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Oxidovanadium(V) Complexes with Aminoethanol Bis(phenolate) [O,N,O,O′] Ligands: Preparations, Structures, *N*-Dealkylation and Condensation Reactions

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The reactions between $[VO(acac)_2]$ ($acac^-$ = acetylacetonate ion) or $[VO(OPr)_3]$ and trianionic tetradentate *N*,*N*-bis(2-methylene-4,6-alkylphenolate)aminoethanolate ligands, [$L1^{3-}$ (4,6-dimethyl), $L2^{3-}$ (4-methyl, 6-*tert*-butyl), $L3^{3-}$ (4-*tert*-butyl, 6-methyl), $L4^{3-}$ (4,6-di-*tert*-butyl)], afford mononuclear complexes [VO(L1)] (**1**) and [VO(L2)] (**2**) with a trigonal bipyramidal coordination sphere around the V^V ion, or dinuclear octahedral complexes $[V_2O_2(L3)_2]$ (**3**) and $[V_2O_2(L4)_2]$ (**4**). In methanol an adduct with the formula [VO(L1)(MeOH)]·1/2MeOH (**5**) is obtained. According to multinuclear NMR spectroscopy all those complexes have a mononuclear structure in $CDCl_3$ solutions. In wet polar solvents complex **1** reacts with water and *N*-dealkylation occurs producing 3,5-dimethylsalicyl alcohol, which condensates with **1** and forms a new oxidovanadium complex **6**. An ether bond links 3,5-dimethylsalicyl alcohol to the $L1^{3-}$ ligand. To support the reaction mechanism, we have found that in dry acetonitrile **1** reacts directly with salicyl alcohol forming compound **7**, which is similar to **6**. All compounds **1**–**7** have been characterized by elemental analysis, multinuclear NMR and X-ray diffraction.

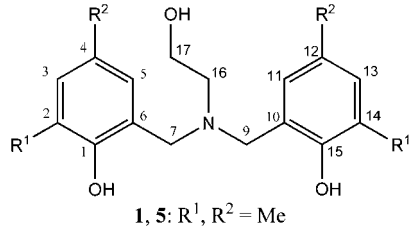
Introduction

The scientific interest in the coordination chemistry of oxidovanadium complexes can be divided into three classes: biological, pharmacological and catalytical. The biological interest[1] lies in the structures of vanadium-dependent haloperoxidases[2,3] and nitrogenases.[4] The primer enzymes are known to catalyze the formation of hypohalous acids from halides in the presence of hydrogen peroxide[5] and hence assist the formation of a variety of halogenated organic compounds. Vanadium-nitrogenases are postulated to bind and reduce dinitrogen.[1,6,7] Since the clarification of the active centre of the haloperoxidases,[8] several articles have been published concerning the binding of multidentate ligands imitating the coordination site.[2,9–11]

The pharmacological interest has arisen since several vanadium complexes have been shown to act as insulin mimetics[12–14] and recent studies have demonstrated the ability of these complexes to inhibit alkylating toxins, and hence minimize DNA damage caused by these compounds.[15,16] Also some vanadium complexes exhibit antitumor activity.[17]

The third major contribution to the vanadium coordination chemistry is the exploration of these compounds in chemical catalysis[18,19] where especially important topics are α-olefin polymerization[20–23] and oxidation of various species.[10,24,25] Generally, vanadium-based polymerization catalysts have been reported to be less active than titanium ones because they suffer deactivating reduction during the catalysis but some advantages are also reported, for instance the synthesis of high molecular weight polymers with a narrow polydispersity.[26]

The chemistry of vanadium is dominated by oxidation states of III, IV and V although lower oxidation states are also met under reducing conditions. Oxido derivatives of vanadium are met at oxidation states IV and V and possess several monomeric and dimeric cores, these starting points lead to a variety of chemically and structurally different species. Thus, the chemistry of oxidovanadium compounds is greatly influenced by the reaction conditions as well as by the nature of the ligands.[27]



1, **5**: R^1, R^2 = Me
2: R^1 = Me, R^2 = *t*Bu
3: R^1 = *t*Bu, R^2 = Me
4: R^1, R^2 = *t*Bu

Scheme 1. The aminoethanol (bis)phenol ligands used in this work and the numbering system.

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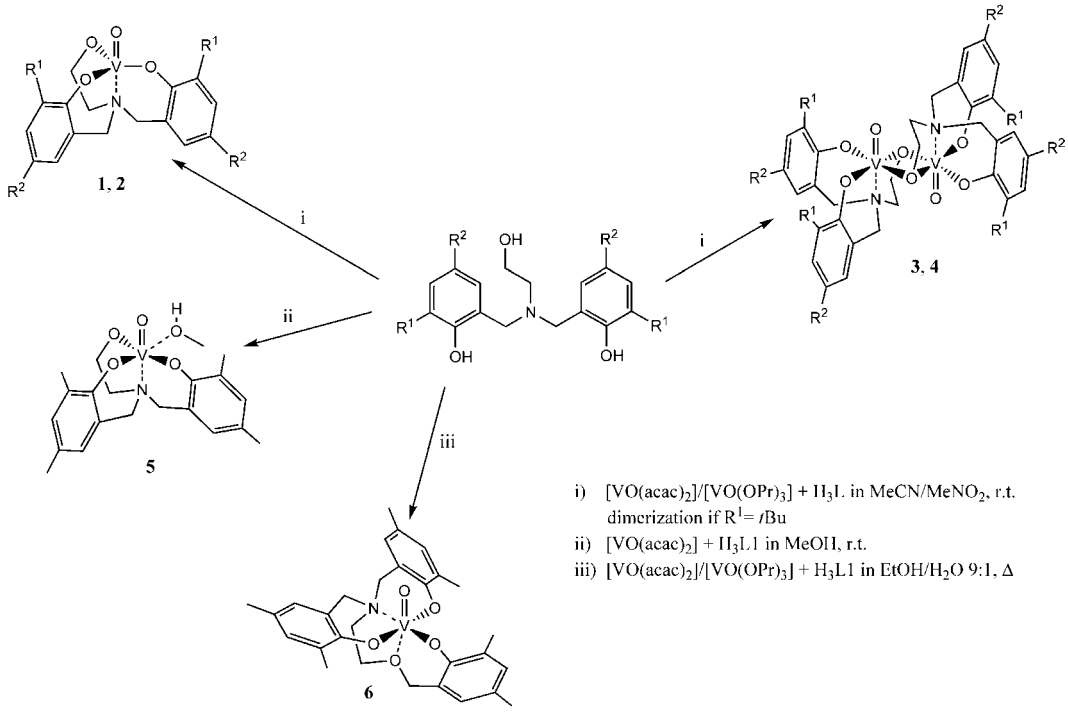
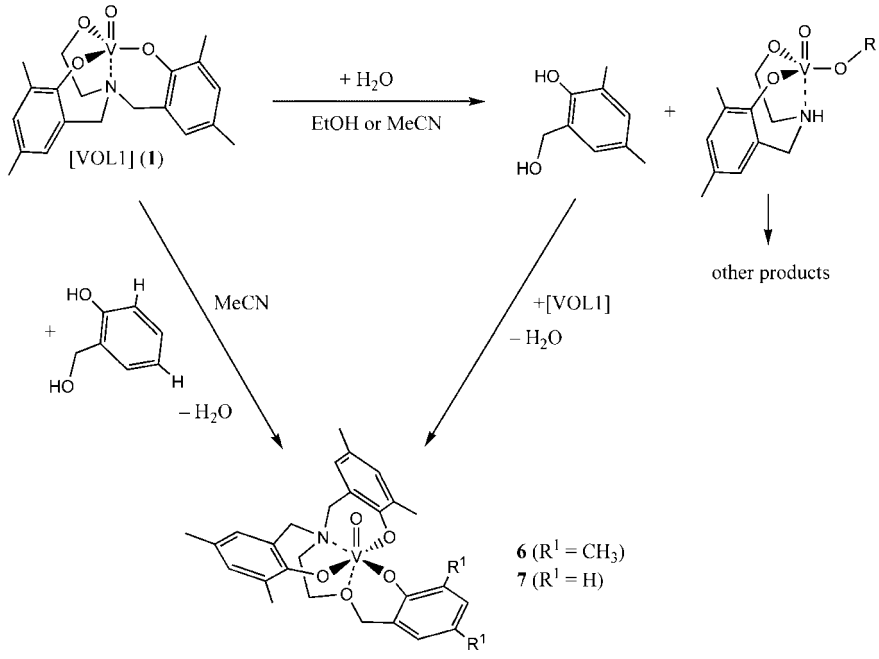


Scheme 2. Reactions of the ligands H_3L1–H_3L4 with $[VO(acac)_2]$ and $[VO(OPr)_3]$.



Scheme 3. The possible course of the condensation reaction. The reaction was observed when group R^1 was methyl or H.

Our primary interest lies in the coordination chemistry of transition metals with amine (bis)phenol ligands carrying various side-arms. In our recent publications, we have demonstrated that such multidentate ligands having alcohol side chains can react either as tridentate dianions (O,N,O donors) or as tetradentate trianions (O,N,O,O′ donors).[28–30] In recent years, the reactions of vanadium compounds with the amine (bis)phenol ligands with nitrogen side-arm donors have been studied from various points of view.[10,25,31–33] However, the reaction outcome of these vanadium based systems is sometimes quite difficult to predict and surprises occur every now and then. One example of such unexpected reactivity is vanadium-induced C–N bond cleavage of a chelating ligand.[34]

Here we report the syntheses and structural characterizations of five new oxidovanadium(V) complexes with four different aminoethanol (bis)phenol ligands (Scheme 1 and Scheme 2) and discuss the structural differences of the iso-

lated VO complexes. We also describe further reactions of vanadium complex **1** (Scheme 3). In these reactions, the C–N bond cleavage (*N*-dealkylation) of the amine group happens first and after that a condensation reaction produces a new complex in which an unexpected triphenolic ligand is formed.

Results and Discussion

Syntheses

Syntheses of the Ligands

The ligands H_3L1–H_3L4 were synthesized according to a previously published procedure with only slight modifications.[35] The purification of the ligands H_3L1 – H_3L3 required crystallization as hydrochlorides; thus complexation reactions were initially carried out using these hydrochlorides as ligand precursors. However, this procedure did not give satisfactory results (demonstrated later by H_3L2), so that the ligands were mainly used as free bases after neutralization (see experimental part). Ligand H_3L1 crystallizes from toluene with the formula $H_3L1 \cdot 1/3PhMe$,[28] and this adduct was used in the preparation of complexes **5** and **6**. The ligand H_3L4 crystallized when the reaction syrup was dissolved in methanol and kept in a refrigerator at 5 °C for overnight. Purity of the ligands was assured by HPLC and by ^{1}H NMR measurements.

Syntheses of the Complexes

Vanadyl acetylacetonate[36] was used as a starting material in the syntheses of complexes **2**–**5**. The reactions were performed in open test tubes under ambient atmosphere to enhance and enable the oxidation process of V^{IV} to V^{V}. The crystals were formed during several days and no recrystallization procedures were needed. The reaction solutions were deep blue (in some cases with a wash of red) and remained so after the removal of the crystals indicating that the complexation was incomplete.

The complexation reactions can be done using ligands as free bases or as hydrochlorides. Although the use of hydrochlorides proved adequate in most cases, the use of free bases is more convenient, as hydrochlorides must be neutralized by triethylamine for the reaction to proceed. When the hydrochlorides were used as starting materials, the reaction solutions tended to be deeply coloured and slightly viscous after complex formation; thus it was difficult to estimate the degree of crystallization prior to the isolation of the products.

To keep the reactions straightforward and more simple, commercially available $[VO(OPr)_3]$ was used in the preparations of complexes **1** and **6**. Identical products were generally isolated also by using vanadyl acetylacetonate as a starting material, but the reactions are much faster and cleaner with $[VO(OPr)_3]$ as there is no need to oxidize V^{IV} to V^{V}.

Solvents played a major role in the crystallization processes of the complexes. For example, complex **2** was originally prepared in an acetonitrile solution, which produced analytically pure crystals of rather poor quality. However, when the same reaction was performed in a nitromethane solution the single crystals that formed were good enough for the X-ray analyses.

The role of the reaction medium was found to be particularly important in reactions of H_3L1 with $[VO(acac)_2]$. In acetonitrile the reaction produced complex **1** as a sole product. When the synthesis was repeated in a methanol solution, methanol adduct **5** was obtained at room temperature. Moreover, when the reaction mixture was heated to the boiling point of methanol for five minutes, traces of a new complex **6** were observed in a ^{1}H NMR spectrum. More evidence of the formation of this new complex was obtained when the reaction of $[VO(acac)_2]$ with $H_3L1 \cdot HCl$ was performed in ethanol at room temperature. The resulting crystalline deposit was found to consist of two types of crystals, i.e. both **1** and **6**, while no ethanol adducts of **1** were obtained. The crystal structure determination of **6** verified that a new ligand was formed upon the coordination process, thus the formation of this unexpected product was thoroughly investigated (Scheme 3).

The experimental conditions were varied in order to have compound **6** as the main product. The metal/ligand ratio was varied from 1:1 to 1:2 and different solvents (methanol, ethanol) and their water mixtures were used. In all these reactions **6** was formed, but the best yields were obtained refluxing the ligand (as a free base) and $[VO(OPr)_3]$ (2:1) in wet ethanol (10% of water). The crystals of **6** were separated by decantation in a 33% yield (based on the metal), while the other products remained in the hot reaction solution. After the collection of the crystals, the cooled solution was evaporated to dryness and upon examining the residue with ^{1}H NMR resonances typical for **1** was seen among others, without ^{1}H NMR signals of **6**. The solid compound **1** was washed with acetonitrile (**1** is only sparingly soluble in acetonitrile) and the solutes were analyzed by ^{1}H NMR spectroscopy. The spectrum consisted of overlapping signals of the remains of **1**, the free ligand and at least one other product, which we were unable to identify. Also ethanol was present in a stoichiometric amount to this new product which indicates that an ethanol adduct could be formed. Disappointingly, all attempts to separate and crystallize these components failed.

The mechanism of formation of the new ligand in **6** is still unclear, although it seems that water is involved in the reaction. When **1** was solely refluxed in an acetonitrile/water (10%) solution, complex **6** was obtained in a 32% yield, which confirmed the participation of water in the reaction. The reaction mixture, after separation of crystallized **6**, was analyzed by NMR spectroscopy. Unfortunately ^{1}H NMR did not give any new information on the by-products. In the ^{51}V NMR, only two strong signals (**1** and **6**) were seen. However, few very weak signals were seen in the broad area between –340 to –540 ppm, which indicates the presence of several vanadium compounds. This complexity of the reaction mixture explains the difficulties in isolating the rest of reaction products in a pure form.

There is one earlier example on *N*-dealkylation of a tertiary amine phenol in the presence of vanadium.[34] A C–N bond was cleaved in one arm of the mixed-valence V^{III}–V^{IV} complex [($VOCl_2$)(VCl_2)bpbp], bpbpH = 2,6-bis{[*N*,*N*-bis(2-picolyl)amino]methyl}-4-*tert*-butylphenol, in a wet acetonitrile solution to give [$VOCl_2$bpa], bpa = bis(2-methylpyridyl)amine, and 2-{[*N*,*N*-bis(2-picolyl)amino]methyl}-6-hydroxymethyl-4-*tert*-butylphenol. This supports the view that during the formation of **6** one of the intermediates is 3,5-dimethylsalicyl alcohol.

The overall reaction for the formation of **6** can be divided into two consecutive steps. The first step is supposedly a hydrolytic *N*-dealkylation of the coordinated ligand, which produces 3,5-dimethylsalicyl alcohol (the final product contains part of 3,5-dimethylsalicyl alcohol) (Scheme 3). In the second step, 3,5-dimethylsalicyl alcohol reacts with **1** to form a bond to the alkoxy group of the aminoethanol part of the ligand and to the V^V ion.

A further experiment was done to study the second step of the reaction. Compound **1** was allowed to react with salicyl alcohol in dry acetonitrile at reflux temperature. As expected, the reaction resulted in a new condensation product **7**, which has an analogous structure with **6**. It seems that the V^V ion can direct 2-hydroxybenzyl alcohols to form benzylic ethers with V-coordinated alkoxides.

We therefore suggest that in wet polar solvents the reaction proceeds via water-induced partial N-dealkylation of **1**, which leads to the formation of 3,5-dimethylsalicyl alcohol (Scheme 3). This diol attacks another molecule of **1** and a condensation reaction takes place between an aliphatic hydroxy group and an alkoxide moiety. At the same time, a phenolic hydroxy group is coordinated to the metal centre. As a result, a new vanadium complex **6** is formed and a molecule of water is released back to the system. According to the NMR spectroscopic data, several unidentified vanadium complexes are also formed during this reaction.

Solution Structures

^{1}H, ^{13}C and ^{51}V NMR spectra of complexes **1**–**7** were recorded in $CDCl_3$. The correlation spectra (HMQC, HMBC) of the complexes **5**–**7** were recorded to assign satisfactorily all proton and carbon shifts; these data were also used to assist in the interpretation of the spectra of **1**–**4**.

The ^{1}H NMR spectra of **1** and **5** are identical except the singlet resonance at δ = 3.35 ppm of the solvate methanol in **5**. The ^{1}H NMR spectra of **1**, **2**, **3**, **4** and **5** are similar in the region of N-CH_2 proton resonances. For ex. in **1**, the signals are at δ = 2.70 ppm (t, 2 H, NCH_2CH_2), 3.43 (d, 2 H, Ar-CH_2-N), 3.73 ppm (d, 2 H, Ar-CH_2-N) and 4.82 ppm (t, 2 H, CH_2CH_2O). The effect of the *para*-substituent on the chemical shifts of the aromatic protons is seen when evaluating the spectra of the studied complexes. The resonances for the protons at C3/C11 and C5/C13 of **2** have shifted downfield by 0.2 ppm compared to the equivalent protons in **1**. A similar shift is observed between the corresponding protons in the spectra of **3** and **4**. In the ^{1}H NMR spectra of **6** and **7**, the *ortho*-methyl groups at C2 and C14 have shifted upfield by 0.4 ppm compared to those in **1**. In the ^{13}C NMR spectra the differences are even smaller and are caused by structural changes of the ligand. The downfield shift is observed in aromatic carbons 4 and 12 of **2** and **4** due to the *tert*-butyl substituents.

According to the proton and carbon NMR spectra of **1**–**5**, all complexes have a mononuclear structure in a $CDCl_3$ solution. It seems that the six-coordinate **5** decomposes in $CDCl_3$ to form methanol and **1**, whereas dinuclear complexes **3** and **4** (see below) dissociate to the mononuclear units. In the literature, there are some reports on a corresponding dissociation of dinuclear vanadium trialkanolamine complexes in the solution.[37,38]

The ^{51}V NMR spectra of complexes **1**–**5** show one signal at –390 to –393 ppm, which supports the observation, that there are complex units of only one composition present in the solution. The monomeric complexes **6** and **7** have resonances at –419 and –438 ppm, respectively, which indicate similar six-coordinate vanadium ions in chloroform as are found in the solid state (see below).[9,32]

Solid-State Structures

Crystal Structures of [VO(L1)] (1) and [VO(L2)] (2)

The complex **1** crystallizes in the orthorhombic space group $Pca2_1$ with four similar mononuclear molecules in the asymmetric unit. One of them is presented in Figure 1. Complex **2** crystallizes in the monoclinic space group $P2_1/c$ with a mononuclear molecule in the asymmetric unit (Figure S1). The relevant bonding parameters for both complexes are presented in Table S3. The ligands H_3L1 and H_3L2 coordinate as an L^{3-} -anion (all hydroxy groups are deprotonated) in a tetradentate manner, i.e. through two phenolate oxygen atoms and the oxygen and nitrogen atoms of the amino alcohol group.

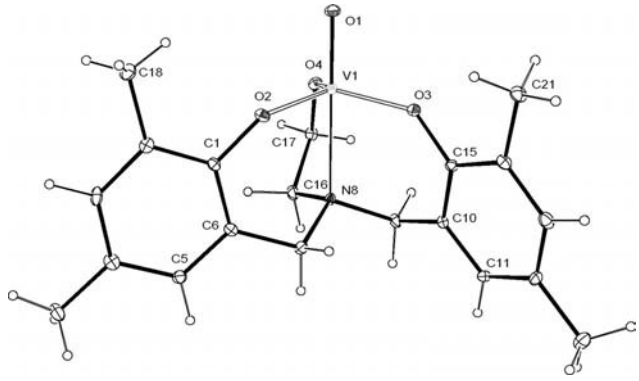


Figure 1. One of the similar four molecules in the asymmetric unit of [VO(L1)] (**1**). Thermal ellipsoids are drawn at the 20% probability level.

As these ligands do not introduce any steric hindrance in the close neighbourhood of the metal centre, one could expect that the coordination number of six would be easily attained either by coordinating the solvent molecules or by

the formation of the dinuclear units. However, in both complexes the vanadium(V) ion has a slightly distorted trigonal bipyramidal VNO_4 coordination sphere. The equatorial positions in **1** and **2** are occupied by phenolate and alcoholate oxygens with V–O bond lengths of approximately 1.80 Å. The oxido group and the neutral nitrogen donor coordinate in the axial positions. The parameter τ, which describes a coordination sphere of five coordinated atoms, has a value of 1 if the structure is pentagonal bipyramidal and 0 if it is square pyramidal.[39] For **1** (four molecules in the asymmetric unit) the τ values are from 0.91 to 0.94 and in **2** (τ = 0.95).

Crystal Structures of [$V_2O_2(L3)_2$] (3) and [$V_2O_2(L4)_2$] (4)

Both complexes **3** and **4** crystallize in the triclinic space group $P\bar{1}$ with one (Figure 2) or two dinuclear molecules, respectively, in the unit cell (Figure S2 in the Supporting Information). The relevant bonding parameters for both complexes are presented in Table S4. The H_3L3 and H_3L4 coordinate as a L^{3-} anion (all the hydroxy groups are deprotonated) in a tetradentate/bridging manner, specifically through two phenolate oxygen atoms and the oxygen and nitrogen atoms of the amino alcohol group. The alcoholate oxygens act as bridging atoms between two VO groups to form a dinuclear unit. Overall, the coordination geometry around the vanadium(V) ions is a distorted octahedron (VNO_5), where the phenolate and alcoholate oxygen atoms lie in the plane and are in *cis* positions to the oxido group and the nitrogen atom. It is interesting that ligands H_3L3 and H_3L4, which have sterically demanding *tert*-butyl groups close to the phenolate oxygen atoms form dinuclear molecules in the solid state. In both structures, the V–O(phenolate) bond lengths are almost the same as those in **1** or **2**, but the V–O(alcoholate) bonds are significantly longer due to the formation of the alkoxide bridges. Especially the bridging V–O bond is long. The different coordination modes of the tetradentate ligands have practically no influence on the V=O (ca. 1.6 Å) and V–N (ca. 2.4 Å) bond lengths in **1**–**4** as the bonding parameters found here are typical for these types of bonds.

Crystal Structure of [VO(L1)(MeOH)]·1/2MeOH (5)

Complex **5**, which is principally a methanol adduct of **1**, crystallizes in the triclinic space group $P\bar{1}$ with a mononuclear molecule in the asymmetric unit (Figure 3). The relevant bonding parameters are presented in Table 1. Again, the ligand H_3L1 coordinates as a tetradentate trianion. The main difference between the structures of **1** and **5** is that in the latter structure one methanol molecule coordinates to the vanadium(V) ion making the overall molecular geometry a distorted octahedron (VNO_5). The phenolate and alcoholate oxygen atoms lie in a plane and are in a *cis* position to the oxido group and the nitrogen donor. The O–V–O bond angles in this plane are approximately 90°. One consequence of the change of the coordination number from 5 (in **1**) to 6 (in **5**) is the dramatic modification in the conformation of the ligands in these two compounds. The aromatic rings in **5** come much closer to each other than in **1** and are almost in a face to face position. However, the distance of the centroids (3.917 Å) of the aromatic rings in **5** is so long, that the structure is not stabilized by π-π stacking. The bond lengths to the vanadium ion are slightly longer in **5** than in **1** due to the increase of the coordination number. The V–O(methanol) bond length, 2.116(1) Å, is of a typical magnitude.[40]

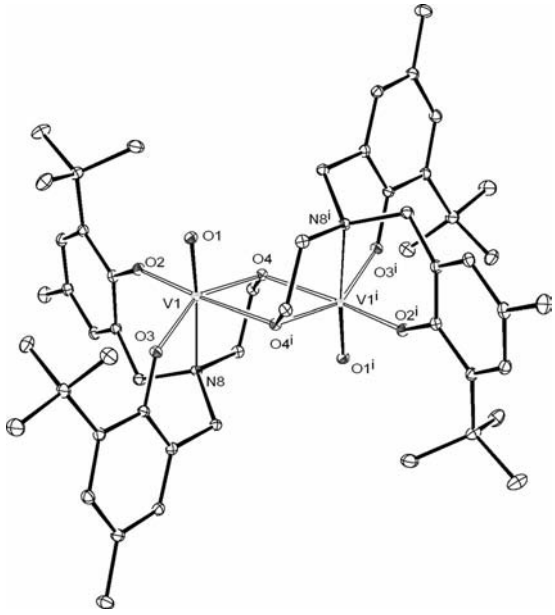


Figure 2. Molecular structure of $[V_2O_2(L3)_2]$ (**3**). Thermal ellipsoids are drawn at the 20% probability level. CH hydrogen atoms are omitted for clarity.

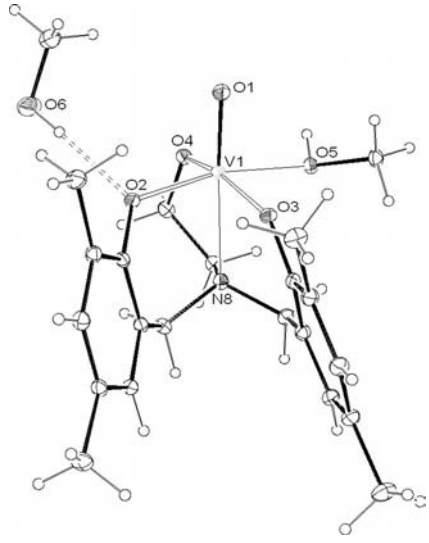


Figure 3. Molecular structure of [VO(L1)(MeOH)]·1/2MeOH (**5**). Thermal ellipsoids are drawn at the 20% probability level. The methanol molecule sits between two vanadium units and is H-bonded at a certain time to only one of them.

Table 1. Selected bond lengths [Å] and angles [°] for **5**–**7**.

	5	**6**	**7**
V=O1	1.6039(14)	1.5985(16)	1.6055(14)
V–O2	1.8666(13)	1.8545(15)	1.8731(14)
V–O3	1.8318(13)	1.8636(15)	1.8600(13)
V–O4	1.8830(14)	1.8347(15)	1.8373(14)
V–O5	2.1159(14)		
V–O18		2.3292(15)	2.3220(13)
V–N8	2.3744(17)	2.2090(19)	2.1844(16)
O1=V–O2	101.98(7)	98.44(8)	98.08(7)
O1=V–O3	101.68(7)	99.73(8)	99.22(7)
O1=V–O4	96.45(7)	105.70(8)	103.92(7)
O1=V–O5	92.63(6)		
O1=V–O18		169.11(7)	169.53(6)
O1–V–N8	172.34(7)	94.67(8)	94.68(7)
O2–V–O3	93.58(6)	159.77(7)	160.57(6)
O2–V–O4	93.17(6)	94.21(7)	93.00(6)
O2–V–N8	84.11(6)	84.65(7)	83.85(6)
O2–V–O5	165.12(6)		
O2–V–O18		80.04(6)	80.14(5)
O3–V–O4	158.88(6)	89.39(7)	91.38(6)
O3–V–O5	86.09(6)		
O3–V–O18		80.44(6)	81.25(5)
O3–V–N8	82.39(6)	85.07(7)	85.98(6)
O4–V–O5	82.31(6)		
O4–V–O18		85.18(6)	86.51(5)
O4–V–N8	78.43(6)	159.53(7)	161.40(6)

Crystal Structures of [VO(L1C1)] (6) and [VO(L1C2)] (7)

Complexes **6** and **7** crystallize in the monoclinic space groups $P2_1/n$ and $P2_1/c$ with a mononuclear molecule in the asymmetric unit (Figures 4 and 5). The relevant bonding parameters are presented in Table 1. Ligand $L1C1^{3-}$ is formed spontaneously during the preparation of complex **1** in water containing media and ligand $L1C2^{3-}$ in the reaction between **1** and salicyl alcohol in dry acetonitrile. Compounds **6** and **7** are isostructural: the coordination spheres consist of the same atoms and molecular geometries are very similar.

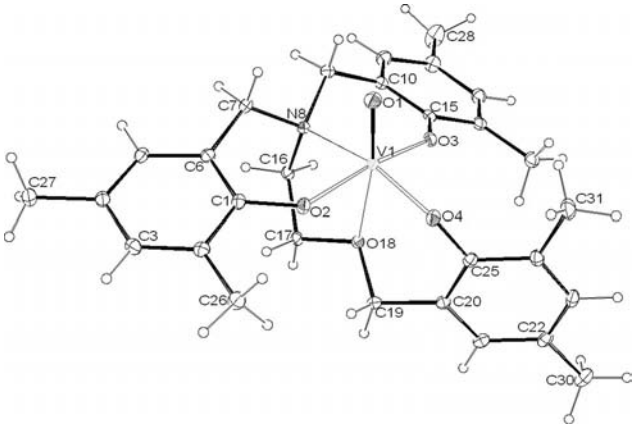


Figure 4. Molecular structure of [VO(L1C1)] (**6**). Thermal ellipsoids are drawn at the 20% probability level.

The molecular geometry of V^V is a distorted octahedron. In both structures the axial position is occupied by the oxido group and the ether oxygen atom (O18). Three phenolate oxygens and the nitrogen atom lie in a plane. The V–N bond lengths in **6** and **7** are significantly (0.2 Å) shorter than in complexes **1**–**5** as the nitrogen atoms in **6**–**7** are in a *trans* position to the phenoxido oxygen, whereas in complexes **1**–**5** the N atoms are in a *trans* position to the oxido group. In **7** the V–N bond is 0.025 Å shorter than in **6**.

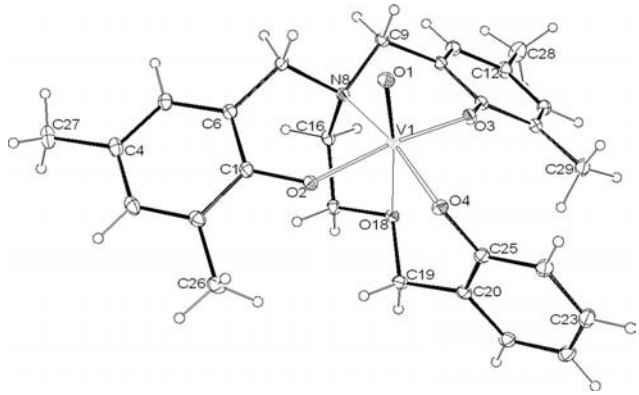


Figure 5. Molecular structure of [VO(L1C2)] (**7**). Thermal ellipsoids are drawn at the 20% probability level.

Conclusions

We have demonstrated that $[VO(acac)_2]$ (under oxidative conditions) and $[VO(OPr)_3]$ can form oxidovanadium(V) complexes with a family of *N*,*N*-bis(2-methylene-4,6-alkylphenol)aminoethan-1-ol ligands. Ligands with *ortho* methyl substituents (H_3L1–H_3L2) react with vanadyl precursors to form compounds that crystallize as trigonal bipyramidal complexes **1**, **2** at room temperature from weakly coordinating polar solvents. Complexes **1** and **2** may be considered to model the active centre of vanadate-dependent haloperoxidases. Conversely, under the same conditions, ligands with *ortho tert*-butyl groups (H_3L3–H_3L4) form dinuclear complexes with a distorted octahedral geometry (**3**, **4**). If the reaction of H_3L1 with $[VO(acac)_2]$ proceeds in methanol at room temperature, a methanol adduct of **1** (i.e., complex **5**) is formed.

The similarity of the ^1H NMR spectra of the compounds **1**–**4** indicates that the dimeric units of **3** and **4** are dissociated to monomeric units in chloroform. The coordinated methanol molecule of **5** also dissociates upon dissolution. The ^{51}V NMR spectra support this observation, as recorded chemical shifts of compounds **1**–**5** are seen as very sharp singlets in a rather narrow range (ca. –392 ppm). Correspondingly, the ^{51}V NMR chemical shifts of complexes **6** and **7** (–419 and –438 ppm, respectively) indicate the persisting octahedral binding also in chloroform solutions.

Solvents play an important role in the complex formation, which is particularly seen in the reactions of H_3L1 with $[VO(OPr)_3]$. When starting materials were refluxed in an ethanol/water solution (9:1 vv), the unexpected new product **6** was obtained in a 33% yield. Complex **6** carries a new triphenolic ligand, which is apparently formed when a new hydroxybenzyl group is attached to the alkoxido oxy-

gen of the coordinated $L1^{3-}$ by an ether linkage. The formation of **6** thus requires that one 2-methylene-4,6-dimethylphenol group must cleave from coordinated $L1^{3-}$ throughout our studies. However, to achieve **6** as a pure product and in a reasonable yield, a catalytic amount of water must be present in the reaction media. This confirms the role of water in the reaction chain. An analogous condensation product **7** is formed when salicyl alcohol is allowed to react with **1** under dry, aprotic conditions. This indicates that the *N*-dealkylation of **1** and the formation of 3,5-dimethylsalicyl alcohol are crucial steps in the condensation process. Unfortunately several NMR studies in the solution did not provide further information about the reaction mechanism. Further studies of the condensation reactions of salicyl alcohols with VO alkoxides are under way.

Experimental Section

General Information: Starting materials for all syntheses were purchased from Aldrich, Merck or Riedel and were of reagent grade and were used as received. The solvents were of HPLC grade and were used as purchased. All syntheses were performed under ambient laboratory atmosphere. The NMR spectra were recorded on a Bruker AVANCE DPX 250 FT-NMR spectrometer or on a Bruker AVANCE DRX 500 FT-NMR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 30 °C. The chemical shifts are reported in ppm and referenced internally using the residual protic solvent resonances relative to tetramethylsilane ($CDCl_3$ δ = 7.26, ^{1}H NMR; δ = 77.0, ^{13}C NMR). The ^{51}V chemical shifts are reported in ppm using an internal $VOCl_3$ standard (δ = 0 ppm). Elemental analyses were performed using a Vario El III elemental analyzer. Single crystal X-ray measurements were performed with an Enraf Nonius Kappa CCD area detector diffractometer using graphite monochromatized Mo-K_α radiation. For liquid chromatography measurements a Perkin–Elmer series 200 equipment was used {Column: Phenomenex Luna 5 u C18 250 × 4.60 mm; solvent: methanol-tris-buffer [97.5% methanol, 2% water and 0.5% tris(hydroxymethyl)aminomethane] 100–90% and water 0–10%; flow rate: 1 mL/min; λ = 254 nm}.

Ligand and Complex Syntheses: The ligands H_3L1·HCl, H_3L2, and H_3L4 were prepared according to the known procedures.[28,35] The ligand H_3L3·HCl was prepared as described below. For the numbering scheme of the complexes **6** and **7**, see Figures 4 and 5.

[H_3L3]·HCl: 3.704 g (22.6 mmol) of 2-*tert*-butyl-4-methylphenol, 0.683 g (22.8 mmol) of paraformaldehyde and 0.635 g (10.4 mmol) of 2-aminoethanol were measured into a 50 mL round bottomed flask. The flask was placed in a beaker and covered with a watchglass. This combined reaction vessel was placed in an oven (120 °C) for 4.5 h. The course of the reaction was followed by HPLC. The resulting yellow syrup was dissolved in diethyl ether (15 mL) and treated with aqueous hydrochloride acid (6 M, 2 mL). The ether solution was then washed with water (10 mL), the ether phase was separated and hexane was added in 1 mL portions until precipitation occurred. The white precipitate was filtered, dried in vacuo and finally recrystallized from hot acetonitrile (20 mL); yield 1.965 g (42%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.41 [s, 18 H, Ar-C(CH_3)$_3$], 2.26 (s, 6 H, Ar-CH_3), 3.29 (t, 2 H, NCH_2CH$_2$), 3.99 (t, 2 H, CH$_2$CH_2O), 4.36 (d, 2 H, Ar-CH_2-N), 6.87, 7.16 (d, 2 H, Ar-*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.8, (Ar-*C*H$_3$), 30.1 [Ar-C(*C*H$_3$)$_3$], 34.7 [Ar-*C*(CH$_3$)$_3$], 55.5 (N*C*H$_2$CH$_2$), 56.8 (Ar-*C*H$_2$-N and CH$_2$*C*H$_2$O), 120.2, 130.2, 130.6, 131.0, 141.5, 151.9 (Ar) ppm. $C_{26}H_{40}ClNO_3$ (450.1): calcd. C 69.4, H 9.0, N 3.1; found C 69.8, H 8.8, N 3.0.

Neutralization of the Ligand Hydrochlorides: The ligand hydrochloride was dissolved in dichloromethane and an excess of saturated aqueous $NaHCO_3$ solution was added. This multiple phase mixture was shaken vigorously until all the organic solids were dissolved. The dichloromethane phase was separated and the solvent was evaporated off.

[VO(L1)] (1): H_3L1·HCl (0.044 g, 0.12 mmol) and triethylamine (0.028 mL, 0.2 mmol) were dissolved in acetonitrile (2 mL). [VO(OCH$_2$CH$_2$CH$_3$)$_3$] (0.023 mL, 0.1 mmol) was added while the color of the solution turned immediately reddish brown. The dark red crystals were formed in 30 min and after two days they were filtered off, washed with diethyl ether (1 mL) and air dried; yield 0.030 g (70%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.26, 2.36 (s, 6 H, Ar-CH_3), 2.70 (t, 2 H, NCH_2CH$_2$), 3.43, 3.73 (d, 2 H, Ar-CH_2-N), 4.82 (t, 2 H, CH$_2$CH_2O), 6.77, 6.91 (d, 2 H, Ar-*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 16.4, 20.6, (Ar-*C*H$_3$), 53.0 (N*C*H$_2$CH$_2$), 56.0 (Ar-*C*H$_2$-N), 75.9 (CH$_2$*C*H$_2$O), 124.4, 124.9, 127.9, 130.4, 132.0, 164.2 (Ar) ppm. ^{51}V NMR (132 MHz, $CDCl_3$): δ = –390.3 ppm. IR: $\nu_{V=O}$, 945 cm^{-1}. $C_{20}H_{24}NO_4V$ (393.36): calcd. C 61.1, H 6.2, N 3.6; found C 60.8, H 6.0, N 3.5. A single-crystal X-ray analysis was performed on one of the crystals.

[VO(L2)] (2): H_3L2 (0.100 g, 0.24 mmol) and [VO(acac)$_2$] (0.054 g, 0.2 mmol) were dissolved in CH_3NO_2 (4 mL). The solution was shaken until all starting material had dissolved and stream of compressed air was passed through the solution to enhance the oxidation of vanadium. The red crystals formed by slow evaporation during two days were filtered off, washed once with diethyl ether (1 mL) and hexane (1 mL) and air dried; yield 0.042 g (44%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.27 [s, 18 H, Ar-C(CH_3)$_3$], 2.38 (s, 6 H, Ar-CH_3), 2.74 (t, 2 H, NCH_2CH$_2$), 3.48, 3.79 (d, 2 H, Ar-CH_2-N), 4.83 (t, 2 H, CH$_2$CH_2O), 6.96, 7.10 (d, 2 H, Ar-*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 16.7 (Ar-*C*H$_3$), 31.5 [Ar-C-(*C*H$_3$)$_3$], 34.2 [Ar-*C*(CH$_3$)$_3$], 53.0 (N*C*H$_2$CH$_2$), 56.0 (Ar-*C*H$_2$-N), 75.9 (CH$_2$*C*H$_2$O), 124.0, 124.2, 124.5, 126.7, 145.5, 164.1 (Ar) ppm. ^{51}V NMR (132 MHz, $CDCl_3$): δ = –392.5 ppm. IR: $\nu_{V=O}$, 960 cm^{-1}. $C_{26}H_{36}NO_4V$ (477.52): calcd. C 65.4, H 7.6, N 2.9; found C 64.6, H 7.5, N 3.0. A single-crystal X-ray analysis was performed on one of the crystals.

[V_2O_2(L3)$_2$] (3): H_3L3·HCl (0.054 g, 0.12 mmol) and [VO(acac)$_2$] (0.027 g, 0.10 mmol) were weighed together, acetonitrile (2 mL) and triethylamine (0.042 mL, 0.3 mmol) were added and the solution was heated until all the solids had dissolved. The reaction mixture was kept under open atmosphere for one hour and then the reaction vessel was sealed. The resulting dark red solution was kept at room temperature for three days leading to the formation of crystals. The dark red crystals were filtered off, washed with diethyl ether (1 mL) and hexane (1 mL) and air dried; yield 0.032 g (65%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.51 [s, 18 H, Ar-C(CH_3)$_3$], 2.29 (s, 6 H, Ar-CH_3), 2.75 (t, 2 H, NCH_2CH$_2$), 3.42, 3.74 (d, 4 H, Ar-CH_2-N), 4.84 (t, 2 H, CH$_2$CH_2O), 6.82, 7.04 (d, 4 H, Ar-*H*) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.0 (Ar-*C*H$_3$), 29.8 [Ar-C-(*C*H$_3$)$_3$], 34.9 [Ar-*C*(CH$_3$)$_3$], 53.1 (N*C*H$_2$CH$_2$), 56.1 (Ar-*C*H$_2$-N), 75.8 (CH$_2$*C*H$_2$O), 125.4, 126.5, 128.5, 131.8, 136.5, 165.2 (Ar) ppm. ^{51}V NMR (132 MHz, $CDCl_3$): δ = –392.0 ppm. IR: $\nu_{V=O}$, 953 cm^{-1}. $C_{26}H_{36}NO_4V$ (477.52): calcd. C 65.4, H 7.6, N 2.9; found C 65.0, H 7.4, N 2.8. A single-crystal X-ray analysis was performed on one of the crystals.

[V_2O_2(L4)$_2$] (4): H_3L4 (0.060 g, 0.12 mmol) and [VO(acac)$_2$] (0.027 g, 0.10 mmol) were weighed together, acetonitrile (2 mL) and

triethylamine (0.028 mL, 0.2 mmol) were added and the solution was heated until all the solids had dissolved. The resulting dark red solution was kept at room temperature and the solvent was allowed to evaporate slowly for three days, which led to the formation of crystals. The dark red crystals were filtered off, washed with acetonitrile (2 mL) and air dried; yield 0.035 g (62%). ^{1}H NMR: δ = 1.29, 1.52 [s, 18 H, Ar-C(CH_3)$_3$], 2.79 (t, 2 H, NCH_2CH$_2$), 3.47, 3.80 (d, 4 H, Ar-CH_2-N), 4.85 (t, 2 H, CH$_2$CH_2O), 7.01, 7.26 (d, 4 H, Ar-*H*) ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ = 29.9, 31.6 [Ar-C(*C*H$_3$)$_3$], 34.5, 35.2 [Ar-*C*(CH$_3$)$_3$], 53.3 (N*C*H$_2$CH$_2$), 56.6 (Ar-*C*H$_2$-N), 75.7 (CH$_2$*C*H$_2$O), 122.8, 124.7, 125.0, 136.0, 145.2, 165.1 (Ar) ppm. ^{51}V NMR (132 MHz, CDCl$_3$): δ = –392.7 ppm. IR: $\nu_{V=O}$, 951 cm^{-1}. $C_{32}H_{48}NO_4V$ (561.68): calcd. C 68.3, H 8.4, N 2.4; found C 68.4, H 8.6, N 2.5. A single-crystal X-ray analysis was performed on one of the crystals.

[VO(L1)(CH$_3$OH)]·0.5CH$_3$OH (5): 0.265 g (1.0 mmol) of [VO(acac)$_2$] and 0.329 g (1.0 mmol) of H$_3$L1·1/3toluene were mixed with 10 mL of methanol. After the dark reaction mixture was kept under open atmosphere for three hours, the reaction vessel was sealed and the mixture was kept at room temperature for a week. Dark, shiny crystals of the complex [VO(L1)(CH$_3$OH)]·0.5CH$_3$OH were isolated and washed with methanol. Yield 280 mg (63%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.25 [s, 6 H, Ar-C(19/20)H_3], 2.35 [s, 6 H, Ar-C(18/21)H_3], 2.70 (t, 2 H, NCH_2CH$_2$O), 3.43, 3.73 (d, 2 H, Ar-CH_2-N), 3.49 (s, 6 H, CH_3O), 4.81 (t, 2 H, NCH$_2$CH_2O), 6.76 [d, 2 H, Ar-*H*(5/11)], 6.90 [d, 2 H, Ar-*H*(3/13)] ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ = 16.4 (C18/C21), 20.6 (C19/C20), 50.8 (*C*H$_3$O) 53.0 (N*C*H$_2$CH$_2$O), 56.0 (Ar-*C*H$_2$-N), 75.9 (NCH$_2$*C*H$_2$O), 124.4 (C6/C10), 124.8 (C4/C12), 127.9 (C5/C11), 130.3 (C3/C13), 132.0 (C2/C14), 164.2 (C1/C15) ppm. ^{51}V NMR (132 MHz, CDCl$_3$): δ = –389.3 ppm. IR: $\nu_{V=O}$, 952 cm^{-1}. $C_{21}H_{25}NO_5V$·1/2CH$_3$OH (438.39): calcd. C 58.9, H 6.2, N 3.2; found C 59.0, H 6.3, N 3.5. A single-crystal X-ray analysis was performed on one of the crystals.

[VO(L1C1)] (6): H$_3$L1·1/3toluene (0.313 g, 0.87 mmol) was dissolved in ethanol (99.5%) (9 mL) and [VO(OCH$_2$CH$_2$CH$_3$)$_3$] (0.092 mL, 0.4 mmol) was added to the solution and it was heated until boiling. Water (1 mL) was added in five 200 μL portions and the solution was refluxed for 18 h. The dark red crystals were filtered off, washed twice with diethyl ether (1 mL) and air dried; yield 0.069 g (33%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.86 [s, 6 H, Ar-C(28/31)H_3], 2.26 [s, 6 H, Ar-C(29/30)H_3], 2.29 [s, 3 H, Ar–C(27)H_3], 2.46 [s, 3 H, Ar-C(26)H_3], 2.89 (t, 2 H, NCH_2CH$_2$O), 3.31 (t, 2 H, CH$_2$CH_2O), 3.76, 4.86 (d, 2 H, Ar-CH_2-N), 4.52 (s, 2 H, Ar-CH_2O), 6.67 (d, 1 H, Ar-*H*21), 6.77 [d, 2 H, Ar-*H*(5/11)], 6.90 [d, 2 H, Ar-*H*(3/13)], 7.01 (d, 1 H, Ar-*H*23) ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ = 15.6 [Ar-*C*(26/29)H$_3$], 16.5 [Ar-*C*(31)H$_3$], 20.4 [Ar-*C*(27/28)H$_3$], 20.6 [Ar-*C*(30)H$_3$], 53.8 (N*C*H$_2$CH_2), 66.4 (Ar-*C*H$_2$-N), 68.5 (CH_2*C*H$_2$O), 72.8 (Ar-*C*H$_2$O), 119.6 (C6/C10), 123.9 (C24), 124.3 (C2/C14), 124.9 (C20), 126.5 (C5/C11), 126.8 (C21), 127.8 (C4/C12), 131.0 (C23), 131.4 (C3/C13), 131.9 (C22), 161.8 (C1/C15), 164.9 (C25) ppm. ^{51}V NMR (132 MHz, CDCl$_3$): δ = –418.7 ppm. IR: $\nu_{V=O}$, 954 cm^{-1}. $C_{29}H_{34}NO_5V$ (527.53): calcd. C 66.0, H 6.5, N 2.7; found C 65.7, H 6.4, N 2.4. A single-crystal X-ray analysis was performed on one of the crystals.

[VO(L1C2)] (7): The complex was prepared by adding **1** (0.079 g, 0.20 mmol) and salicyl alcohol (0.40 mmol, 0.050 g) in dry acetonitrile. The solvent was dried beforehand with molecular sieves (4 Å) and a CaCl$_2$ tube was added to the experimental setup. The solution was refluxed for 20 h and cooled to 5 °C. Dark matter precipitated on the bottom of the reaction vessel during two hours. The precipitate (40.7 mg) was washed twice with diethyl ether (2 mL) and its subsequent ^{1}H NMR spectrum consisted of the signals of **7** and **1** in a 1.6:1 ratio. A recrystallization by slow evaporation from a mixture of acetonitrile and dichloromethane (9 mL, 5:4) yielded dark, shiny crystals of **7**, which were washed twice with diethyl ether (1 mL) and air dried. To improve the poor yield (8.6 mg) of the first recrystallization, the solvent was evaporated to dryness, washed with diethyl ether (2 × 1 mL), and a similar recrystallization process was performed twice on the remains. Complex **7** seemed to be practically insoluble to diethyl ether, which helped to reduce the amount of **1** (soluble in small amounts) in the precipitates; yield 22.3 mg (22%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.87 [s, 6 H, Ar-C(26/29)H_3], 2.25 [s, 6 H, Ar-C(27/28)H_3], 2.91 (t, 2 H, NCH_2CH$_2$O), 3.34 (t, 2 H, CH$_2$CH_2O), 3.79, 4.86 (d, 2 H, Ar-CH_2-N), 4.57 (s, 2 H, Ar-CH_2O), 6.78 [d, 2 H, Ar-*H*(5/11)], 6.92 [d, 2 H, Ar-*H*(3/13)], 6.92 [m, 2 H, Ar-*H*(22/23)], 7.01 (d, 1 H, Ar-*H*24), 7.32 (t, 1 H, Ar-*H*21) ppm. ^{13}C NMR (126 MHz, CDCl$_3$): δ = 15.7 [Ar-*C*(26/29)H$_3$], 20.5 [Ar-*C*(27/28)H$_3$], 53.9 (N*C*H$_2$CH_2), 66.4 (Ar-*C*H$_2$-N), 68.7 (CH_2*C*H$_2$O), 72.8 (Ar-*C*H$_2$O), 115.9 (C24), 119.6 (C6/C10), 122.3 (C23), 124.3 (C2/C14), 125.4 (C20), 126.5 (C5/C11), 128.2 (C4/C12), 128.7 (C21), 129.6 (C22), 131.6 (C3/C13), 162.1 (C1/C15), 167.1 (C25) ppm. ^{51}V NMR (132 MHz, CDCl$_3$): δ = –437.9 ppm. IR: $\nu_{V=O}$, 943 cm^{-1}. $C_{27}H_{30}NO_5V$ (499.48): calcd. C 64.9, H 6.1, N 2.8; found C 65.4, H 5.8, N 3.1. A single-crystal X-ray analysis was performed on one of the crystals.

X-ray Crystallography: Crystals suitable for single-crystal X-ray measurements were obtained directly from reaction tubes before filtration. The crystal data for compounds **1**–**7** along with other experimental details are summarized Tables S1–S2. The crystallographic data were collected at 123 or 173 K on an Enraf Nonius Kappa CCD area detector diffractometer using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). The data were collected with ϕ and ω scans and were processed using DENZO-SMN v0.95.373.[41,42] An SADABS[43] absorption correction was applied to the data sets. The structures were solved by direct methods using the SHELXS-97[44] or SIR-97[45] programs and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97[46] program. The heavy atoms were refined anisotropically except the disordered carbon atoms in the side chains of the aromatic rings of **2**, which were refined isotropically. The CH hydrogen atoms were included at fixed distances using fixed displacement parameters from their host atoms while other H atoms were refined using fixed displacement parameters. Structure figures were drawn using ORTEP-3 for Windows.[47]

CCDC-802518 (for **1**), -802519 (for **2**), -802520 (for **3**), -802521 (for **4**), -802522 (for **5**), -802523 (for **6**), -802524 (for **7**) contain the supplementary crystallographic data for compounds **1**–**7** presented in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figures S1 and S2 for compounds **2** and **4**. Tables S1 and S2 (crystal data for compound **1**–**7**). Tables S3–S4 (selected bond lengths and angles for compounds **1**–**4**).

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