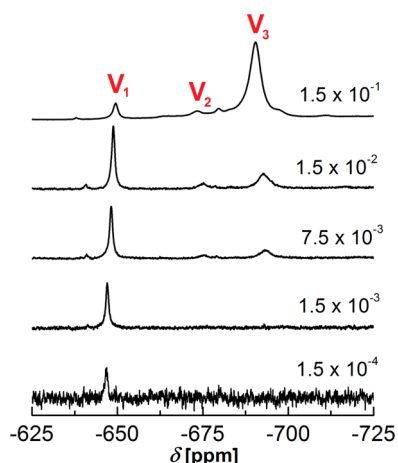
The  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  anion adopts only C<sub>1</sub> symmetry, with the three vanadium atoms being nonequivalent; thus, three resonances are expected in its <sup>51</sup>V NMR spectrum. In solution, however, the resonances merge into one signal. We suppose that this coalescence might be explained by fast exchange on the <sup>51</sup>V NMR time scale.<sup>28</sup> This is supported by evident broadening of the signal with decreasing temperature (Figure S3 in the SI).

Compound **1** dissolved in acetonitrile shows one dominant signal at –674 ppm<sup>29</sup> (Figure 2). This chemical shift has previously also been observed but not identified by Slebošnick and Pecoraro, who investigated the solvent effects on the <sup>51</sup>V NMR chemical shifts of peroxidovanadates in a mixed CH<sub>3</sub>CN/H<sub>2</sub>O solvent.<sup>23</sup> They found that (a) the chemical shifts move systematically downfield with increasing CH<sub>3</sub>CN content (this is evidently valid also for other organic solvents)<sup>15</sup> and (b) there is a strong preference of higher oligomers with increasing concentration of CH<sub>3</sub>CN. Both of these findings are in agreement with our observations in mixed CH<sub>3</sub>CN/H<sub>2</sub>O solvents.

In the spectra depicted in Figures 2 and 3, traces of vanadates and monoperoxido complexes, which are species formed by hydrolysis, are also observable, occurring because of the



**Figure 2.**  $^{51}\text{V}$  NMR spectra of solutions of **1** in solvent with variable ratio  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (% vol) and with fixed concentration  $c(\text{V}) = 1.5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ .  $\text{V}_1$ :  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ .  $\text{V}_3$ :  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ .



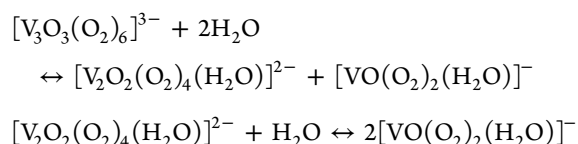
**Figure 3.**  $^{51}\text{V}$  NMR spectra of solutions of **1** in the solvent composed of 95:5 (% vol)  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  and with variable vanadium concentrations ( $\text{mol}\cdot\text{dm}^{-3}$ ).

presence of water of crystallization (mainly for pure  $\text{CH}_3\text{CN}$  as the solvent) and because of the partial decomposition of the peroxido ligand.

The increase of the relative peak area with increasing vanadium concentration is proof for the formation of oligomeric species. The dependence of the distribution of individual species present in the mixture 95:5  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  upon concentration (Figure 3) confirms that increasing vanadium concentration causes (1) a decrease of the relative area of the  $\sim -648 \text{ ppm}^{30}$  peak ( $\text{V}_1$ ) from 100% at  $c(\text{V}) = 1.5 \times 10^{-4}$  to 4% at  $1.5 \times 10^{-1}$  and (2) an increase of the relative intensity of the  $\sim -692 \text{ ppm}^{30}$  peak ( $\text{V}_3$ ) from 0.0% at  $1.5 \times 10^{-4}$  to 60% at  $1.5 \times 10^{-1}$ .

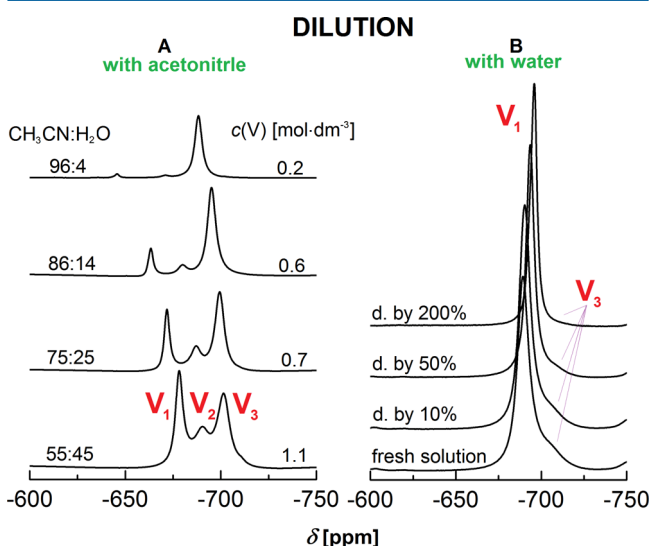
The relative area of the signal at  $\sim -675 \text{ ppm}$  reaches its maximum at  $c(\text{V}) = 1.5 \times 10^{-2}$  (0.0% at  $1.5 \times 10^{-4}$  and  $1.5 \times 10^{-3}$ , 4% at  $7.5 \times 10^{-3}$ , 5% at  $1.5 \times 10^{-2}$ , and 1% at  $1.5 \times 10^{-1}$ ). This behavior is consistent with a dinuclear species, and we assign this signal to the  $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$  ( $\text{V}_2$ ) species, which is already known from X-ray single-crystal analyses.<sup>19–21</sup> The assignment of the signal of  $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$  cannot be straightforwardly confirmed because, upon dissolution of  $(\text{NMe}_4)_2[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}^{19}$  in the mixed  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvents, the equilibrium is established quickly (Figure S5 in the SI) and the distribution of the species present in the solutions is consistent with that in Figure 2.

We suppose that, with rising water concentration in the  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures, the following reactions take place:



It should be noted that the dominant signal at  $m/Z$  131 in the electrospray ionization mass spectrometry (ESI-MS) spectrum of the peroxido vanadium solution in 1:1  $\text{H}_2\text{O}/\text{EtOH}$  (pH = 6.8 before the addition of EtOH), previously assigned to the naked  $[\text{VO}(\text{O}_2)_2]^-$  fragment,<sup>16</sup> can correspond also to the  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  species.

To confirm the presence of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  in concentrated solutions, we have conducted studies on two different systems (Figure 4). First, we prepared  $\text{NBu}_4\text{VO}_3$  by the dissolution of



**Figure 4.**  $^{51}\text{V}$  NMR spectra of solutions of  $[\text{N}(\text{C}_4\text{H}_9)_4]\text{VO}_3 + \text{H}_2\text{O}_2$  in solvents with variable ratio  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (% vol) and  $c(\text{V})$  (A) and the decomposition of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  by dilution of its freshly prepared concentrated aqueous solution (B).

$\text{V}_2\text{O}_5$  in  $\text{NBu}_4\text{OH}$  and evaporation to dryness, while the residue was dissolved in solvents having a variable ratio  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  in the presence of excess of hydrogen peroxide (2.5–5 equiv). The corresponding spectra (A) nicely demonstrate that the monomer, dimer, and trimer are the only species in such solutions. Furthermore, regardless of the decreasing concentration of vanadium(V), a higher concentration of  $\text{CH}_3\text{CN}$  enforces the formation of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ . On the other hand, upon preparation of a fresh solution of **1** in water<sup>31</sup> and the immediate measurement of its  $^{51}\text{V}$  NMR spectrum (B), a nearly complete decomposition into  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  was detected. The peak of  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  bears a shoulder at  $\sim -710 \text{ ppm}$ , which quickly disappears by subsequent dilution of the solution and is most likely the resonance of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ . The position of the shoulder peak follows the tendency of the movement of the chemical shift of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  in mixed  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvents (Figure 2) toward the signal of  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  in conjunction with increasing concentration of water. The presence of the anion in an aqueous solution was confirmed under different conditions (Figure S4 in the SI).

**$^{51}\text{V}$  NMR Spectroscopy in Other Solvents.** The  $^{51}\text{V}$  NMR spectra of solutions of **1** in  $\text{CH}_2\text{Cl}_2$  and acetone exhibit one signal that could be attributed to  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  (Table 3).

**Table 3.**  $^{51}\text{V}$  NMR Chemical Shifts of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  in Different Solvents,  $c(\text{V}) = 1.5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$

solvent	$\delta$ [ppm]
$\text{H}_2\text{O}$	-710
$\text{CH}_3\text{CN}$	-674
$\text{CH}_2\text{Cl}_2$	-675 <sup>a</sup>
$\text{CHCl}_3$	-676 <sup>a</sup>
acetone	-670 <sup>a</sup>

<sup>a</sup>These assignments need to be confirmed by further experiments.

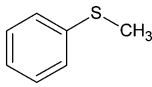
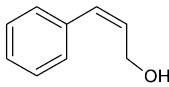
A chloroform solution exhibits one dominant signal at -676 ppm (77%; together with -613, -584, -541, and -520 ppm), which could be assigned to  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ , but after several minutes, this resonance disappears and new resonances attributable to simple vanadates are present: -545 ppm (33%), -566 ppm (12%), and -580 ppm (55%, perhaps  $\text{V}_4\text{O}_{12}^{4-}$ ). One peak is also observed in dimethyl sulfoxide (-598 ppm). A *N,N*-dimethylformamide solution showed two signals (-613 ppm, 70%; -635 ppm, 30%). We strongly emphasize that the assignment of resonances close to the chemical shift of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  in  $\text{CH}_3\text{CN}$  based only on the NMR is insufficient and further experiments will be necessary. One of the most satisfactory supporting experiments would be isolation of a crystalline sample from the solution, but we have been unsuccessful in this task so far.

**Intervention of the Trinuclear Species in Vanadium-Catalyzed Reactions.** Dinuclear peroxidovanadates are believed to play a role in vanadium-catalyzed oxidations,<sup>3,32</sup> among which the most important are alkane oxidations,<sup>32</sup> asymmetric sulfoxidations, and epoxidations.<sup>33</sup> The catalytic reaction is routinely performed using a vanadium precursor and excess hydrogen peroxide, all in an appropriate solvent. Elucidation of the mechanism of vanadium-catalyzed oxidation reactions remains a serious challenge even today. Despite the almost 40 years elapsed from the introduction of a protocol for stereoselective vanadium-catalyzed epoxidation,<sup>34</sup> the identity of the catalytic particle still remains unclear. Even though there is an exhausting data set of  $^{51}\text{V}$  NMR chemical shifts of species present in different catalytic systems, almost all of them are left unidentified or only tentatively ascribed to unspecified monoperoxido and diperoxido complexes of vanadium, which are the most probable terminal oxidizing agents in vanadium-catalyzed reactions. Efforts to elucidate the composition of the reaction mixtures were put on solutions in many relevant solvents, including acetonitrile,<sup>32,35,36</sup>  $\text{CHCl}_3$ ,<sup>37</sup> and  $\text{CH}_2\text{Cl}_2$ <sup>38</sup> (exhibiting low coordination ability), together with some noninnocent solvents, where the situation may become even more complicated, resulting from the possible coordination of the solvent molecules to the vanadium atom. This is the case of water, methanol,<sup>16</sup> and isopropyl alcohol.<sup>35,39</sup> After a careful study of the works listed above, we noticed that several of them pointed to  $^{51}\text{V}$  NMR chemical shifts, which could also be quite reliably assigned to  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ . Our results are most consistent with the work of Shul'pin and co-workers.<sup>35</sup> In the catalytic system in a mixed  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent, they found two major peaks attributed to monoperoxido complexes (-543 and -558 ppm) together with minor peaks of  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  (-644 ppm) and  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  (-699

ppm), which they have assigned to  $[\text{VO}(\text{O}_2)_2(\text{NCCH}_3)]^-$ . We deduce that the coordination of acetonitrile to peroxidovanadium species is a rather unfavorable process and that acetonitrile is capable of stabilizing higher oligomers, which is evident from Figures 2 and 4. The experimentally confirmed fact that the signal of  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  in wet  $\text{CH}_3\text{CN}$  shifts to  $\sim -614$  ppm (compared to -697 ppm in water) and the fact that a similar downfield shift can be expected in other solvents lead us to the crucial proposal that the signal of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  in nonaqueous solvents could lie in the region of -670 to -700 ppm, where until now the signal of  $[\text{VO}(\text{O}_2)_2(\text{solvent})_x]^-$  has been looked for.

Compound **1** is capable of oxidizing thioanisole to the corresponding sulfoxide in  $\text{CDCl}_3$  and cinnamyl alcohol to the undesired aldehyde (instead of epoxide) in  $\text{CD}_3\text{CN}$  and  $\text{CD}_2\text{Cl}_2$  (Table 4), so it appears to us that the intervention of

**Table 4.** Oxidation of Thioanisole and Cinnamyl Alcohol with  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$

Substrate	Entry	Solvent	Conditions	Yield	
				Sulfoxide	Sulfone
	1	$\text{CDCl}_3$	30 min, 5°C	23 %	0 %
	2	$\text{CDCl}_3$	3 h, 5°C	39 %	1 %
	3	$\text{CD}_2\text{Cl}_2$	30 min, 5°C	< 1 %	0 %
	4	$\text{CD}_2\text{Cl}_2$	3 h, 5°C	5 %	0 %
				Epoxide	Aldehyde
	5	$\text{CD}_3\text{CN}$	30 min, RT	0 %	0 %
	6	$\text{CD}_3\text{CN}$	20 h, RT	0 %	99 %
	7	$\text{CD}_2\text{Cl}_2$	30 min, RT	0 %	50 %
8	$\text{CD}_2\text{Cl}_2$	20 h, RT	0 %	99 %	

$[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  in catalytic systems has to be seriously considered. Together with  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ , they may act as powerful oxidizing agents and influence both the yield and enantioselectivity in asymmetric reactions. It is obvious that  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  and  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  are formed in situ from a vanadium (pre)catalyst, usually a chiral complex. While the monomer is achiral and lowers the enantiomeric excess,<sup>38</sup>  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  is itself chiral. If the chirality of the precursor could have an influence on the chirality of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ , this would necessitate a dramatic change on the conception of the mechanism of vanadium-catalyzed oxidations.

The signals in the  $^{51}\text{V}$  NMR spectra of the  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_3$  solutions (Figure 5, entries 1–4, 7, and 8) observable at  $\sim -612$  ppm could be assigned to  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ , while the signals at  $\sim -675$  ppm may correspond to  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  if the positions of their  $^{51}\text{V}$  NMR chemical shifts in these solvents would be similar to those of acetonitrile (entries 5 and 6). Such an assignment seems to be reasonable because of the consistent positions of the signals in all of the solvents and good agreement with the data presented in Table 3.

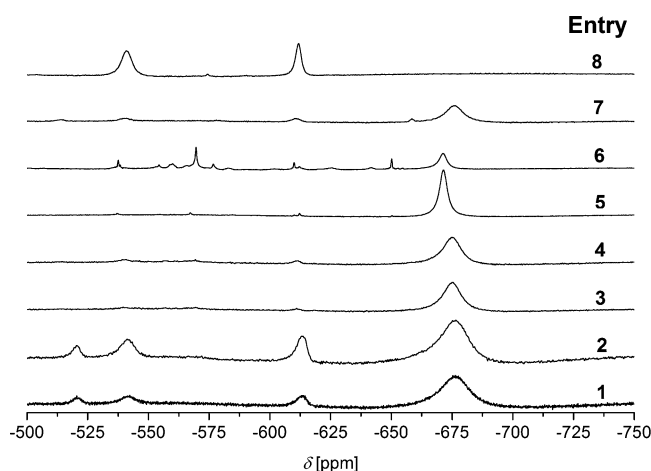


Figure 5.  $^{51}\text{V}$  NMR spectra of reaction mixtures listed in Table 3.

## CONCLUSIONS

In conclusion, we presented the synthesis and structural characterization of the  $(\text{NBu}_4)^+$  salt of the first chiral trinuclear peroxidovanadate,  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$ , with an unprecedented cyclic structure and the yet-unobserved  $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$  coordination mode of one of its peroxido ligands. The  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  anion is stable in an acetonitrile solution, and we ran several speciation studies in a two-component  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solvent to demonstrate that the formation of  $[\text{V}_2\text{O}_2(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$  and  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  is supported by a higher vanadium concentration and a higher  $\text{CH}_3\text{CN}$  content.  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  oxidizes thioanisole to the corresponding sulfoxide and cinnamyl alcohol to the aldehyde, and it is most likely an integrant of catalytic systems involving a vanadium precursor and excess hydrogen peroxide. Very importantly, for the first time, it was possible to perform a speciation study in an organic solvent using a peroxidovanadate having a defined composition and without the presence of a heteroligand. Concluding our observations, it is of utmost importance to emphasize the necessity of isolation and structural characterization of compounds present in solution for a better understanding of speciation and a more reliable elucidation of the mechanism of oxidation reactions.

## EXPERIMENTAL SECTION

**General Remarks.** All reagents and solvents were obtained from commercial sources and used without further purification.  $\text{V}_2\text{O}_5$  was prepared by thermal decomposition of previously purified  $\text{NH}_4\text{VO}_3$ . Elemental analyses (C, H, and N) were performed on a Vario MIKRO cube (Elementar). Vanadium(V) was determined volumetrically by titration with a standardized solution of  $\text{FeSO}_4$  using diphenylamine as the indicator. The sample was annealed in a porcelain dish prior to titration to release the peroxido oxygen. The content of  $\text{O}_2^{2-}$  was determined volumetrically by titration with a standardized solution of  $\text{KMnO}_4$  with a potentiometric indication of the equivalence point. IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT IR spectrometer in a Nujol mull and using two KRS-5 (TlBr–TlI) windows for the liquid sample. The UV–vis spectrum was recorded on the Jasco V-530 instrument in the range 200–1000 nm. The NMR spectra were registered at 278 K on a Varian VNMRs 600 MHz spectrometer operating at 157.88 MHz ( $^{51}\text{V}$ ) in 5 mm tubes.  $^{51}\text{V}$  NMR chemical shifts ( $\delta$ ) are given in ppm relative to  $\text{VOCl}_3$  as the external standard ( $\delta = 0$  ppm).

**Synthesis.**  $\text{V}_2\text{O}_5$  (0.2 g, 1.1 mmol) was dissolved in  $\text{NBu}_4\text{OH}$  (1.45 mL, 40% w/w, 2.2 mmol), and water (5 mL) was added to the solution. L-Glutamic acid (0.324 g, 2.2 mmol) was dissolved in

$\text{NBu}_4\text{OH}$  (1.45 mL, 40% w/w, 2.2 mmol), and water (5 mL) was added. The combined solution was cooled in an ice bath, and  $\text{H}_2\text{O}_2$  (0.44 mL, 30% w/w, 4.4 mmol) was added. A clear yellow solution was stirred for 5 min, filtered, and placed in a Petri dish. On the fifth day of standing at 5 °C, bright-orange-yellow blocky crystals of **1** were filtered off, washed with ice-cooled water, and dried over silica. Yield: 20%. Anal. Calcd for **1**,  $\text{C}_{48}\text{H}_{112}\text{N}_3\text{O}_{17}\text{V}_3$  (1156.24): C, 49.86; H, 9.76; N, 3.63; V, 13.22;  $\text{O}_2^{2-}$ , 16.60. Found: C, 50.54; H, 9.53; N, 3.67; V, 13.35;  $\text{O}_2^{2-}$ , 17.00.

Compound **1** is stable at  $-15$  °C for several months, and handling of the compound possesses no hazards. The L-glutamate anion (glu) does not coordinate to the vanadium atom; however, the absence of L-glutamic acid during the synthesis leads to failure. We suppose that the role of tetrabutylammonium L-glutamate used in the synthesis is predominantly acido–basic. Replacement of  $\text{NBu}_4(\text{gluH})$  by  $\text{NBu}_4\text{NO}_3$  (but not  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{SO}_4^{2-}$ ) and adjustment of the pH by  $\text{NBu}_4\text{OH}$  to the value of 6.7 resulted in a mixture of three products: white rods, yellow crystals, and orange crystals of the title compound (vide infra). Interestingly, the use of enantiomerically pure L-glutamic acid did not cause stereoselective formation of  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  or preferential crystallization of a single enantiomer.

**Single-Crystal X-ray Diffraction.** Diffraction data were collected using a Kappa Apex II (Bruker) diffractometer equipped with a Cryostream cooler (Oxford Cryosystems). Data were collected using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) and corrected for radiation absorption by methods incorporated in the diffractometer software. The phase problem was solved by direct methods (*SHELXS97*)<sup>40</sup> and refined by full-matrix least squares based on  $F^2$  (*SHELXL97*).<sup>40</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined as riding atoms. Geometric data were obtained with a recent version of the *PLATON* program.<sup>41</sup> Graphics were obtained with *DIAMOND*.<sup>42</sup> CCDC: 1050678. Crystal data and structure refinement details are summarized in Table 2.

**Computational Details.** DFT calculations have been carried out at the *bose* cluster at the J. Heyrovský Institute of Physical Chemistry, The Czech Academy of Sciences, v.v.i., using *Gaussian 09*, revision D.01.<sup>43</sup> The solid-state structure has been used as input geometry. Atoms of cations and crystal water molecules residing in the asymmetric part of the unit cell have been discarded, and only the anionic part has been retained. The single-point calculation utilized an ultrafine integration grid, the M06 functional,<sup>44</sup> and the 6-31+G(d,p) basis set for all atoms. Prior to carrying out population analysis, the wave function has been verified for stability.

**Oxidation Reactions.** General procedure: 0.7 mmol of the substrate (methylphenylsulfide or cinnamyl alcohol) and 0.7 mmol of **1** [ $c(\text{V}) = 2 \times 10^{-2}$  mol·dm<sup>-3</sup>] were dissolved in 1 mL of the chosen solvent in a 5 mm NMR tube. After the desired time, the reaction mixture was monitored by  $^1\text{H}$  NMR spectroscopy to determine the conversion.  $^{51}\text{V}$  NMR spectra were collected afterward.

## ASSOCIATED CONTENT

### Supporting Information

Vibrational and additional NMR spectra, bond lengths, and X-ray crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00600.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: krivosudskyl@fns.uniba.sk. Tel.: +421 2 602 96 273.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the Grant Agency of the Ministry of Education of the Slovak Republic and Slovak Academy of Sciences VEGA Project 1/0336/13.

## REFERENCES

- (1) Bevan, A. P.; Drake, P. G.; Yale, J.-F.; Shaver, A.; Posner, B. I. *Mol. Cell. Biochem.* **1995**, *153*, 49–58.
- (2) Posner, B. I.; Faure, R.; Burgess, J. W.; Bevan, A. P.; Lachance, D.; Zhang-Sun, G.; Fantus, I. G.; Ng, J. B.; Hall, D. A.; Soo Lum, B.; Shaver, A. *J. Biol. Chem.* **1994**, *269*, 4596–4604.
- (3) Tracey, A. S.; Willsky, G. R.; Takeuchi, E. S. *Vanadium Chemistry, Biochemistry, Pharmacology, and Practical Applications*; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2007.
- (4) Rehder, D. *Bioinorganic Vanadium Chemistry*; John Wiley & Sons: Chichester, U.K., 2007; pp 119–121.
- (5) Colpas, G. J.; Hamstra, B. J.; Kampf, J. W.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1996**, *118*, 3468–3478.
- (6) Hwang, J. H.; Larson, R. K.; Abu-Omar, M. M. *Inorg. Chem.* **2003**, *42*, 7967–7977.
- (7) Djordjevic, C.; Wampler, G. L. *J. Inorg. Biochem.* **1985**, *25*, 51–55.
- (8) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 625–638.
- (9) Conte, V.; Floris, B. *Dalton Trans.* **2011**, *40*, 1419–1436.
- (10) Howarth, O. W.; Hunt, J. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1388–1391.
- (11) Harrison, A. T.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1173–1177.
- (12) Campbell, N. J.; Dengel, A. C.; Griffith, W. P. *Polyhedron* **1989**, *8*, 1379–1386.
- (13) Jaswal, J. S.; Tracey, A. S. *Inorg. Chem.* **1991**, *30*, 3718–3722.
- (14) Conte, V.; Di Furia, F.; Moro, S. *J. Mol. Catal.* **1994**, *94*, 323–333.
- (15) Conte, V.; Di Furia, F.; Moro, S. *Inorg. Chim. Acta* **1998**, *272*, 62–67.
- (16) Conte, V.; Bortolini, O.; Carraro, M.; Moro, S. *J. Inorg. Biochem.* **2000**, *80*, 41–49.
- (17) Andersson, I.; Angus-Dunne, S.; Howarth, O.; Pettersson, L. *J. Inorg. Biochem.* **2000**, *80*, 51–58.
- (18) Gorzsás, A.; Andersson, I.; Pettersson, L. *J. Inorg. Biochem.* **2009**, *103*, 517–526.
- (19) Lapshin, A. E.; Smolin, Y. I.; Shepelev, Y. F.; Gyepesová, D.; Schwendt, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *45*, 1477–1479.
- (20) Lapshin, A. E.; Smolin, Y. I.; Shepelev, Y. F.; Schwendt, P.; Gyepesová, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 738–741.
- (21) Suchá, V.; Sívák, M.; Tyršlová, J.; Marek, J. *Polyhedron* **1997**, *16*, 2837–2842.
- (22) Schwendt, P.; Liščák, K. *Collect. Czech. Chem. Commun.* **1996**, *61*, 868–876.
- (23) Slebodnick, C.; Pecoraro, V. L. *Inorg. Chim. Acta* **1998**, *283*, 37–43.
- (24) Won, T.-J.; Barnes, C. L.; Schlemper, E. O.; Thompson, R. C. *Inorg. Chem.* **1995**, *34*, 4499–4503.
- (25) Stomberg, R.; Olson, S.; Svensson, I.-B. *Acta Chem. Scand., Ser. A* **1984**, *38*, 653–656.
- (26) Campbell, N. J.; Flanagan, J.; Griffith, W. P.; Skapski, A. C. *Transition Met. Chem.* **1985**, *10*, 353–354.
- (27) Hamilton, E. E.; Fanwick, P. E.; Wilker, J. J. *J. Am. Chem. Soc.* **2002**, *124*, 78–82.
- (28) Bühl, M.; Parrinello, M. *Chem.—Eur. J.* **2001**, *7*, 4487–4494.
- (29) See the SI for further details and additional  $^{51}\text{V}$  NMR spectra.
- (30) The positions of the peaks are slightly dependent on  $c(\text{V})$ .
- (31) Because  $[\text{V}_3\text{O}_3(\text{O}_2)_6]^{3-}$  is rapidly decomposed by dissolving it in water, it was impossible to obtain its saturated solution. The solution under discussion was prepared by vigorous stirring of 500 mg of 1 in 2 mL of water, followed by quick filtering and immediate measurement.
- (32) Kirillova, M. V.; Kuznetsov, M. L.; Kozlov, Y. N.; Shul'pina, L. S.; Kitaygorodskiy, A.; Pombeiro, A. J. L.; Shul'pin, G. B. *ACS Catal.* **2011**, *1*, 1511–1520.
- (33) Pellissier, H. *Coord. Chem. Rev.* **2015**, *284*, 93–110.
- (34) Michaelson, R. C.; Palermo, R. E.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 1990–1992.
- (35) Kirillova, M. V.; Kuznetsov, M. L.; Romakh, V. B.; Shul'pina, L. S.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Shul'pin, G. B. *J. Catal.* **2009**, *267*, 140–157.
- (36) Shul'pin, G. B.; Kozlov, Y. N.; Nizova, G. V.; Süß-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1351–1371.
- (37) Lippold, I.; Becherb, J.; Klemm, D.; Plass, W. *J. Mol. Catal. A: Chem.* **2009**, *299*, 12–17.
- (38) Karpyshev, N. N.; Yakovleva, O. D.; Talsi, E. P.; Bryliakov, K. P.; Tolstikova, O. V.; Tolstikov, A. G. *J. Mol. Catal. A: Chem.* **2000**, *157*, 91–95.
- (39) Kozlov, Y. N.; Romakh, V. B.; Kitaygorodskiy, A.; Buglyó, P.; Süß-Fink, G.; Shul'pin, G. B. *J. Phys. Chem. A* **2007**, *111*, 7736–7752.
- (40) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.
- (41) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
- (42) Brandenburg, K. In *Diamond, Crystal and Molecular Structure Visualization*, version 3.2; Brandenburg, K., Putz, H., Eds.; Crystal Impact GbR: Bonn, Germany, 2009.
- (43) Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2013.
- (44) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–41.