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Mono and oligonuclear vanadium complexes as catalysts for alkane oxidation: synthesis, molecular structure, and catalytic potential

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Abstract

A series of mono- and oligonuclear vanadium(V) and vanadium(IV) complexes containing various chelating *N*,*O*-, N_3-, and O_2-ligands have been prepared. The biphasic reaction of an aqueous solution of ammonium vanadate and a dichloromethane solution of hexamethylphosphoramide (hmpa) and pyrazine-2-carboxylic acid (pcaH) or pyrazine-2,5-dicarboxylic acid ($pdcaH_2$) or pyridine-2,5-dicarboxylic acid ($pycaH_2$) yields yellow crystals of $[VO_2(pca)(hmpa)]$ (**1**), $[(VO_2)_2(pdca)(hmpa)_2]$ (**2**), and $[VO_2(pycaH)(hmpa)]$ (**3**), respectively. The single-crystal X-ray structure analyses reveal **1** and **3** to be mononuclear vanadium(V) complexes, in which a VO_2 unit coordinates to one nitrogen and one oxygen atom of a pca or pycaH chelating ligand, and **2** to be a dinuclear vanadium(V) complex, in which two VO_2 units are coordinated through one nitrogen and one oxygen atom of a pdca bridging ligand; in the three complexes the vanadium atoms also coordinate to the oxygen atom of a hmpa ligand. The reaction of *N*,*N*,*N*′,*N*′-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane (hptbH) and $VOSO_4$ in methanol gives the cationic complex $[(VO)_4(hptb)_2(\mu\text{-}O)]^{4+}$ (**4**), which can be crystallized as the perchlorate salt. In this tetranuclear complex, two dinuclear vanadium(IV) units are held together by a μ-oxo bridge. The known complex $[VOCl_2(tmtacn)]$ (**5**) was synthesized from the reaction of 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) and VCl_3 in acetonitrile; the reaction of tetrabutylammonium vanadate with *pyro*-cathecol ($catH_2$) in acetonitrile gives the known anionic complex $[V(cat)_3]^-$ (**6**), in which the vanadium(V) center is bonded to three cat chelating ligands through the oxygen atoms, obtained as the tetrabutylammonium salt. All compounds synthesized are highly efficient oxidation catalysts for the reaction of cyclohexane with air and hydrogen peroxide in the presence of four equivalents of pcaH per vanadium, although the catalytic activity of the complexes containing bulky chelating ligands **4** and **5** is somewhat lower in the initial period of the reaction. During this period the active species are formed from the complexes and final turnover numbers are high. The catecholate ligands of complex **6** may reduce from V(V) to V(IV) in the beginning of the process, thus providing very high initial oxidation rates.

Keywords: Alkanes; Oxidation; Vanadium complexes

1. Introduction

Vanadium complexes play a very important role in catalytic organic chemistry (see books and reviews [1–7] and recent original papers [8–12]) and also in living organisms (books and reviews [9–21]). Vanadium can mimic insulin's actions [22–25], its complexes with certain amino acids have been proposed as anti-tumor and anti-leukemic agents [26], they initiate the photo-cleavage of DNA [27] and are finally known as potent toxicants and carcinogens [28–33] which can act via generation of hydroxyl radicals. These radicals formed from molecular oxygen or hydrogen peroxide under the action of vanadium complexes in a living cell [34,35] attack various cell components leading to damage and induce aerobic peroxidation of liposomal membranes [36]. In recent years, many papers have been published on the

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synthesis of biomimetic vanadium complexes and on their activity in various metabolisms [37–44].

Hydroxyl radicals, very efficiently generated from H_2O_2 (or less efficiently from O_2 and a reducing agent) under the action of vanadium catalysts, have been successfully used for organic synthesis in vitro [45–51]. As all these systems contained certain amino acids as additives to vanadium derivatives or as ligands at vanadium center, they can be considered as biomimetic models which oxidize with very high turnover numbers (TONs): aliphatic [45–49], olefinic [50], and aromatic [51] hydrocarbons.

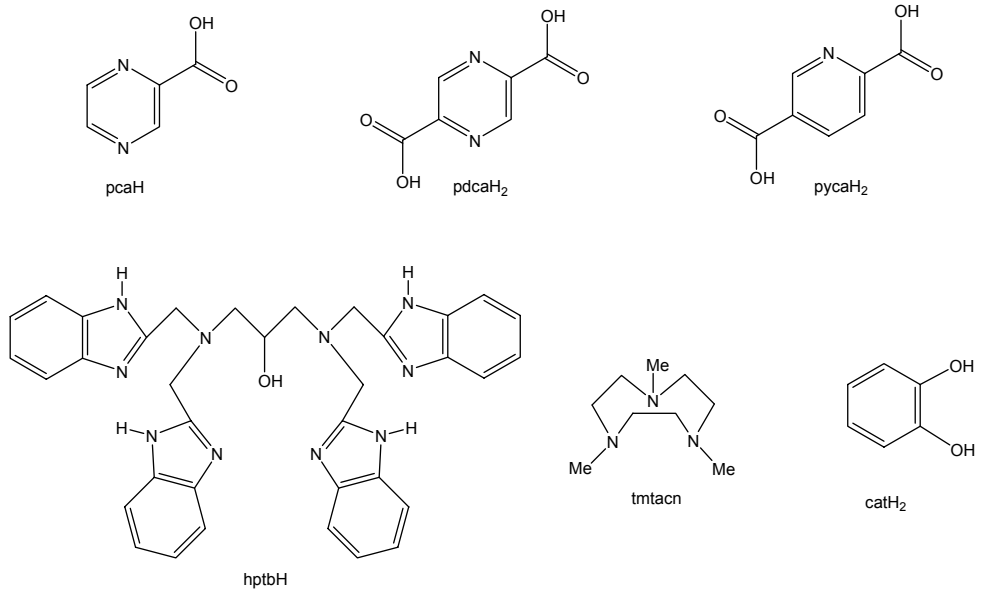
$$RH + \tfrac{1}{2}O_2 + H_2O_2 \rightarrow ROOH + H_2O$$

Typically, the simple vanadate anion (in the form of its n-Bu_4N^+ salt soluble in acetonitrile) was used as a catalyst in combination with pyrazine-2-carboxylic acid (pcaH), a mixture from which the anion $[VO_2(pca)_2]^-$ has been isolated as the tetrabutylammonium salt [52]. On the basis of kinetic studies, a mechanism of hydroxyl radical generation was proposed [7,53,54] which included as the rate-limiting step the monomolecular decomposition of a complex containing one coordinated pca ligand as well as one hydrogen peroxide molecule ("V^{5+}" + H_2O_2 → "V^{4+}" + $HOO^{\cdot}$ + H^+). The V(IV) species thus formed reacts further with a second H_2O_2 molecule to generate the hydroxyl radical ("V^{4+}" + H_2O_2 → "V^{5+}" + $HO^{\cdot}$ + OH^-). It was assumed that the accelerating role of pcaH is due to facilitating the proton transfer between oxo and hydroxo ligands of the vanadium complex on the one hand and the molecules of hydrogen peroxide and water on the other hand (a biomimetic robot's arm mechanism) [54]. Very recently, systems which mimic the generation of hydroxyl radicals in certain vanadium-dependent biological processes have been reported. Thus, the vanadate anion catalyzes aerobic hydroxylation of hydrocarbons in the presence of solid ascorbic acid or zinc and with the obligatory participation of pyridine, pcaH, and acetic acid as mediators of proton and electron transfer [55].

It was interesting to extend a set of vanadium complexes bearing various N,O-, N_3-, and O_2-chelating ligands as potential biomimetic systems, which are capable of generating hydroxyl radicals from hydrogen peroxide. In order to test the catalytic activity, cyclohexane was used as a substrate, as it is known to be a trap for hydroxyl radicals, leading to the formation of cyclohexyl hydroperoxide as a main product.

2. Results and discussion

In this work, we used N,O-chelating ligands, anions of pyrazine-2-carboxylic acid (pcaH) and pyrazine-2,5-dicarboxylic acid ($pdcaH_2$) for the synthesis of vanadium(V) oxo derivatives. In a previous paper, we had reported the synthesis of anionic complexes $[VO_2(pca)_2]^-$ which contain two pca ligands in the molecule [52]. Inspired by the pioneering work of Mimoun et al. [56], we decided to block a vanadium(V) coordination site by the bulky hexamethylphosphoramide $(Me_2N)_3PO$ (hmpa), in order to prevent the coordination of a second pca ligand. The same strategy was applied to the synthesis of a dinuclear dioxovanadium(V) complex containing a N,O-chelating ligand derived from pyrazine-2,5-dicarboxylic acid. It was interesting to compare the latter ligand with that derived from pyridine-2,5-dicarboxylic acid ($pycaH_2$) which can give rise to the formation of a similar mononuclear vanadium derivative (Scheme 1).



Scheme 1. N,O-, N_3-, and O_2- containing molecules used as ligands or ligand precursors for the coordination to vanadium(V) or vanadium(IV).

Furthermore, it was important to compare the catalytic properties of these vanadium complexes containing *N*,*O*-chelating ligands as well as weakly coordinating hmpa ligands with vanadium complexes containing strongly coordinating chelating ligands. For this purpose, we prepared complexes containing 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) as a ligand, and complexes containing ligands derived from *N*,*N*,*N*′,*N*′-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane (hptb) and from *pyro*-catechol ($catH_2$).

2.1. Syntheses

The reaction of pyrazine-2-carboxylic acid, pyrazine-2,5-dicarboxylic or pyridine-2,5-dicarboxylic acid with ammonium vanadate in the correct metal to ligand ratio gives, in the presence of excessive hexamethylphosphoramide, rise to the formation of the neutral complexes **1**, **2**, and **3** according to Eqs. (1)–(3). The use of an excess of hmpa helps to avoid the coordination of a second *N*,*O*-chelating ligand to the vanadium(V) center. Complexes **1**, **2** and **3** are easily extracted in dichloromethane and recrystallized from a mixture of dichloromethane and diethyl ether (Scheme 2).

$$[VO_3]^- + \mathrm{pcaH} + \mathrm{hmpa} \rightarrow \underset{(\mathbf{1})}{[VO_2(\mathrm{pca})(\mathrm{hmpa})]} + OH^- \quad (1)$$

$$2[VO_3]^- + \mathrm{pdcaH_2} + 2\mathrm{hmpa} \rightarrow \underset{(\mathbf{2})}{[(VO_2)_2(\mathrm{pdca})(\mathrm{hmpa})_2]} + 2OH^- \quad (2)$$

$$[VO_3]^- + \mathrm{pycaH_2} + \mathrm{hmpa} \rightarrow \underset{(\mathbf{3})}{[VO_2(\mathrm{pycaH})(\mathrm{hmpa})]} + OH^- \quad (3)$$

The reaction of $VOSO_4$ with hptbH in methanol, the metal to ligand ratio being 2:1, yields, in the presence of $NaClO_4 \cdot nH_2O$ after some weeks at room temperature green crystals of $[(VO)_4(\mathrm{hptb})_2(H_2O)_2(\mu\text{-}O)][ClO_4]$ (cation **4**), according to Eq. (4). Complex **4** has a tetrameric structure composed of two dinuclear vanadium(IV) moieties held together by a μ-oxo bridge. Each dinuclear moiety is formed by two vanadyl moieties chelated through two imidazol-nitrogen atoms, one amino nitrogen and the oxygen atom of the alkoxo function of the hptb ligands.

$$4[VO]^{2+} + 2\mathrm{hptbH} + 3H_2O \rightarrow \underset{(\mathbf{4})}{[(VO)_4(\mathrm{hptb})_2(H_2O)_2(\mu\text{-}O)]^{4+}} + 4H^+ \quad (4)$$

$$2VCl_3 + 2\mathrm{tmtacn} + H_2O + \frac{1}{2}O_2 \rightarrow \underset{(\mathbf{5})}{2[VOCl_2(\mathrm{tmtacn})]} + 2HCl \quad (5)$$

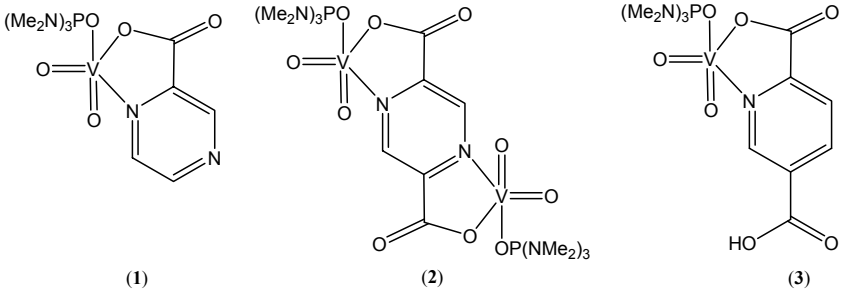
$$[VO_3]^- + 3\mathrm{catH_2} \rightarrow \underset{(\mathbf{6})}{[V(\mathrm{cat})_3]^-} + 3H_2O \quad (6)$$

The known [57,62] vanadium(IV) 1,4,7-trimethyl-1,4,7-triazacyclononane complex $[VOCl_2(\mathrm{tmtacn})]$ (**5**) is synthesized by a slightly modified procedure with respect to that of the original paper [57]: Vanadium(III) chloride is reacted in wet acetonitrile at 0 °C with tmtacn, after the color change from violet to black, the reaction solution is refluxed in air to allow the oxidation of vanadium(III) to vanadium(IV), according to Eq. (5). Blue crystals of **5** are obtained by recrystallization from acetonitrile. The known [58] vanadium(V) catecholate complex $[V(cat)_3]^-$ (**6**) is accessible as the tetrabutylammonium salt from $[n\text{-}Bu_4N][VO_3]$ and catechol (1:3) in acetonitrile, in the presence of triethylamine to facilitate the deprotonation of catechol, according to Eq. (6) (Scheme 3).

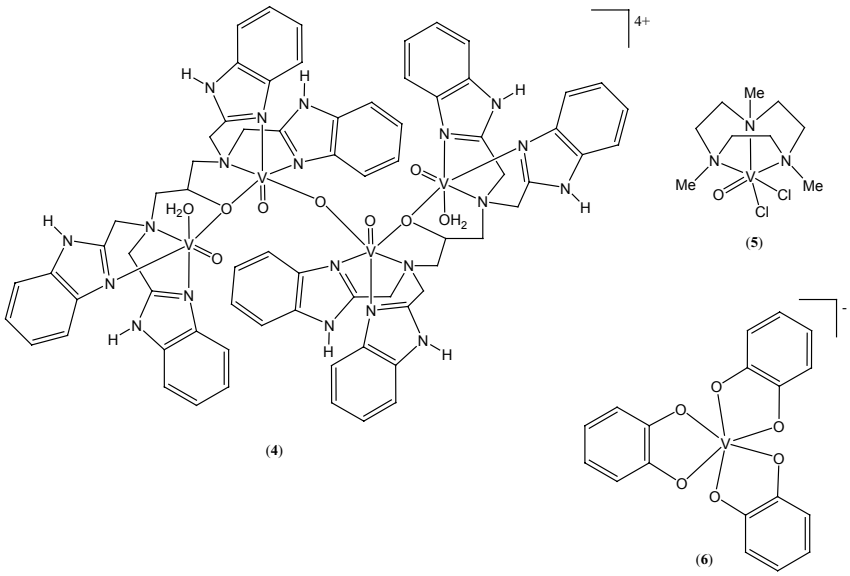
2.2. Molecular structures

The molecular structures of compounds **1**, **2**, **3**, and **4**$[ClO_4]_4$ have been determined by single-crystal X-ray structure analysis. Due to poor crystal quality, the structure analysis for **2** is not good enough for a precise structure determination; nevertheless, it was possible to elucidate the molecular constitution and configuration. Selected bond distances and angles are given in Tables 1 and 2.

The X-ray crystal structure analysis of **1** (Fig. 1) reveals a trigonal-bipyramidal environment of the vana-



Scheme 2. Mono- and dinuclear vanadium(V) complexes containing *N*,*O*-chelating ligands.



Scheme 3. The tetranuclear vanadium(IV) complex **4** and the known mononuclear vanadium complexes **5** and **6**.

Table 1
Selected bond distances (Å) and angles (°) of complexes **1**, **2**, and **3**

	1	**2**		**3**
V(1)–O(1)	1.606(4)	1.670(15)	V(1)–O(5)	1.617(4)
V(1)–O(2)	1.600(4)	1.607(16)	V(1)–O(6)	1.628(4)
V(1)–O(3)	2.001(4)	2.065(15)	V(1)–O(9)	1.987(5)
V(1)–O(5)	1.967(4)	1.968(17)	V(1)–O(1)	1.976(3)
V(1)–N(1)	2.173(4)	2.17(2)	V(1)–N(1)	2.137(4)
V(2)–N(2)		2.132(2)	O(11)–H(11)	0.840
V(2)–O(2)		1.966(17)	H(11)–O(3)	1.670
V(2)–O(7)		1.622(16)		
V(2)–O(8)		1.633(15)		
V(2)–O(13)		2.004(15)		
O(1)–V(1)–O(2)	109.2(2)	104.6(8)	O(5)–V(1)–O(6)	109.3(2)
N(1)–V(1)–O(3)	75.34(16)	74.8(7)	N(1)–V(1)–O(9)	75.27(18)
O(3)–V(1)–O(5)	80.59(16)	85.2(7)	O(1)–V(1)–O(9)	82.45(17)
V(1)–O(5)–P(1)	139.5(3)	135.6(11)	V(1)–O(1)–P(1)	137.3(3)
V(2)–O(2)–P(2)		140.0(11)	O(11)–H(11)–O(3)	169.87

dium atom, which agrees with that of the analogous picolinato complex [56]. In the dioxovanadium moiety, the two terminal oxo ligands are *cis* positioned with respect to each other. The V=O distances are 1.606 and 1.600 Å, and the O=V=O angle is 109.2°. The pca ligand is coordinated to the dioxovanadium moiety by an oxygen atom of the carboxylato function and by the nitrogen atom of the aromatic cycle in the α position with respect to the carboxylato substituent; this coordination gives an almost planar five-membered metallocyclic moiety. The V–O bond is 2.001 Å and the V–N bond is 2.173 Å, and the O–V–N angle is 75.34°. The hmpa ligand is bonded to the vanadium atom through the oxygen atom, with a distance of 1.967 Å and a V–O–P angle of 139.5°.

In **2** (Fig. 2), both vanadium atoms also have a trigonal-bipyramidal environment, both being coordinatively equivalent due to the symmetry of the molecule. The pdca ligand is chelated to both VO_2 moieties by one oxygen atom of the carboxylato function and by a nitrogen atom of the aromatic ring in the α-position. The carboxylato function and the aromatic nitrogen form with the vanadium atom an almost planar five-membered metallocyclic moiety. One hmpa ligand is bonded to each vanadium atom by its oxygen atom, the coordination geometry of both vanadium atoms in **2** is similar to that found in **1**. As the final *R* value is only 21%, the bond angles and distances are not reliable enough for precise values.

The molecular structure of **3** is similar to that of **1**. The vanadium center is bonded to two terminal oxo ligands, the V–O bond distances being 1.617 and 1.628 Å, respectively, and the O–V–O angle 109.3°. The vanadium atom is coordinated to the pycaH ligand through

Table 2
Selected bond distances (Å) and angles (°) of complex **4**$[ClO_4]_4$

V(1)–N(1)	2.040(9)	O(2)–V(1)–O(3)	108.9(3)
V(1)–N(3)	2.054(6)	O(2)–V(1)–N(1)	98.6(3)
V(1)–N(5)	2.361(7)	O(3)–V(1)–N(1)	152.5(3)
V(2)–N(7)	2.057(6)	O(2)–V(1)–O(1)	99.5(2)
V(2)–N(9)	2.065(6)	O(3)–V(1)–O(1)	88.3(2)
V(2)–N(6)	2.359(6)	N(1)–V(1)–O(1)	85.9(3)
V(1)–O(1)	2.045(5)	O(2)–V(1)–N(3)	98.1(3)
V(1)–O(2)	1.609(5)	O(3)–V(1)–N(3)	90.6(2)
V(1)–O(3)	2.017(6)	N(1)–V(1)–N(3)	86.8(3)
V(2)–O(3)	2.052(5)	O(1)–V(1)–N(3)	161.7(3)
V(2)–O(4)	1.603(5)	O(2)–V(1)–N(6)	171.7(3)
V(2)–O(5)	1.8102(16)	O(3)–V(1)–N(6)	77.1(2)
		N(1)–V(1)–N(6)	75.7(3)
		O(1)–V(1)–N(6)	86.2(2)
		N(3)–V(1)–N(6)	75.8(3)
		V(2)–O(5)–V(2)#1	180.0
		O(4)–V(2)–O(5)	102.1(2)
		O(4)–V(2)–O(3)	95.6(3)
		O(5)–V(2)–O(3)	162.34(17)
		O(4)–V(2)–N(7)	104.4(2)
		O(5)–V(2)–N(7)	85.6(2)
		O(3)–V(2)–N(7)	89.8(2)
		O(4)–V(2)–N(9)	105.0(3)
		O(5)–V(2)–N(9)	89.60(19)
		O(3)–V(2)–N(9)	86.0(2)
		N(7)–V(2)–N(9)	150.5(3)
		O(4)–V(2)–N(6)	172.3(3)
		O(5)–V(2)–N(6)	85.55(17)
		O(3)–V(2)–N(6)	76.8(2)
		N(7)–V(2)–N(6)	75.7(2)
		N(9)–V(2)–N(6)	75.0(3)

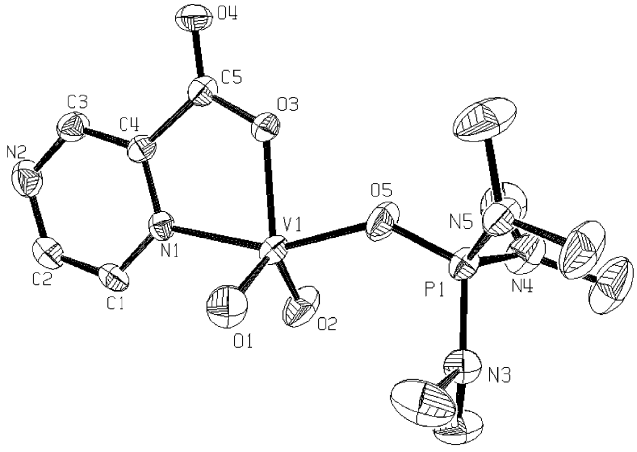


Fig. 1. Molecular structure of **1**.

the oxygen atom of the α-carboxylato function, the bond distance being 1.987 Å, and through the nitrogen atom of the aromatic cycle, with a V–N distance of 2.137 Å. The N–V–O angle is 75.27°. The vanadium center is also bonded to the oxygen atom of the hmpa ligand with a bond distance of 1.976 Å and a V–O–P angle of 137.3°. As in **3** only one of the carboxylic functions is coordinated, while the other one is present as a free carboxylic

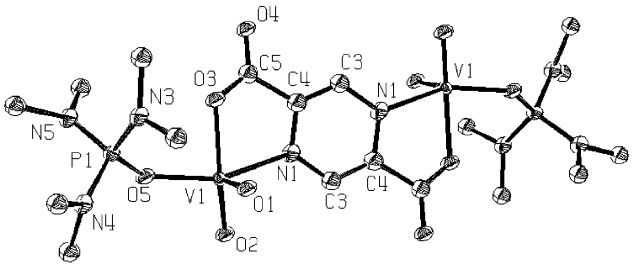


Fig. 2. Molecular structure of **2**.

function, the crystal structure reveals an adduct of **3** with an additional hmpa molecule linked by hydrogen bonding: The H atom is bonded to the oxygen of the carboxylic function with a bond distance of 0.840 Å and to the oxygen of the additional hmpa ligand with a bond distance of 1.670 Å. The O–H–O angle is 169.87° (see Fig. 3).

Complex **4** (Fig. 4) was found to contain four vanadium atoms and two N_3O- ligands, two $V_2(hptb)(O)_2(H_2O)$ moieties being connected by an μ-oxo bridge

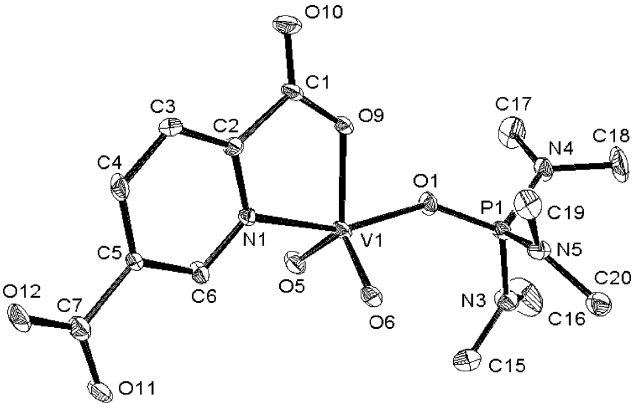


Fig. 3. Molecular structure of **3**.

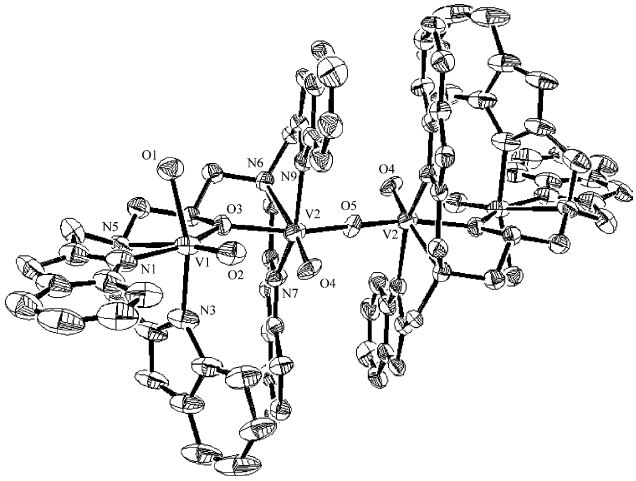


Fig. 4. Molecular structure of **4**.

situated at the center of symmetry of the molecule. The four vanadium atoms are six-coordinated in a distorted octahedral geometry, two of which being pairwise equivalent. Both V(2) atoms are bonded to the μ-O bridge with a V–O distance of 1.810 Å and an V–O–V angle of 180°. The environment of these two vanadium atoms is formed by three nitrogen atoms and one oxygen atom of the hptb ligand, a terminal oxo ligand and the bridging oxo ligand. The hptb ligand chelates these V(2) atoms through two imidazol nitrogen atoms with the V–N distances of 2.054 and 2.057 Å, one amino nitrogen atom with a V–N distance of 2.359, and one alkoxo oxygen atom with a V–O distance of 2.052; the terminal oxo ligand is bonded to each V(2) with a V–O distance of 1.603 Å, and forms an angle of 162.34° with the μ-oxo bridge. The other two equivalent vanadium atoms V(1) also have an octahedral coordination geometry, formed by three nitrogen atoms and one oxygen atom of the hptb ligand, a terminal oxo ligand, and a water ligand. Each hptb ligand bonds one V(1) by two imidazol nitrogen atoms with the V–N distances of 2.040 and 2.054 Å, one nitrogen amino ligand with the V–N distance of 2.361 Å, and one alkoxo oxygen atom with the V–O distance of 2.017 Å. The oxo ligand in each V(1) center bonds to vanadium with a V–O distance of 1.609 Å and a water molecule is bonded to each V(1) with a V–O distance of 2.045 Å. The angle between the oxo ligand, the V(1) center, and the oxygen atom of the water molecule is 99.5°. In each V_2(hptb)$(O)_2(H_2O)$ moiety, the two terminal oxo ligands are *syn* and they are *anti* with respect to the corresponding oxo ligands in the other moiety, comparable to the structure of $[(VO)_4(btppnol)_2(\mu\text{-}O)_2](ClO_4)_2 \cdot 2DMF \cdot 2H_2O$ published very recently [63].

2.3. Catalytic oxidation of cyclohexane

We studied the catalytic activity of all compounds synthesized for the oxidation of cyclohexane with hydrogen peroxide and air in acetonitrile. Based on our previous publication [54], we carried out the reactions at 40 °C. In accordance with our previous findings [45–55], we added pcaH as a co-catalyst (V/pcaH ratio 1:4) which accelerates the reaction, even in the cases where the vanadium complexes contain already one or two pca ligands. We followed the course of the reaction normally for 24 h. The samples were analyzed twice, i.e., before and after the addition of the excess of solid PPh_3, a method which allows to detect alkyl hydroperoxides and to measure also the real concentrations of all three products [6,7,45–47,67–72].

The data obtained are summarized in Table 3. The vanadium complexes differ significantly in their catalytic behavior, the most efficient catalyst (per vanadium) being complex **1**. It oxidizes cyclohexane with high initial rate and high TON after 24 h. The reaction gives initially cyclohexyl hydroperoxide which decomposes significantly in the course of the reaction to give cyclohexanone and cyclohexanol, the decomposition being catalyzed by **1**.

$$C_6H_{12} + H_2O_2 + \tfrac{1}{2}O_2 \rightarrow C_6H_{11}OOH + H_2O$$

$$2C_6H_{11}OOH \rightarrow C_6H_{11}OH + C_6H_{10}O$$

After 24 h, the content of CyOOH is only 29%. The dinuclear complex **2** catalyzes the reaction with approximately the same activity, but the efficiency per vanadium is only half of that of **1**. Complex **3** exhibits a high activity in combination with only three equivalent

Table 3
Cyclohexane oxidation by various systems[a]

Catalyst ($\times 10^4$ mol dm^{-3})	pcaH added ($\times 10^4$ mol dm^{-3})	Initial rate ($\times 10^6$ mol dm^{-3} s^{-1})	TOF[b] (h^{-1})	TON[c]	Oxygenates (mol dm^{-3}) (after 24 h)			CyOOH in the mixture (%)[d]
					Cyclohexanone	Cyclohexanol	CyOOH	
1 (1.0)	3.0	3.9	256	1370	0.017	0.080	0.040	29
2 (0.5)	3.5[e]	3.5	98	550	0.005	0.040	0.010	18
3 (1.0)	3.0	6.6	121	1140	0.014	0.014	0.086	75
4 (0.25)	4.0	0.8	14	570	0.002	0.002	0.053	93
5 (1.0)	4.0	1.8	23	290	0.0008	0.001	0.027	94
6 (1.0)	4.0	6.7	224	980	0.010	0.087	0.001	1

[a] Conditions: solvent, acetonitrile; $[cyclohexane]_0$, 0.46 mol dm^{-3}; $[H_2O_2]_0$, 0.50 mol dm^{-3}; 40 °C. In all cases concentration of a single vanadium ion was 1.0×10^4 mol dm^{-3} and the vanadium/*O*,*N*-chelating group of amino acid ratio was 1:4.

[b] Turnover frequency, i.e., number of moles of all products produced per one mol of vanadium during the first hour.

[c] Turnover number, i.e., number of moles of all products per one mol of vanadium ions after 24 h.

[d] Relative content of cyclohexyl hydroperoxide in the mixture of oxygenates after 24 h; estimated by comparison of chromatograms before and after the reduction with PPh_3 (for this method, see [6,7,45–47,67–72]).

[e] $pdcaH_2$ was used instead of pcaH.

of pcaH; one can assume that the free carboxylic group in the pycaH ligand takes part in the proton transfer processes and thus replaces one equivalent of pcaH (see Fig. 5).

The behavior of complexes **4** and **5** containing strongly complexing chelating and voluminous ligands is remarkable, because they give rise to the formation of almost pure cyclohexyl hydroperoxide, although their activity is not as high. The accumulation of oxidation products occurs with auto-acceleration (Fig. 6), which is apparently due to a gradual destruction of **4** in the course of the reaction leading to more catalytically efficient species. These species presumably contain weaker ligands (for example, acetonitrile, water, and fragments of hptb) which provide easier access of H_2O_2 to the vanadium center.

Complex **6** surprisingly catalyzes the oxidation with the highest initial rate (6.7×10^{-6} versus 3.9×10^{-6} mol dm^{-3} s^{-1} in the case of **1**). This behavior suggests that the catecholate ligands can be easily removed in the beginning of the reaction and that this detachment

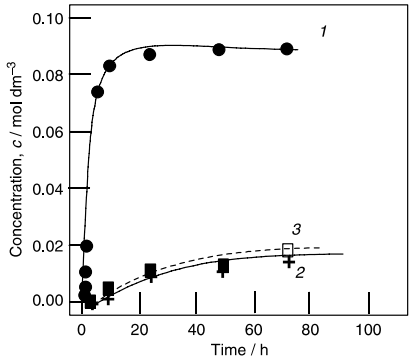


Fig. 5. Accumulation of oxygenates (cyclohexyl hydroperoxide, curve 1; cyclohexanone, curve 2; cyclohexanone, curve 3) with time in oxidation of cyclohexane (0.46 mol dm^{-3}) by H_2O_2 (0.50 mol dm^{-3}) catalyzed by complex **3** (0.25×10^{-4} mol dm^{-3}) in acetonitrile at 40 °C.

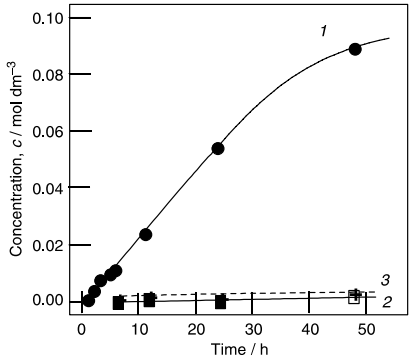


Fig. 6. Accumulation of oxygenates (cyclohexyl hydroperoxide, curve 1; cyclohexanone, curve 2; cyclohexanone, curve 3) with time in oxidation of cyclohexane (0.46 mol dm^{-3}) by H_2O_2 (0.50 mol dm^{-3}) catalyzed by complex **4** (0.25×10^{-4} mol dm^{-3}) in acetonitrile at 40 °C.

proceeds via the reduction from V(V) to (IV) by the strongly reducing catecholate ions. It has been shown previously that the reduction of vanadium by H_2O_2 is the first step of the catalytic cycle [53,54]. Electron transfer from one of the catecholate ligands (which can be transformed into semiquinone) may allow hydrogen peroxide to coordinate to a vacant site thus formed at V(IV). It is noteworthy that **6** catalyzes also the complete decomposition of cyclohexyl hydroperoxide into cyclohexanol and cyclohexanone.

3. Experimental

3.1. Materials

All solvents used were of analytical grade (>90% for dichloromethane and >99% for acetonitrile) and water was bidistilled. NH_4VO_3, pyrazine-2-carboxylic acid, hexamethylphosphoramide, tetrafluoroboric acid (40% in water), H_2O_2 (35% in water), and cyclohexane were used as received from Fluka. Pyrazine-2,5-dicarboxylic acid was synthesized according to published methods [64]. The reagents for this synthesis were used as received from Fluka and Aldrich, hptbH was synthesized as described in the literature [65], using reagents from Fluka, tmtacn was received from Lonza. Catechol (Fluka) was recrystallized from benzene prior to use. Tetrabutylammonium vanadate was synthesized as reported before [54,66].

3.2. Spectroscopic and analytic measurements

The ^1H, ^{31}P NMR spectra were recorded using a Bruker 400 MHz instrument, the IR spectra were measured with a Perkin–Elmer FT-IR 1720 X, the mass spectra were recorded using a LCQ Finnigan instrument. Microanalyses were performed by the Mikroelementarnalytisches Laboratorium of the ETH Zürich, and the Service de Microanalyse of the University of Geneva, Switzerland. Gas chromatographic analyses were carried out with a DANI-86.10 instrument (capillary column 50 m × 0.25 mm × 0.25 μm, Carbowax 20M; integrator SP-4400; the carrier gas was helium).

3.3. Syntheses

*3.3.1. [VO_2(pca)(hmpa)] (**1**)*

To an aqueous solution (10 ml) of 1.18 g (10 mmol) NH_4VO_3, a dichloromethane solution (60 ml) of 1.24 g (10 mmol) of pcaH and 3.5 ml (20 mmol) of hmpa was added, giving rise to the formation of a biphasic system composed of a bright yellow aqueous phase and a light yellow organic phase. After 15 min of vigorous stirring, 2 ml of HBF_4 (40% in water) was added, which caused the aqueous phase to turn orange and the organic phase

to turn bright yellow. The organic phase was then decanted and dried over Na_2SO_4. Slow evaporation of this solution yielded yellow crystals of **1** which were recrystallized from a mixture of CH_2Cl_2 and diethyl ether. Yield: 3 g (77%). IR (KBr, cm^{-1}): 935, 945 ($\nu_{V=O}$), 1181 (ν_{P-O}), 1682 ($\nu_{C=O}$). ^1H NMR (400 MHz, $CDCl_3$): δ 2.7 (d, 18H), 8.9 (d, 2H), 9.4 (s, 1H). ^{31}P NMR (400 MHz, $CDCl_3$): δ 32.4 (s). ESI MS: m/z 385.9 $[\mathbf{1}+H]^+$. *Anal.* Calc. for $C_{11}H_{21}N_5O_5P_1V_1$: C, 34.30; H, 5.49; N, 18.18. Found: C, 34.06; H, 5.51; N, 18.15%.

*3.3.2. [$(VO_2)_2$(pdca)$(hmpa)_2$] (**2**)*

Complex **2** was synthesized by the same method described for **1**, using 234 mg (2 mmol) of NH_4VO_3 in 10 ml of water, and 168 mg (1 mmol) of $pdcaH_2$ and 0.7 ml (4 mmol) of hmpa in 10 ml of dichloromethane; 0.3 ml of HBF_4 was added in the course of the reaction. Yield: 0.5 g (36%). IR (KBr, cm^{-1}): 942 ($\nu_{V=O}$), 1198 (ν_{P-O}), 1678 ($\nu_{C=O}$). ^1H NMR (400 MHz, $CDCl_3$): δ 2.77 (d, 36H), 9.3 (dd, 2H). ^{31}P NMR (400 MHz, $CDCl_3$): δ 27.4 (s). ESI MS: m/z 712.9 $[\mathbf{2}+Na]^+$. *Anal.* Calc. for $C_{18}H_{38}N_8O_{10}P_2V_2$: C, 31.32; H, 5.55; N, 16.23. Found: C, 31.84; H, 5.74; N, 15.97%.

*3.3.3. [VO_2(pycaH)(hmpa)] (**3**)*

Complex **3** was synthesized by the same method described for **1**, using 1.17 g (10 mmol) of NH_4VO_3 in 10 ml of water, and 1.67 g (10 mmol) of $pydcaH_2$ and 3.5 ml (20 mmol) of hmpa in 50 ml of dichloromethane; 2 ml of HBF_4 was added in the course of the reaction. Yield: 2.5 g (88%). IR (KBr, cm^{-1}): 942 ($\nu_{V=O}$), 1191 (ν_{P-O}), 1689 ($\nu_{C=O}$). ^1H NMR (400 MHz, $CDCl_3$): δ 2.7 (d, 18H), 8.27 (d, 1H), 8.7 (dd, 1H), 9.65 (s, 1H). ^{31}P NMR (400 MHz, $CDCl_3$): δ 28.3 (s). ESI MS: m/z 428.25 $[\mathbf{3}+Na]^+$. *Anal.* Calc. for $C_{19}H_{40}N_7O_8P_2V$ (**3** + hmpa): C, 37.57.46; H, 6.64; N, 16.14. Found: C, 36.97; H, 6.76; N, 16.27%.

*3.3.4. [$(VO)_4$(hptb)$_2(H_2O)_2(\mu$-O)] [ClO_4]$_4$ and [$(VO)_4$(hptb)$_2(H_2O)_2(\mu$-O)] [CF_3SO_3]$_4$ (cation **4**)*

To a solution of hptbH (120 mg, 0.2 mmol) in methanol (20 ml) was added an excess (100 mg) of $NaClO_4 \cdot nH_2O$ and then $VOSO_4$ (75 mg, 0.4 mmol) of $VOSO_4$. This mixture was stirred at room temperature: After a few minutes the solution became clear, after a few hours the color had turned from blue to green. After a few weeks, green crystals had formed mixed with white crystals of $NaClO_4$. The green crystals (**4**[ClO_4]) were separated manually for X-ray crystal structure analysis. For the isolation of **4** devoid of $NaClO_4$, the triflate salt was prepared in the same way, using 75 mg of KCF_3SO_3 instead of $NaClO_4$; in this case a green, analytically pure powder of **4**[CF_3SO_3]$_4$ precipitated. Yield: 50 mg (11%). IR (KBr, cm^{-1}): 845.77 ($\nu_{V=O}$). *Anal.* Calc. for $C_{74}F_{12}H_{70}N_{20}O_{21}S_4V_4$: C, 41.62; H, 3.30; N, 13.12. Found: C, 41.98; H, 3.92; N, 13.22%.

*3.3.5. [(tmtacn)$VOCl_2$] (**5**)*

To a solution of VCl_3 (160 mg, 1mmol) in 10 ml of acetonitrile was added dropwise a solution of 1,4,7-trimethyl-1,4,7-triazacyclononane (176 mg, 1 mmol) in 10 ml of acetonitrile under nitrogen atmosphere at 0 °C. An immediate color change from dark brown to deep violet was observed. After stirring at room temperature under nitrogen atmosphere for 30 min, the mixture was refluxed for 18 h in the presence of air and the resulting deep green solution was cooled, filtered, and evaporated to give a green solid. After redissolution in acetonitrile and filtration, slow crystallization at room temperature yielded after one week blue crystals of **5**. Yield: 57 mg (18%) IR (KBr, cm^{-1}): 749.40, 790.76 (ν_{V-N}), 965.79 ($\nu_{V=O}$), 1061.66 (ν_{C-N}); MS (electrospray, positive mode): 331.1 ($[M+Na]^+$); *Anal.* Calc. for $C_9Cl_2H_{21}N_3OV$: C: 34.97; H: 6.85; N: 13.59. Found: C: 34.46; H: 6.78; N: 13.43%.

*3.3.6. [NBu_4][$V(cat)_3$] (anion **6**)*

To an acetonitrile solution (50 ml) of catechol (1.4204 g, 0.0129 mol) and triethylamine (10 ml) was added 1.4683 g (0.0043 mol) of NBu_4VO_3. The color of the solution immediately changed from colorless to black-blue. The reaction solution was refluxed in a nitrogen atmosphere for 5 h and the reaction mixture was evaporated to 1/3 of its volume, giving a dark blue precipitate of $[NBu_4]\mathbf{6} \cdot 0.5CH_3CN \cdot 1.5H_2O$, which was filtered and washed five times with small amounts of acetonitrile. Yield: 0.9 g (11%). IR (KBr, cm^{-1}): 871 (ν_{V-O}) ^1H NMR (400 MHz, acetone-d_6): δ 0.9602 (d, 12H, CH_3), 1.4204 (m, 8H, CH_2), 1.8961 (m, 8H, CH_2), 3.4260 (m, 8H, CH_2), 6.2480 (d, 6H), 6.7085 (t, 6H). ESI MS: (negative mode) m/z 375.0 $[V(cat)_3]^-$, (positive mode) m/z 242.29 $[NBu_4]^+$. *Anal.* Calc. for $C_{35}H_{52.5}N_{1.5}O_{7.5}V$: C, 63.20; H, 7.90; N, 3.16. Found: C, 63.26; H, 7.83; N, 3.20.

3.4. X-ray structure analyses

Crystals of **1**, **2**, **3**, and **4**[ClO_4] were mounted on a Stoe Image Plate Diffraction System [59] equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range from 0° to 200°, increment between 0.7° and 1.7°, $D_{max} - D_{min} = 12.45 - 0.81$ Å. The structures were solved by direct methods using the program SHELXS-97 [60]. The refinement and all further calculations were carried out using SHELXL-97 [61]. All non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 4. Figures were drawn with ORTEP [73]. Full crystallographic data for compounds **1**–**4** may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, quoting the CIF deposition numbers: CCDC 209749 for **1**, CCDC 209751 for **2**, CCDC 209750 for **3**, and CCDC 209752 for **4.**

Table 4
Selected crystallographic and experimental data for complexes **1**, **2**, **3**, and **4**[a]

	[**1**]	[**2**]	[**3**]	[**4**]
Chemical formula	$C_{11}H_{21}N_5O_5PV$	$C_{36}H_{76}N_{16}O_{20}P_4V_4$	$C_{38}H_{80}N_{14}O_{16}P_4V_2$	$C_{35}H_{30}N_{10}O_{12.5}V_2$
Formula weight	385.24	690.38	1214.92	961.45
Crystal system	orthorhombic	monoclinic	triclinic	triclinic
Space group	*P ca*21	$P21/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	15.0443(14)	7.7084(6)	13.383(2)	12.9187(14)
b (Å)	7.9632(8)	11.4712(11)	14.329(2)	14.3458(16)
c (Å)	14.430(3)	16.6926(14)	16.053(2)	16.8609(19)
α (°)	90	90	103.778(18)	71.831(13)
β (°)	90	92.796(10)	97.791(18)	68.359(13)
γ (°)	90	90	101.048(19)	70.054(13)
V (Å^3)	1728.7(4)	1441.6(3)	2881.0(8)	2667.7(5)
Z	4	2	2	2
T (K)	153(2)	153(2)	153(2)	293(2)
D_{calc} (g cm^{-3})	1.480	1.591	1.401	1.199
μ (mm^{-1})	0.696	0.823	0.508	0.508
Scan range (°)	$2.56 < 2\theta 25.92$	$2.18 < 2\theta < 25.77$	$1.91 < 2\theta < 25.78$	$2.00 < 2\theta < 24.1$
Collected reflections	5710	9835	21859	19564
Reflections used	2717	2642	10237	9740
R_{int}	0.0344	0.1791	0.1410	0.1145
Final R indices	0.0438,	0.2095,	0.0626,	0.0773,
$[I > 2\sigma(I)]$	wR_2 0.0911	wR_2 0.4966	wR_2 0.1331	wR_2 0.1722
R indices (all data)	0.0616,	0.2606,	0.1629,	0.2042,
	wR_2 0.0929	wR_2 0.5161	wR_2 0.1601	wR_2 0.2141
Goodness-of-fit	1.516	1.166	0.783	0.724
Max./min. $\Delta\rho$ (e Å^{-3})	0.422, −0.296	3.472, −1.038	0.436, −0.536	0.783, −0.495

[a] Conditions for all complexes: Stoe Image Plate Diffraction system [59] using Mo Kα graphite monochromated radiation, $\lambda = 0.71073$ Å. Image plate distance 70 mm, ϕ oscillation scans 0°–180°, and step $\Delta\phi = 1.5°$. The structures were solved by direct methods using the program SHELXS-97 [60]. The refinement and all further calculations were carried out using SHELXL-97 [61]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

3.5. Catalytic runs

The oxidations of cyclohexane were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 5 ml. Initially, a portion of 35% aqueous solution of hydrogen peroxide was added to the solution of the catalyst, co-catalyst, and substrate in acetonitrile. The samples were analyzed twice, i.e., before and after the addition of the excess of solid PPh_3.

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References

[1] G.B. Shul'pin, Organic Reactions Catalyzed by Metal Complexes, Nauka, Moscow, 1988.
[2] J.-M. Brégeault, Catalyse Homogène par les Complexes des Métaux de Transition, Masson, Paris, 1992.
[3] A. Butler, M.J. Clague, G.E. Meister, Chem. Rev. 94 (1994) 625.
[4] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879.
[5] V. Conte, F. Di Furia, G. Licini, Appl. Catal. A 157 (1997) 335.
[6] A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Academic Publishers, Dordrecht, 2000, Chapter IX (Homogeneous catalytic oxidation of hydrocarbons by molecular oxygen), Chapter X (Homogeneous catalytic oxidation of hydrocarbons by peroxides and other oxygen atom donors).
[7] G.B. Shul'pin, J. Mol. Catal. A 189 (2002) 39.
[8] I. Yamanaka, K. Morimoto, M. Soma, K. Otsuka, J. Mol. Catal. A 133 (1998) 251.
[9] M. Ishida, Y. Masumoto, R. Hamada, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc., Perkin Trans. 2 (1999) 847.
[10] L. El Aakel, F. Launay, A. Atlamsani, J.-M. Brégeault, Chem. Commun. (2001) 2218.
[11] Y. Maeda, N. Kakiuchi, S. Matsumura, T. Nishimura, S. Uemura, Tetrahedron Lett. 42 (2001) 8877.
[12] M. Vennat, P. Herson, J.-M. Brégeault, G.B. Shul'pin, Eur. J. Inorg. Chem. (2003) 908.
[13] H. Sigel, A. Sigel (Eds.), Vanadium and its Role in Live, Marcel Dekker, New York, 1995.
[14] A.S. Tracey, D.C. Crans (Eds.), Vanadium Compounds: Chemistry, Biochemistry, and Therapeutic Applications, Oxford University Press, New York, 1998.
[15] D. Rehder, Coord. Chem. Rev. 182 (1999) 297.
[16] A. Butler, Coord. Chem. Rev. 187 (1999) 17.
[17] E.J. Baran, J. Inorg. Biochem. 80 (2000) 1.
[18] T. Hirao, J. Inorg. Biochem. 80 (2000) 27.
[19] A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Academic Publishers, Dordrecht, 2000, Chapter XI (Oxidation in living cells and its chemical models).
[20] S. Bhattacharyya, A.S. Tracey, J. Inorg. Biochem. 85 (2001) 9.
[21] K.H. Thompson, C. Orvig, Coord. Chem. Rev. 219–221 (2001) 1033.

[22] M. Tsaramyrsi, D. Kavousanaki, C.P. Raptopoulou, A. Terzis, A. Salifoglou, Inorg. Chim. Acta 320 (2001) 47.
[23] D.C. Crans, J. Inorg. Biochem. 80 (2000) 123.
[24] G.R. Willsky, A.B. Goldfine, P. Kostyniak, J.H. McNeill, L.Q. Yang, H.R. Khan, D.C. Crans, J. Inorg. Biochem. 85 (2000) 33.
[25] D. Rehder, J. Costa Pessoa, C.F.G.C. Geraldes, M.M.C.A. Castro, T. Kabanos, T. Kiss, B. Meier, G. Micera, L. Pettersson, M. Rangel, A. Salifoglou, I. Turel, D. Wang, J. Biol. Inorg. Chem. 7 (2002) 384.
[26] Y. Dong, R.K. Narla, E. Sudbeck, F.M. Uckun, J. Inorg. Biochem. 78 (2000) 321.
[27] C. Hiort, J. Goodisman, J.C. Dabrowiak, Biochemistry 35 (1996) 12354.
[28] X.L. Shi, H.G. Jiang, Y. Mao, J.P. Ye, U. Saffiotti, Toxicology 106 (1996) 27.
[29] M. Ding, J.J. Li, S.S. Leonard, J.P. Ye, X.L. Shi, N.H. Colburn, V. Castranova, V. Vallyathan, Carcinogenesis 20 (1999) 663.
[30] V. Castranova, V. Vallyathan, X.L. Shin, J. Biol. Chem. 275 (2000) 32516.
[31] C.S. Huang, M. Ding, J.X. Li, S.S. Leonard, Y. Rojanasakul, V. Castranova, V. Vallyathan, G. Ju, X.L. Shi, J. Biol. Chem. 276 (2001) 22397.
[32] Z. Zhang, C.S. Huang, J.X. Li, S.S. Leonard, R. Lanciotti, L. Butterworth, X.L. Shi, Arch. Biochem. Biophys. 392 (2001) 311.
[33] Z. Zhang, C. Huang, J. Li, X. Shi, J. Inorg. Biochem. 89 (2002) 142.
[34] M. Ding, P.M. Gannett, Y. Rojanasakul, K.J. Liu, X.L. Shi, J. Inorg. Biochem. 55 (1994) 101.
[35] E.G. Ferrer, E.J. Baran, Biol. Trace Element Res. 83 (2001) 111.
[36] A.T. Kotchevar, P. Ghosh, D.D. DuMez, F.M. Uckun, J. Inorg. Biochem. 83 (2001) 151.
[37] S.W. Taylor, B. Kammerer, E. Bayer, Chem. Rev. 97 (1997) 333.
[38] K.H. Thomson, J.H. McNeil, C. Orvig, Chem. Rev. 99 (1999) 2561.
[39] H. Sakurai, Y. Kojima, Y. Yoshikawa, K. Kawabe, H. Yasui, Coord. Chem. Rev. 226 (2002) 187.
[40] S.-X. Liu, S. Gao, Inorg. Chim. Acta 282 (1998) 149.
[41] M.R. Maurya, S. Khurana, W. Zhang, D. Rehder, J. Chem. Soc., Dalton Trans. (2002) 3015.
[42] S.B. Etcheverry, D.A. Barrio, A.M. Cortizo, P.A.M. Williams, J. Inorg. Biochem. 88 (2002) 94.
[43] T. Sasagawa, Y. Yoshikawa, K. Kawabe, H. Sakurai, Y. Kojima, J. Inorg. Biochem. 88 (2002) 108.
[44] S. Yano, M. Nakai, F. Sekiguchi, M. Obata, M. Kato, M. Shiro, I. Kinoshita, M. Mikuriya, H. Sakurai, C. Orvig, Chem. Lett. (2002) 916.
[45] G.B. Shul'pin, D. Attanasio, L. Suber, Russ. Chem. Bull. 42 (1993) 55.
[46] G.B. Shul'pin, D. Attanasio, L. Suber, J. Catal. 142 (1993) 147.
[47] G.B. Shul'pin, M.C. Guerreiro, U. Schuchardt, Tetrahedron 52 (1996) 13051.
[48] G.V. Nizova, G. Süss-Fink, G.B. Shul'pin, Tetrahedron 53 (1997) 3603.
[49] G. Süss-Fink, G.V. Nizova, S. Stanislas, G.B. Shul'pin, J. Mol. Catal. A 130 (1998) 163.
[50] G.B. Shul'pin, Y. Ishii, S. Sakaguchi, T. Iwahama, Russ. Chem. Bull. 48 (1999) 887.
[51] M.H.C. de la Cruz, Yu.N. Kozlov, E.R. Lachter, G.B. Shul'pin, New J. Chem. 27 (2003) 634.
[52] G. Süss-Fink, S. Stanislas, G.B. Shul'pin, G.V. Nizova, H. Stoeckli-Evans, A. Neels, C. Bobillier, S. Claude, J. Chem. Soc., Dalton Trans. (1999) 3169.
[53] Yu.N. Kozlov, G.V. Nizova, G.B. Shul'pin, Russ. J. Phys. Chem. 75 (2001) 770.
[54] G.B. Shul'pin, Yu.N. Kozlov, G.V. Nizova, G. Süss-Fink, S. Stanislas, A. Kitaygorodskiy, V.S. Kulikova, J. Chem. Soc., Perkin Trans. 2 (2001) 1351.
[55] G.B. Shul'pin, E.R. Lachter, J. Mol. Catal. A 197 (2003) 65.
[56] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, R. Weiss, J. Am. Chem. Soc. 105 (1983) 3101.
[57] M. Köppen, G. Fresen, K. Wieghardt, R.M. Llusar, B. Nuber, J. Weiss, Inorg. Chem. 27 (1988) 721.
[58] S.R. Cooper, Y.B. Koh, K.N. Raymond, J. Am. Chem. Soc. 104 (1982) 5092.
[59] Stoe and Cie, IPDS Software, Stoe and Cie, GmbH, Darmstadt, Germany, 2000.
[60] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[61] G.M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1999.
[62] D. Fiedler, O.S. Miljanic, E.J. Welch, Acta Cryst. E (2002) m347.
[63] A. Neves, L.M. Rossi, A.J. Bortoluzzi, A.S. Mangrich, W. Haase, O. Nascimento, Inorg. Chem. Commum. 5 (2002) 418.
[64] W.J. Schut, H.I.X. Mayer, W. Berends, Rec. Trav. Chim. Pays-Bas 80 (1961) 391.
[65] L. Wersterheide, F. Müller, R. Than, B. Krebs, J. Dietrich, S. Schindler, Inorg. Chem. 40 (2001) 1951.
[66] V.W. Day, W.G. Klemperer, A. Yagasaki, Chem. Lett. 8 (1990) 1266.
[67] G.B. Shul'pin, A.N. Druzhinina, React. Kinet. Catal. Lett. 47 (1992) 207.
[68] G.B. Shul'pin, G.V. Nizova, React. Kinet. Catal. Lett. 48 (1992) 333.
[69] G.B. Shul'pin, A.N. Druzhinina, Petrol. Chem. 33 (1993) 247.
[70] G.B. Shul'pin, A.N. Druzhinina, L.S. Shul'pina, Petrol. Chem. 33 (1993) 321.
[71] G.B. Shul'pin, M.M. Bochkova, G.V. Nizova, J. Chem. Soc., Perkin Trans. 2 (1995) 1465.
[72] G.B. Shul'pin, G.V. Nizova, Yu.N. Kozlov, New J. Chem. 20 (1996) 1243.
[73] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.