

## From vanadium(V) to vanadium(IV)—and backwards\*

Esther C. E. Rosenthal

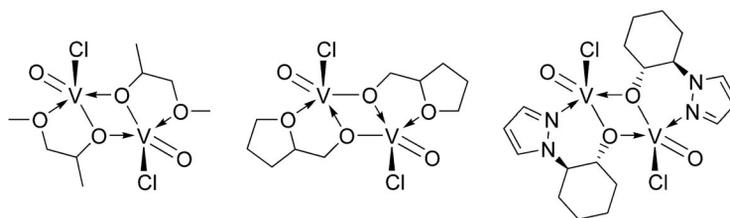
Department of Chemistry, Technische Universität Berlin, 10623 Berlin, Germany

**Abstract:** With bidentate alkoxy alkoxide and alkoxy alcohol ligands, respectively, a series of oxovanadium complexes in the oxidation state +4 is synthesized starting from oxovanadium(V) compounds. The reaction of two or more equivalents of 2-methoxyethanol with  $\text{VOCl}_3$  in *n*-hexane yields a mixture of the monomeric oxovanadium(IV) complex *cis*- $[\text{VOCl}_2(\text{HOCH}_2\text{CH}_2\text{OMe}-\kappa^2\text{O})(\text{HOCH}_2\text{CH}_2\text{OMe}-\kappa\text{O}^1)]$  and the alkoxide-bridged oxovanadium(IV) dimer *syn*- $[\text{VOCl}(\mu\text{-OCH}_2\text{CH}_2\text{OMe}-\kappa^2\text{O})]_2$ , which are separated by fractionated crystallization. The same reaction with 2-ethoxy- and 2-*iso*-propoxyethanol gives only the alkoxide-bridged oxovanadium(IV) dimers *anti*- $[\text{VOCl}(\mu\text{-OCH}_2\text{CH}_2\text{OR}-\kappa^2\text{O})]_2$  (R = Et, <sup>*i*</sup>Pr). All alkoxide-bridged oxovanadium(IV) dimers are furthermore obtained as decomposition products of the chloride-bridged oxovanadium(V) complexes  $[\text{VO}(\mu\text{-Cl})\text{Cl}(\text{OCH}_2\text{CH}_2\text{OR}-\kappa^2\text{O})]_2$  (R = Me, Et, <sup>*i*</sup>Pr) by  $\text{Cl}_2$  elimination and react inversely with  $\text{Cl}_2$  to the vanadium(V) compounds.

**Keywords:** oxovanadium; alkoxides; reduction; vanadium(IV); X-ray structure.

### INTRODUCTION

In opposition to vanadium oxytrichloride, solutions of vanadyl dichloride react with dry alcohols to Lewis acid/Lewis base adducts of the composition  $\text{VOCl}_2(\text{ROH})_3$  without substitution of chloride [1]. Hovnanian and coworkers synthesized the first chloro oxovanadium(IV) alkoxide in 1993 by reduction of  $\text{VOCl}_3$  [2]. Exothermic reaction of  $\text{VOCl}_3$  with three equivalents of sodium (1-methoxy-2-propanolate) in a mixture of toluene and 1-methoxy-2-propanol as well as reaction of  $\text{VOCl}_3$  with 1-methoxy-2-propanol in tetrahydrofuran (THF) and use of  $\text{NH}_3$  gas gave the dark blue dimer  $[\text{VOCl}\{\text{OCH}(\text{Me})\text{CH}_2\text{OMe}\}]_2$  in Scheme 1. Sobota and his group obtained an analogous compound (Scheme 1) in 1997 initially in low yield by equimolar conversion of  $\text{VCl}_3$  with sodium (2-tetrahydrofuran)methanolate) in THF, finally with higher yields by direct reaction of  $\text{VOCl}_2$  and the sodium salt of the ligand in THF [3].



**Scheme 1** Chloro oxovanadium(IV) alkoxides with square pyramidal coordination sphere.

\*Paper based on a presentation at the 6<sup>th</sup> International Symposium on Chemistry and Biological Chemistry of Vanadium, 17–19 July 2008, Lisbon, Portugal. Other presentations are published in this issue, pp. 1187–1330.

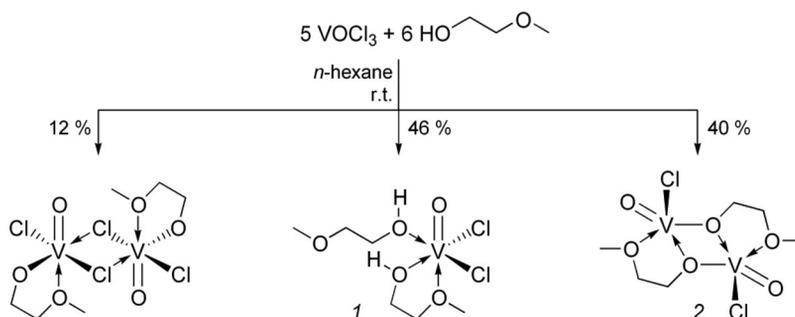
In 2001, Thiel and coworkers made similar observations [4] as Hovnanian when they reacted  $\text{VOCl}_3$  in  $\text{CH}_2\text{Cl}_2$  with the bidentate ligand *rac-trans*-2-(pyrazol-1-yl)cyclohexan-1-ol at  $0^\circ\text{C}$  in the presence of  $\text{K}_2\text{CO}_3$  as base to obtain an orange–brown solution. The primary product decomposed already below  $-20^\circ\text{C}$ . Besides a black oily precipitate, which has not been investigated further, a small amount of dark blue crystals formed. X-ray crystal structural analysis revealed the dinuclear, nitrogen-stabilized V(IV) complex in Scheme 1. They developed a direct synthesis for the latter compound starting from  $\text{VOSO}_4$ , which gave the oxovanadium(IV) product with high yield through reaction with *rac-trans*-2-(pyrazol-1-yl)cyclohexan-1-ol in  $\text{CH}_3\text{CN}$  at  $60^\circ\text{C}$  in the presence of an excess  $\text{LiCl}$ .

Previously we synthesized and characterized a series of oxovanadium(V) alkoxides with bidentate ligands and investigated their catalytic behavior [5]. Alkoxy and aryloxy alkoxide ligands were chosen due to their ability to stabilize vanadium complexes in high oxidation states by forming chelate structures with the additional oxygen donor coordinated to the vanadium atom. Anyhow, the complexes with alkoxy alkoxide ligands are not indefinitely stable under inert conditions [5b–d]. They decompose even in the dark and at low temperatures to the corresponding V(IV) complexes. Expedited reduction is observed by color change from the yellow, orange, or red V(V) compounds to the blue–green color of V(IV) in solution as well as on exposition to sunlight. With 2-methoxyethanol, reduction already takes place during the reaction [5b]. Stable reduction products were isolated and characterized, and their properties are described. Possible decomposition pathways are the oxidation of the alcoholic ligands or the formation of chlorine from the remaining chloride ligands in the complexes. Electrochemical methods are not conclusive on the reduction and oxidation products formed [5c]. No positive proof of aldehydes as oxidation products could be made, which had been identified as those for simple alcohols [6]. In this paper, the evolution of chlorine from the reactions is presented as a reversible process.

## RESULTS AND DISCUSSION

### Oxovanadium complexes by reaction of $\text{VOCl}_3$ with 2-methoxyethanol

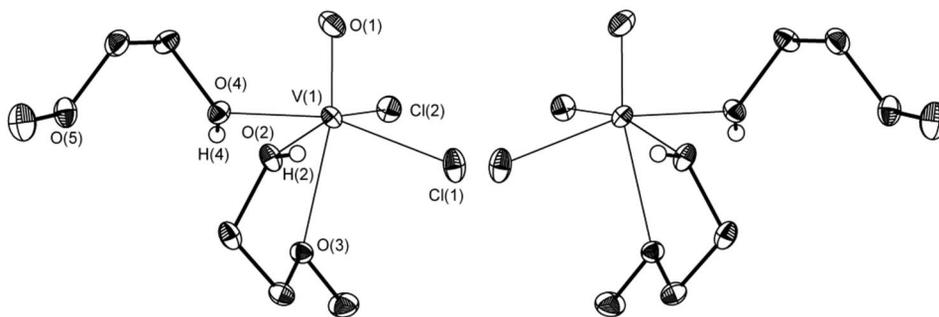
Two equivalents of 2-methoxyethanol react with  $\text{VOCl}_3$  rather to V(IV) compounds than to the expected doubly substituted oxovanadium(V) complexes. Even for a 1:1 ratio a significant extent of reduction takes place if pure *n*-hexane is the solvent [5b]. The chloride-bridged V(V) dimer is isolated from this solution in only 12 % yield (Scheme 2). Within a few hours after addition of  $\text{VOCl}_3$  to a solution of at least one equivalent of 2-methoxyethanol in *n*-hexane, the originally red–brown solution turns blue. About two days later, blue oil precipitates from the blue solution. By fractionated crystallization of the oil from  $\text{CH}_2\text{Cl}_2$ , the two different V(IV) species in Scheme 2 are obtained. Due to its lower solubility in  $\text{CH}_2\text{Cl}_2$ , the turquoise, monomeric complex  $[\text{VOCl}_2(\text{HOCH}_2\text{CH}_2\text{OMe})_2]$  **1** crystallizes first at low temperatures. The royal blue, dimeric oxovanadium(IV) complex  $[\text{VOCl}(\text{OCH}_2\text{CH}_2\text{OMe})_2]_2$  **2** crystallizes only after concentration of the remaining  $\text{CH}_2\text{Cl}_2$  solution and addition of *n*-pentane.



**Scheme 2** Synthesis of oxovanadium complexes from  $\text{VOCl}_3$ .

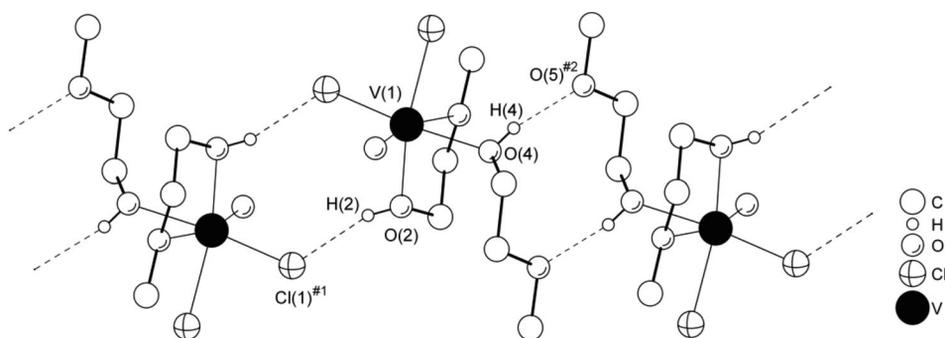
The monomeric oxovanadium(IV) complex **1** melts at 72 °C. The IR spectrum shows two O–H-deformation vibrations at 1285 and 1272 cm<sup>-1</sup> as well as a broad band at 3171 cm<sup>-1</sup>, suggesting O–H-valence vibration in a hydrogen bond. The V=O stretching frequency is found at 1001 cm<sup>-1</sup>. The electron paramagnetic resonance (EPR) spectrum in THF at room temperature shows a hyperfine structure consisting of eight lines due to coupling with the vanadium nucleus (<sup>51</sup>V, *I* = 7/2) and is typical for a mononuclear VO<sup>2+</sup> species. The isotropic parameters are *g* = 1.9661 and *A*(<sup>51</sup>V) = 11.035 mT. Likewise, the mass spectrum shows only monomeric fragments.

Due to the *cis*-configuration of the chloride ligands, the distorted octahedral monomer [VOCl<sub>2</sub>(HOCH<sub>2</sub>CH<sub>2</sub>OMe-κ<sup>2</sup>O)(HOCH<sub>2</sub>CH<sub>2</sub>OMe-κO<sup>1</sup>)] **1** is chiral and both enantiomers crystallize together with a disordered molecule of 2-methoxyethanol in the cell. The molecular structure in Fig. 1 shows two neutral alcohol ligands, one coordinated terminal through the hydroxyl oxygen, the other chelating through both oxygen atoms. With an O(1)–V(1)–O(3) angle of 165.48(11)° and O(1)–V(1)–Cl angles above 100°, the complex is fairly distorted from an ideal octahedron. The vanadium oxo bond V(1)–O(1) of 1.591(3) Å is similar to the V=O bond lengths in the octahedral coordinated oxovanadium(IV) complexes [VOCl<sub>2</sub>(CH<sub>3</sub>CN){pyCONH(C<sub>6</sub>H<sub>4</sub>-2-NO<sub>2</sub>)}] [7] and [VOCl<sub>2</sub>(thf)(pyNHpy)] [8] of 1.587 Å each. Due to the *trans*-influence of the oxo group, the bond from the vanadium atom to the ether oxygen O(3) of 2.300(2) Å is significantly longer than the two vanadium alcohol oxygen bond lengths of 2.089(3) and 2.072(3) Å.



**Fig. 1** Molecular structure of the  $\Lambda$ -enantiomer (left) and the  $\Delta$ -enantiomer (right) of *cis*-[VOCl<sub>2</sub>(HOCH<sub>2</sub>CH<sub>2</sub>OMe-κ<sup>2</sup>O)(HOCH<sub>2</sub>CH<sub>2</sub>OMe-κO<sup>1</sup>)] **1**. Selected bond lengths in Å and bond angles in °: V–O(1) 1.591(3), V–O(2) 2.089(3), V–O(3) 2.300(2), V–O(4) 2.072(3), V–Cl(1) 2.3587(10), V–Cl(2) 2.3152(10), O(1)–V–O(2) 93.77(12), O(1)–V–O(3) 165.48(11), O(1)–V–O(4) 95.42(12), O(1)–V–Cl(1) 101.78(11), O(1)–V–Cl(2) 102.15(11).

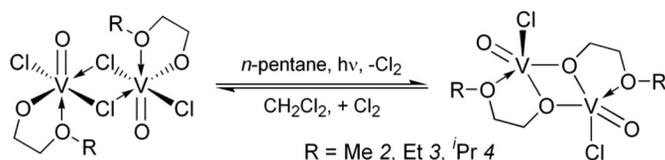
The two hydrogen atoms in the two alcohol ligands are responsible for the formation of molecular chains through hydrogen bonds. Both enantiomers alternate in the chain (Fig. 2). The chain contains two different types of hydrogen bonds. The molecules form hydrogen bonds through oxygen as well as chlorine atoms. Each molecule is connected to the neighboring molecule by two hydrogen bonds of the same type.



**Fig. 2** Hydrogen bonds in *cis*-[VOCl<sub>2</sub>(HOCH<sub>2</sub>CH<sub>2</sub>OMe- $\kappa^2$ O)(HOCH<sub>2</sub>CH<sub>2</sub>OMe- $\kappa^1$ O)] **1**. Bond lengths in Å: O(2)...Cl(1)<sup>#1</sup> 3.012(3), O(4)...O(5)<sup>#2</sup> 2.645(4). Symmetry operations used to generate equivalent atoms: <sup>#1</sup> 1 - x, 1 - y, 2 - z, <sup>#2</sup> 2 - x, 1 - y, 1 - z.

### Alkoxide-bridged oxovanadium(IV) complexes

While reduction of the V(V) precursor is the main process observed for 2-methoxyethanol in every stoichiometric proportion exceeding one equivalent of alcohol, the use of three and more equivalents of the free ligand leads to reduction products for all alkoxy alcohols. In neither case is complete substitution of all three chlorine atoms observed. On the other hand, the dimeric V(IV) compounds **2–4** form from the chloride-bridged V(V) complexes [VO( $\mu$ -Cl)Cl(OCH<sub>2</sub>CH<sub>2</sub>OR- $\kappa^2$ O)]<sub>2</sub> (R = Me, Et, *i*Pr) by decomposition (Scheme 3). The composition of the oxovanadium(IV) dimers **2–4** and the oxovanadium(V) dimers differs only in one chlorine atom per vanadium. This suggests the oxidation product of this redox reaction to be elemental chlorine formed through oxidation of the chloride ligands.



**Scheme 3** Decomposition of chloride-bridged oxovanadium(V) dimers.

To probe this reaction mechanism, a series of experiments has been performed: (i) in the presence of *trans*-stilbene in the decomposing solution dichloro diphenylethane, which was detected by mass spectrometry, forms due to Cl<sub>2</sub> addition to the double bond; (ii) bubbling N<sub>2</sub> through the decomposing solution and into a methyl red solution afterwards leads to chlorine bleaching of the dye; (iii) a downstream KI/starch solution turns blue under these conditions due to iodide oxidation. Reversely, the V(IV) complexes can be oxidized with elemental chlorine: passing chlorine gas through a CH<sub>2</sub>Cl<sub>2</sub> solution of the oxovanadium(IV) dimers leads to color change from blue to brown and finally the chloride-bridged oxovanadium(V) dimers are isolated from the brown solution. Attempts to oxidize the V(IV) compounds electrochemically ended in immediate decomposition of the initially formed V(V) products.

All V(IV) complexes are significantly more stable against moisture, light, and temperature than the V(V) complexes [5b–d]: they melt away in air very slowly to give blue oils. The V(IV) compounds are hardly soluble in THF and CH<sub>2</sub>Cl<sub>2</sub> and completely insoluble in hydrocarbons. The melting points of the V(IV) dimers in Table 1 are considerably higher than those of the V(V) complexes [5].

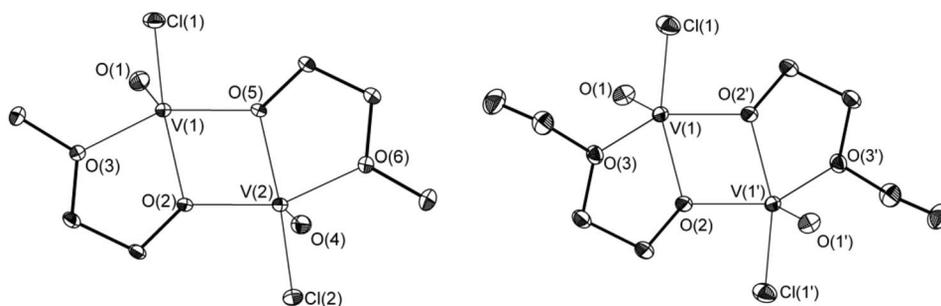
**Table 1** Selected physical and analytical data of oxovanadium(IV) complexes **2–4**.

Complex	M.p./°C	Color	$\tilde{\nu}$ in nujol/cm <sup>-1</sup>				EPR in THF	
			V=O	V–O–V	V–OR	V–Cl	A( <sup>51</sup> V)/mT	g
<b>2</b> (R = Me)	164	royal blue	1004	828	678	461, 421	11.09	1.9655
<b>3</b> (R = Et)	178	dark blue	1006	788	676	436	11.17	1.9493
<b>4</b> (R = <sup>i</sup> Pr)	254	blue	1003	773	676	452	10.98	1.9749

The dimeric nature of the V(IV) compounds is obvious from mass spectrometric data showing the dinuclear molecular ion in all cases. The IR data are consistent with a dimeric formulation as well: they particularly show bands for V–O–V vibration. The EPR spectra in THF at room temperature consist of eight principal lines (<sup>51</sup>V,  $I = 7/2$ ) and are more typical for mononuclear VO<sup>2+</sup> species. Possibly the dinuclear form of the solid state is not maintained in solution or interactions are negligible. The isotropic parameters are similar to the analogous oxovanadium(IV) complexes [VOCl{OCH(Me)CH<sub>2</sub>OMe}]<sub>2</sub> [2] and [VOCl{OCH<sub>2</sub>(C<sub>4</sub>H<sub>7</sub>O)}]<sub>2</sub> [3].

The molecular structures of complexes **2** and **3** were determined by single-crystal X-ray diffraction. The solid-state structures of [VOCl(μ-OCH<sub>2</sub>CH<sub>2</sub>OMe-κ<sup>2</sup>O)]<sub>2</sub> **2** and [VOCl(μ-OCH<sub>2</sub>CH<sub>2</sub>OEt-κ<sup>2</sup>O)]<sub>2</sub> **3** in Fig. 3 confirm the alkoxide-bridged dimers. Bond lengths and angles in Table 2 support approximate square pyramidal coordination around the vanadium atom with the oxo group in apical position. As in [VOCl{OCH(Me)CH<sub>2</sub>OMe}]<sub>2</sub> [2], the vanadium oxo bond average of 1.59 Å is slightly higher than for the V=O bonds in the corresponding V(V) compounds [5b,c].

The alkoxide bridge between the vanadium atoms is symmetrical: the bond lengths average 1.96 Å to both vanadium atoms as in [VOCl{OCH(Me)CH<sub>2</sub>OMe}]<sub>2</sub> [2] and [VOCl{OCH<sub>2</sub>(C<sub>4</sub>H<sub>7</sub>O)}]<sub>2</sub> [3]. The difference in vanadium oxygen bond lengths between alkoxide and ether oxygen of 0.1 Å is comparable to [VOCl{OCH(Me)CH<sub>2</sub>OMe}]<sub>2</sub> [2]. The longer bond to the ether oxygen is caused by the weaker π-donor strength of the neutral ethers compared to the negatively charged alkoxide. Vanadium chloride bond lengths average 2.30 Å as in [VOCl{OCH(Me)CH<sub>2</sub>OMe}]<sub>2</sub> [2] and [VOCl{OCH<sub>2</sub>(C<sub>4</sub>H<sub>7</sub>O)}]<sub>2</sub> [3]. Values for the intermetallic distance of 3.0748(5) Å in the methyl derivative **2** and 3.1062(7) Å in the ethyl derivative **3** compare well to the V–V distance in [VOCl{OCH(Me)CH<sub>2</sub>OMe}]<sub>2</sub> (3.084(3) Å) [2] and [VOCl{OCH<sub>2</sub>(C<sub>4</sub>H<sub>7</sub>O)}]<sub>2</sub> (3.070(1) Å) [3].

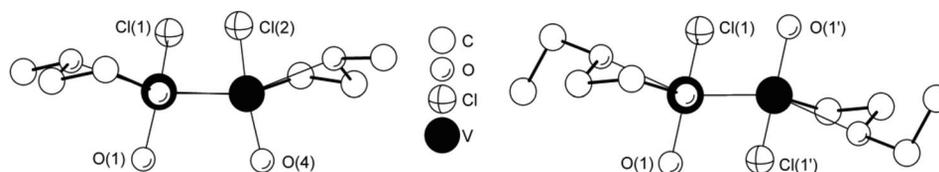


**Fig. 3** Molecular structures of *syn*-[VOCl(μ-OCH<sub>2</sub>CH<sub>2</sub>OMe-κ<sup>2</sup>O)]<sub>2</sub> **2** (left) and *anti*-[VOCl(μ-OCH<sub>2</sub>CH<sub>2</sub>OEt-κ<sup>2</sup>O)]<sub>2</sub> **3** (right). Symmetry operations used to generate equivalent atoms: 1 - x, -y, 1 - z.

**Table 2** Selected bond lengths (Å) and bond angles (°) of V(IV) complexes **2** and **3**.

<b>2</b> (R = Me)		<b>3</b> (R = Et)			
V(1)–O(1)	1.5843(17)	V(2)–O(4)	1.5941(16)	V(1)–O(1)	1.5902(17)
V(1)–O(2)	1.9688(14)	V(2)–O(5)	1.9571(14)	V(1)–O(2)	1.9555(15)
V(1)–O(3)	2.0584(15)	V(2)–O(6)	2.0878(15)	V(1)–O(3)	2.0525(15)
V(1)–O(5)	1.9670(15)	V(2)–O(2)	1.9542(14)	V(1)–O(2')	1.9654(16)
V(1)–Cl(1)	2.3086(6)	V(2)–Cl(2)	2.2974(6)	V(1)–Cl(1)	2.2890(7)
O(1)–V(1)–O(2)	94.21(4)	O(4)–V(2)–O(5)	111.72(7)	O(1)–V(1)–O(2)	110.81(8)
O(1)–V(1)–O(3)	99.40(8)	O(4)–V(2)–O(6)	102.34(7)	O(1)–V(1)–O(3)	105.40(8)
O(1)–V(1)–O(5)	105.08(8)	O(4)–V(2)–O(2)	107.06(7)	O(1)–V(1)–O(2')	106.53(8)
O(2)–V(1)–O(3)	79.35(6)	O(5)–V(2)–O(6)	77.64(6)	O(2)–V(1)–O(3)	77.71(6)
O(2)–V(1)–O(5)	76.49(6)	O(2)–V(2)–O(5)	77.06(6)	O(2)–V(1)–O(2')	75.22(7)
O(3)–V(1)–O(5)	150.16(6)	O(2)–V(2)–O(6)	146.61(6)	O(3)–V(1)–O(2')	143.72(7)
O(1)–V(1)–Cl(1)	102.86(6)	O(4)–V(2)–Cl(2)	106.96(6)	O(1)–V(1)–Cl(1)	107.27(6)
O(2)–V(1)–Cl(1)	147.24(5)	O(5)–V(2)–Cl(2)	141.09(5)	O(2)–V(1)–Cl(1)	141.91(6)
O(3)–V(1)–Cl(1)	94.21(4)	O(6)–V(2)–Cl(2)	90.35(5)	O(3)–V(1)–Cl(1)	93.23(5)
O(5)–V(1)–Cl(1)	96.67(4)	O(2)–V(2)–Cl(2)	95.84(4)	O(2')–V(1)–Cl(1)	93.38(5)

Despite the similarities in bond lengths and angles, both oxovanadium(IV) dimers differ significantly in their spatial arrangement. In the unsymmetrical methyl derivative **2** the molecule is bent leading to the boat conformation in Fig. 4. An analogous arrangement is found in the other crystallographically characterized representatives of this class of compounds,  $[\text{VOCl}\{\text{OCH}(\text{Me})\text{CH}_2\text{OMe}\}]_2$  [**2**] and  $[\text{VOCl}\{\text{OCH}_2(\text{C}_4\text{H}_7\text{O})\}]_2$  [**3**] as well as in the alkoxide-bridged oxovanadium(IV) complex  $[\text{VOCl}(\text{OCy-2-py})]_2$  [**4**] (Scheme 1). The vanadyl groups in these compounds adopt a *syn* position in relation to the V–O–V–O ring.

**Fig. 4** Side view of *syn*- $[\text{VOCl}(\mu\text{-OCH}_2\text{CH}_2\text{OMe-}\kappa^2\text{O})]_2$  **2** (left) and *anti*- $[\text{VOCl}(\mu\text{-OCH}_2\text{CH}_2\text{OEt-}\kappa^2\text{O})]_2$  **3** (right) along the V–O–V–O plane.

Remarkably, the inversion symmetric ethyl derivative **3** is the only *anti* isomer relating to oxo group and chloride. Merely the structurally related oxovanadium(V) complex  $[\text{VOCl}(\text{OCMe}_2\text{CMe}_2\text{O})]_2$  [**9**] shows an *anti* conformation of the V=O units. Corresponding to the inversion symmetry the central  $\text{V}_2\text{O}_2$  ring in ethyl derivative **3** is planar, and the two five-membered rings formed by the chelating glycol ether ligands lie above and below this plane. Figure 4 shows the chair-like arrangement, which matches that in  $[\text{VOCl}(\text{OCMe}_2\text{CMe}_2\text{O})]_2$  [**9**]. One reason for the different arrangements might be the different steric demand of the alkoxides.

## CONCLUSION

Using alkoxy alcohols as bidentate ligands, two types of oxovanadium(IV) alkoxides with different coordination modes of the ligands were prepared from V(V) starting materials. Reacting  $\text{VOCl}_3$  with excess of ethylene glycol mono alkyl ethers does not lead to the expected multiple substituted V(V) products, but to oxovanadium(IV) complexes  $[\text{VOCl}_2(\text{HOCH}_2\text{CH}_2\text{OMe})]_2$  **1** and  $[\text{VOCl}(\text{OCH}_2\text{CH}_2\text{OR})]_2$

(R = Me **2**, Et **3**, *i*Pr **4**). The dimeric V(IV) complexes **2–4** are as well available through decomposition of the corresponding V(V) complexes  $[\text{VO}(\mu\text{-Cl})\text{Cl}(\text{OCH}_2\text{CH}_2\text{OR}-\kappa^2\text{O})]_2$  (R = Me, Et, *i*Pr). The reduction of vanadium takes place with simultaneous oxidation of chloride ligands to elemental chlorine, which was proven for the first time. The V(IV) complexes were oxidized with chlorine gas conversely to the dimeric, chloride-bridged V(V) complexes.

The octahedral V(IV) monomer *cis*- $[\text{VOCl}_2(\text{HOCH}_2\text{CH}_2\text{OMe}-\kappa^2\text{O})(\text{HOCH}_2\text{CH}_2\text{OMe}-\kappa\text{O}^1)]$  **1** exists as a racemic mixture in the crystal. The oxovanadium(IV) dimers **2–4** are alkoxide-bridged with square pyramidal coordination at the vanadium atoms. The configuration of the vanadyl groups depends on the steric demand of the ether function: *syn*-configuration is found for the methyl derivative *syn*- $[\text{VOCl}(\mu\text{-OCH}_2\text{CH}_2\text{OMe}-\kappa^2\text{O})]_2$  **2**, for the larger ethyl and *iso*-propyl groups *anti*-configuration is observed in *anti*- $[\text{VOCl}(\mu\text{-OCH}_2\text{CH}_2\text{OR}-\kappa^2\text{O})]_2$  (R = Et **3**, *i*Pr **4**) for the first time in an oxovanadium(IV) chelate complex.

## EXPERIMENTAL

### *cis*-Dichloro(2-methoxyethanol- $\kappa^2\text{O}$ )(2-methoxyethanol- $\kappa\text{O}^1$ )oxovanadium(IV) **1** and *syn*-bis[chloro( $\mu$ -2-methoxyethanolato- $\kappa^2\text{O}$ )oxovanadium(IV)] **2**

At room temperature (r.t.), 1.0 ml (11 mmol)  $\text{VOCl}_3$  was added to a colorless solution of 2.5 ml (32 mmol)  $\text{MeOCH}_2\text{CH}_2\text{OH}$  (both as obtained from Aldrich) in 160 ml *n*-hexane (distilled from rotary evaporator). The reaction mixture darkened immediately and after 2 days of stirring blue oil separated. The slightly colored *n*-hexane solution was decanted off and discarded. The oily residue was dried in vacuum, extracted with 50 ml dry  $\text{CH}_2\text{Cl}_2$  and concentrated to 30 ml. Storing of the resulting blue–green solution at  $-30$  °C for 1 week yielded 1.22 g (40 %) crystals of **1**.  $\text{C}_6\text{H}_{16}\text{Cl}_2\text{O}_5\text{V}$  (290.03 g mol<sup>-1</sup>): C 24.60 (calcd. 24.85), H 5.45 (5.56), V 17.41 (17.56) %. MS (117 °C): *m/z* 290 (2)  $[\text{M} + \text{H}]^+$ , 289 (0.4)  $[\text{M}]^+$ , 288 (7)  $[\text{M} - \text{H}]^+$ , 260 (14)  $[\text{C}_4\text{H}_{11}\text{Cl}_2\text{O}_5\text{V}]^+$ , 217 (100)  $[\text{VO}(\text{OCH}_2\text{CH}_2\text{OMe})_2]^+$ .

Concentration of the mother liquor to 10 ml and layering with 10 ml of dry *n*-pentane gave 0.90 g (46 % based on V) crystals of **2** after 2 weeks.  $\text{C}_6\text{H}_{14}\text{Cl}_2\text{O}_6\text{V}_2$  (354.96 g mol<sup>-1</sup>): C 20.40 (calcd. 20.30), H 3.81 (3.98), V 28.53 (28.70) %. MS (103 °C): *m/z* 354 (60)  $[\text{M}]^+$ , 338 (1)  $[\text{M} - \text{CH}_4]^+$ , 319 (5)  $[\text{M} - \text{Cl}]^+$ , 318 (6)  $[\text{M} - \text{HCl}]^+$ , 217 (100)  $[\text{C}_6\text{H}_{14}\text{O}_5\text{V}]^+$ .

### $[\text{VO}(\mu\text{-Cl})\text{Cl}(\text{OCH}_2\text{CH}_2\text{OR}-\kappa^2\text{O})]_2$ (R = Me, Et, *i*Pr)

#### General procedure

Exposing  $[\text{VO}(\mu\text{-Cl})\text{Cl}(\text{OCH}_2\text{CH}_2\text{OR}-\kappa^2\text{O})]_2$  to daylight for several months at r.t. leads to quantitative decomposition of the compound accompanied by color change from red to blue. Recrystallization of the blue material through layering of a saturated solution of dry toluene with dry *n*-pentane gave blue crystalline needles.

#### *anti*-Bis[chloro( $\mu$ -2-ethoxyethanolato- $\kappa^2\text{O}$ )oxovanadium(IV)] **3**

$\text{C}_8\text{H}_{18}\text{Cl}_2\text{O}_6\text{V}_2$  (383.01 g mol<sup>-1</sup>): C 24.98 (calcd. 25.09), H 4.61 (4.74)%. MS (182 °C): *m/z* 382 (81)  $[\text{M}]^+$ , 368 (12)  $[\text{M} - \text{CH}_2]^+$ , 347 (10)  $[\text{M} - \text{Cl}]^+$ , 346 (13)  $[\text{M} - \text{HCl}]^+$ , 318 (21)  $[\text{M} - \text{Cl} - \text{Et}]^+$ , 302 (13)  $[\text{M} - \text{Cl} - \text{OEt}]^+$ , 293 (25)  $[\text{M} - \text{OCH}_2\text{CH}_2\text{OEt}]^+$ , 274 (47)  $[\text{C}_4\text{H}_9\text{ClO}_5\text{V}_2]^+$ , 245 (100)  $[\text{VO}(\text{OCH}_2\text{CH}_2\text{OEt})_2]^+$ .

#### *anti*-Bis[chlorooxo( $\mu$ -2-*iso*-propoxyethanolato- $\kappa^2\text{O}$ )vanadium(IV)] **4**

$\text{C}_{10}\text{H}_{22}\text{Cl}_2\text{O}_6\text{V}_2$  (411.07 g mol<sup>-1</sup>): C 29.07 (calcd. 29.22), H 5.20 (5.39) %. MS (202 °C): *m/z* 410 (8)  $[\text{M}]^+$ , 375 (4)  $[\text{M} - \text{Cl}]^+$ , 368 (8)  $[\text{M} - \text{C}_3\text{H}_6]^+$ , 332 (66)  $[\text{M} - \text{C}_3\text{H}_6 - \text{HCl}]^+$ , 326 (15)  $[\text{M} - 2\text{C}_3\text{H}_6]^+$ , 290 (90)  $[\text{M} - 2\text{C}_3\text{H}_6 - \text{HCl}]^+$ , 272 (13)  $[\text{C}_5\text{H}_{11}\text{ClO}_4\text{V}_2]^+$ , 43 (100)  $[\text{C}_3\text{H}_7]^+$ .

## X-ray crystallography

Crystal data and details of data collection for compounds **1–3** are listed in Table 3.

**Table 3** Summary of crystallographic data for compounds **1–3**.

	<b>1</b> (R = Me)	<b>2</b> (R = Me)	<b>3</b> (R = Et)
Formula	C <sub>6</sub> H <sub>16</sub> Cl <sub>2</sub> O <sub>5</sub> V · ½C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>14</sub> Cl <sub>2</sub> O <sub>6</sub> V <sub>2</sub>	C <sub>8</sub> H <sub>18</sub> Cl <sub>2</sub> O <sub>6</sub> V <sub>2</sub>
<i>M</i> <sub>formula</sub> /g mol <sup>-1</sup>	328.08	354.95	383.00
Crystal system	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>Pbca</i> (No. 61)
<i>a</i> /Å	6.9242(2)	17.0715(3)	12.0817(2)
<i>b</i> /Å	9.8601(4)	7.8439(1)	9.9974(2)
<i>c</i> /Å	12.1025(4)	9.7535(1)	12.6308(2)
$\alpha$ /°	66.701(1)	90	90
$\beta$ /°	73.661(1)	102.520(1)	90
$\gamma$ /°	71.826(1)	90	90
<i>V</i> /Å <sup>3</sup>	709.13(4)	1275.01(3)	1525.62(5)
<i>Z</i>	2	4	8
$\rho$ <sub>calcd</sub> /g cm <sup>-3</sup>	1.536	1.849	1.668
$\mu$ /mm <sup>-1</sup>	1.086	1.891	1.587
<i>R</i> values	<i>R</i> <sub>1</sub> = 0.0511	<i>R</i> <sub>1</sub> = 0.0287	<i>R</i> <sub>1</sub> = 0.0347
[ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>wR</i> <sub>2</sub> = 0.1109	<i>wR</i> <sub>2</sub> = 0.0647	<i>wR</i> <sub>2</sub> = 0.0818
<i>R</i> values	<i>R</i> <sub>1</sub> = 0.0787	<i>R</i> <sub>1</sub> = 0.0393	<i>R</i> <sub>1</sub> = 0.0408
(all data)	<i>wR</i> <sub>2</sub> = 0.1318	<i>wR</i> <sub>2</sub> = 0.0688	<i>wR</i> <sub>2</sub> = 0.0873

## REFERENCES

1. V. K. Belyaeva, I. S. Filippova, E. P. Turevskaya, N. Ya. Turova, I. N. Marov. *Z. Neorg. Khim.* **34**, 830 (1989).
2. G. Foulon, J.-D. Foulon, N. Hovnanian. *Polyhedron* **12**, 2507 (1993).
3. Z. Janas, P. Sobota, M. Klimowicz, S. Szafert, K. Szczegot, L. B. Jerzykiewicz. *J. Chem. Soc., Dalton Trans.* 3897 (1997).
4. H. Glas, K. Köhler, E. Herdtweck, P. Maas, M. Spiegler, W. R. Thiel. *Eur. J. Inorg. Chem.* 2075 (2001).
5. (a) E. C. E. Rosenthal, F. Girgsdies. *Z. Anorg. Allg. Chem.* **628**, 1917 (2002); (b) E. C. E. Rosenthal, H. Cui, K. C. H. Lange, S. Dechert. *Eur. J. Inorg. Chem.* 4681 (2004); (c) E. C. E. Rosenthal, H. Cui, J. Koch, P. Escarpa Gaede, M. Hummert, S. Dechert. *Dalton Trans.* 3108 (2005); (d) E. C. E. Rosenthal, H. Cui, J. Koch. In *Vanadium: The Versatile Metal*, K. Kustin, J. Costa-Pessoa, D. C. Crans (Eds.), ACS Symposium Series No. 974, pp. 70–79, American Chemical Society, Washington, DC (2007); (e) E. C. E. Rosenthal, H. Cui, M. Hummert. *Inorg. Chem. Commun.* **11**, 918 (2008).
6. (a) H. Prandtl, L. Hess. *Z. Anorg. Chem.* **82**, 103 (1913); (b) H. Funk, W. Weiss, M. Zeising. *Z. Anorg. Allg. Chem.* **296**, 36 (1958).
7. T. A. Kabanos, A. D. Keramidis, A. Papaioannou, A. Terzis. *Inorg. Chem.* **33**, 845 (1994).
8. H. Kumagai, M. Endo, M. Kondo, S. Kawata, S. Kitagawa. *Coord. Chem. Rev.* **237**, 197 (2003).
9. D. C. Crans, R. A. Felty, M. M. Miller. *J. Am. Chem. Soc.* **113**, 265 (1991).