Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

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ARTICLE

Vanadium complexes with multidentate amine bisphenols

Cite this: DOI: 10.1039/xoxxoooooox

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Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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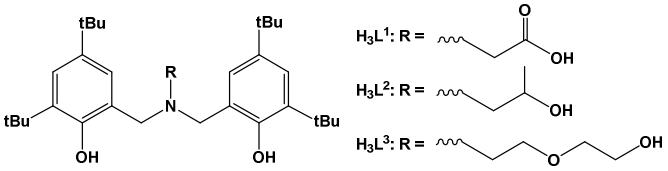
The reaction of $VO(acac)_2$ ($acac^-$ = acetyl acetonate) with tripodal glycine bisphenol H_3L^1 under ambient atmosphere yields a hexacoordinated vanadium(IV) complex $[V(acac)(L^1)]$ (**1**). Corresponding reactions with tripodal 2-propanolamine bisphenol H_3L^2 and potentially pentadentate ethoxyethanolamine bisphenol H_3L^3 lead to the oxidation of the metal centre and formation of mononuclear oxovanadium(V) complexes $[VO(L^2)]$ (**2**) and $[VO(L^3)]$ (**3**), respectively. Alternatively, these latter two complexes can be prepared using $VOSO_4 \cdot 5H_2O$ or $VO(OPr)_3$ as a precursor. The CV of **1** in a ACN solution show a reversible one-electron process at $E_{1/2}$ = +1.18 V, whereas **2** and **3** have an irreversible redox response at -1.6 V and -1.2 V, respectively. Complexes **2** and **3** show moderate activity in the epoxidation of *cis*-cyclooctene by *tert*-BuOOH at 50 °C.

Introduction

A common idea in coordination chemistry is to control the environment of the metal centre by using diverse ligands. Particularly, the electronic and steric properties of ligands are used to tune the reactivity of metal species. For example, to obtain robust complexes which are stable under catalytic conditions, certain multidentate ligands such as salens and aminotrisphenols are frequently used.[1,2] Correspondingly, aminobisphenols with different side-arm donors are potentially tetradentate ligands which can form stable complexes with most main group and transition metals.[3] The coordination geometry of the metal centre can be controlled by the ligand design. Especially, the *ortho*-substituents of the phenolate moieties as well as the nature of side-arm donor influence the structure and reactivity of the complexes formed.

The coordination chemistry of vanadium is largely studied due to the biological relevance and catalytic properties of different vanadium-based systems.[4,5] Especially, the role of vanadium in certain haloperoxidase and nitrogenase enzymes as well as the insulin-like effect of vanadium compounds have motivated synthetic chemists to prepare model compounds for structural studies as well as for reactivity tests. For example, the active sites of haloperoxidase enzymes have been modelled by vanadium phenoxides and catecholates.[6,7,8] During such investigations, the reactions of vanadium compounds with multidentate aminotrisphenols and aminobisphenols have been studied.[7-13] Oxovanadium(V) trispropoxide $VO(OPr)_3$ is an obvious starting material for new oxovanadium(V) aminobisphenolate complexes as it undergoes readily alkoxide displacement reactions with the phenolic ligand precursors. However, a stable oxovanadium(IV) precursor $VO(acac)_2$ ($acac^-$ = acetyl acetonate) can also be used as it oxidises easily when treated with amine bisphenol ligands in alcohol solution under ambient atmosphere yielding oxovanadium(V) complexes.[10,14] For example, tripodal ethanolamine bisphenols react with abovementioned vanadium starting materials to form monomeric, pentacoordinated complexes which can dimerize upon crystallisation.[14] In the present study, aminobisphenols with different side-arm hydroxyl groups (Scheme 1) are used to prepare new oxovanadium species. The syntheses, solid and solution state structures and catalytic behaviour of the complexes are reported.



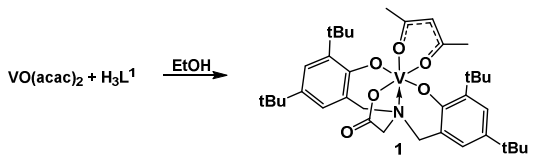
Scheme 1.

Results and discussion

Syntheses

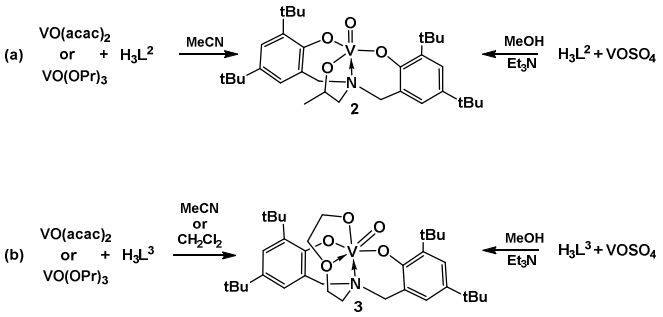
The reaction of $[VO(acac)_2]$ with one equivalent of H_3L^1 was performed in ethanol solution under ambient atmosphere

following a similar procedure used for the preparation of V(V) complexes with aminoalcohol bisphenols.[14] The reaction yielded a dark solution from which black, shiny crystals were separated after few days (Scheme 2). The crystals were analysed by X-ray diffraction and characterized as a monomeric complex [V(acac)(L^1)] **1**. Surprisingly, the metal centre was not oxidised during the complexation reaction and the oxidation state remained as vanadium(IV). The reaction of H_3L^1 with $VO(acac)_2$ can be compared with the reactivity of aminotrisphenol tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (H_3L^{tris}).[9] This ligand forms structurally very similar V(IV) complex [V(acac)(L^{tris})], but the product is air-sensitive and must be prepared under an atmosphere of dry argon to prevent oxidation of the metal centre during the coordination reaction. Conversely, **1** is stable under air in solid state as well as in solution. Furthermore, to enhance the oxidation of the metal, the complexation was repeated under an atmosphere of pure oxygen in different solvents, but all these reactions led to the formation of **1** as the only isolable product and no V(V) species were found. The different redox behaviour of **1** and [V(acac)(L^{tris})] can be clearly seen in their cyclic voltammograms (CV). The CV of **1** in a acetonitrile (ACN) solution shows a reversible one-electron process at $E_{1/2}$ = +1.18 V (*vs*. Fc^+/Fc) due to the oxidation of V(IV) to V(V) whereas the corresponding process for [V(acac)(L^{tris})] is seen at +0.374 V.[9] The overall mechanism for the formation of complex **1** includes an alcoholysis of one of the V–O_{acac} bonds as well as a condensation of the V=O double bond, which leads to the tetradentate dianionic coordination mode of the ligand. Even rather weak acids can protonate the oxo group and such reactivity of M=O moiety with multidentate phenols is well known e.g. in vanadium[9,15] and molybdenum[16] chemistry. Other attempts to make a corresponding oxovanadium(V) complex involved the reactions of bisphenol H_3L^1 with [$VO(OPr)_3$] in various solvents. However, in all cases the reactions led to the dark mixtures and precipitates, which were in most cases insoluble and non-crystalline. In methanol, few crystals of a methyl ester derivative [VO(OMe)(MeL^1)] (**S4**) were formed.† During this reaction, two propoxides were replaced by phenoxide parts of the glycine bisphenol ligand whereas the third propoxide was substituted by methoxide. The carboxylic acid group of the side arm has undergone an esterification to form a methyl ester.



Scheme 2.

Reaction of racemic 2-propanolamine bisphenol H_3L^2 with $VO(acac)_2$ in acetonitrile solution under ambient atmosphere gave a dark solution from which the red crystals of **2** deposited in a few days (Scheme 3a). Alternatively, the identical product can be prepared in a basic methanol solution using $VOSO_4{\cdot}5H_2O$ as a starting material. During these reactions, the V(IV) ion is oxidized to form a new V(V) complex in a high yield. The nearly quantitative yield was achieved when the reaction was repeated using $VO(OPr)_3$ in dry acetonitrile. This reaction is fast and clean since there is no necessity for V(IV) to V(V) oxidation upon complexation reaction. The air- and moisture-stable complex **2** is soluble in common organic solvents but insoluble in water.



Scheme 3.

The studied vanadium precursors ($VO(acac)_2$, $VOSO_4{\cdot}5H_2O$, $VO(OPr)_3$), also reacted with aminoethoxyethanol bisphenol H_3L^3 to form a dark greenish solution from which transparent green crystals of **3** could be separated after few days (Scheme 3b). The $VO(OPr)_3$ precursor afforded the highest yield of all studied starting materials. Complex **3** is stable under ambient conditions, soluble in chloroform and DMSO and moderately soluble in other common organic solvents but insoluble in water. The CV of pentacoordinated **2** and hexacoordinated **3** in an acetonitrile solution show an irreversible redox response at -1.6 V and -1.2 V (*vs*. Fc^+/Fc), respectively, due to the reduction of V(V) to V(IV). As reported earlier, [$V_2O_2(L^{2'})_2$] is the ethanolamine bisphenol analogue of complex **2**, which has an octahedral coordination in solid state due to the dimerization.[14] Interestingly, it has a similar irreversible redox response at -1.2 V as octahedrally coordinated **3**.[±] The reactions of $VO(acac)_2$ with ligands H_3L^1 – H_3L^3 indicate that the nature of the side arm hydroxyl donor has a significant role in the oxidation of the vanadium centre, which is in line with the earlier observations on the reactivity of tripodal amino acid and amino alcohol ligands. For example, the aerobic reaction of triethanol amine (H_3tea) with $VO(acac)_2$ yields a V(V) complex [VO(tea)][17] whereas the reaction of *N*-(2-hydroxyethyl)iminoacetic acid (H_3hida) leads to the formation of a monomeric V(IV) complex [VO(Hhida)(H_2O)]·MeOH[18].

The IR spectra show strong absorptions at 970 cm^{-1} for **2** and at 974 cm^{-1} for **3**, corresponding the V=O stretching frequencies.[6,10,19] The ^{1}H and ^{13}C NMR spectra of complexes **2** and **3** in $CDCl_3$ solution show the anticipated resonances for aminoalcohol bisphenolate ligands, once an apparent plane of symmetry in **3** is taken into account. The resonances could be assigned with the help of conventional 2D NMR correlation spectroscopy (COSY, NOESY, HSQC, HMBC), except for a

couple of nearly-isochronous ^{13}C shifts from the *t*Bu substituents of **2**. The assignment of chemical shifts is provided in the Experimental section under the chemical shift list of the complexes, using the atom numbering from Figs. 2 and 3. The carbons in the aminoalcohol side-arm are numbered as 16, 17, (18), (19), starting from the amino end. Furthermore, the diastereotopic benzylic hydrogens (at C7 and C9) are labelled with α if they are *syn* (on the same side) with the aminoalcohol side-arm, and with β otherwise. In **2**, labels α and β are also used to distinguish between the diastereotopic hydrogens at C16; 16-Hα being *syn* with the 17-Me substituent.

The ^{1}H and ^{13}C NMR spectra of the complex **3** indicate a presence of an effective plane of symmetry in solution phase, defined by the atoms O1, O4, O5, V1 and N8. Thus the two phenolate moieties of **3** are chemically equivalent due to symmetry (i.e. the pairs C1/C15, C2/C14, 3-H/13-H, etc. display isochronous chemical shifts), as are the geminal pairs of hydrogens within the aminoethoxyethanol side-arm (16-H_2, 17-H_2, etc.). This symmetry element arises as a result of dynamic averaging over asymmetric instantaneous conformations in solution; for each asymmetric conformation, such as the one observed in the crystal structure (Fig. 3), there exists an equally-energetic and equally-populated mirror conformation accessible via ring inversion. This averaging is evident from the CH_2 proton signals of the ethoxyethanol side-arm of **3**, which appear as four 1:2:1 triplets (each with an integral of 2 H) in the ^{1}H NMR spectrum, and display a peak-splitting of 5-6 Hz due to averaged $^{3}J_{HH}$-coupling constants.

In contrast, distinct chemical shifts for both phenolate side-arms are seen in the ^{1}H and ^{13}C NMR spectra of **2**, with the exception of the accidentally isochronous 2-$\underline{C}(CH_3)_3$ and 14-$\underline{C}(CH_3)_3$ ^{13}C shifts. The lack of an effective plane of symmetry in this complex is due to the asymmetric C17 carbon carrying the methyl substituent. The large vicinal *J*-coupling constant ^{3}J(16-Hα,17-H) (11.0 Hz) and small ^{3}J(16-Hβ,17-H) (3.7 Hz) indicate that the complex **2** adopts a preferred conformation in solution, which is close to its crystal structure. This conclusion is also supported by 1D NOE NMR results. An NOE enhancement can be observed between all the pairs of protons which are spatially close to each other in the solid-state structure ($d \approx 2.9$ Å or less), excluding the pair 7-Hβ/9-Hα for which the overlapping signals obscure the detection of NOE. Conversely, "unexpected" NOEs were not observed. The non-innocent, (i.e. redox-active) behaviour of catecholate ligands in vanadium-based haloperoxidase models can be studied by ^{51}V NMR as it is sensitive to small changes in the electronic structure of the complexes.[20,21] The ^{51}V NMR spectra of **2** and **3** consist of a single broad singlet in each case, resonating at -397.0 ppm (**2**) and -409.5 ppm (**3**) vs. $VOCl_3$(calcd.). The corresponding peak widths are 308 Hz (**2**, at $B_0 \sim 132$ MHz) and 240 Hz (**3**, at 105 MHz); these peaks show (quadrupolar) broadening due to the quadrupolar vanadium nucleus (I_{51V} = 7/2) experiencing a non-zero local electric field gradient. The ^{51}V chemical shifts are within the expected range for an oxidation state V(V), which indicates a redox-inactive behaviour of the phenolate ligands.[21] It should also be noted that the vanadium cations in oxidation states 0, II, and IV are paramagnetic and their complexes (for example **1**) would generally not be observable with NMR.

Description of the structures

In solid state, complex **1** is formed of mononuclear molecules in which the central vanadium ion is surrounded by one nitrogen and five oxygen donors to form a distorted octahedral coordination sphere. The equatorial plane is formed by three oxygen donors of the tripodal ligand and one of the acetyl acetonato oxygens. The axial positions are occupied by other acetyl acetonato oxygen and the tertiary nitrogen atom while the O5-V1-N8 angle is 173.90°. The phenolate groups of the tripodal ligand are located *trans* to each other with a O1-V1-O2 angle of 170.96° whereas the two oxygen atoms of the acetyl acetonate ligand are positioned *cis* with a O5-V1-O6 angle of 90.13°. Complex **1** crystallises with one molecule of solvent ethanol in the crystal lattice. Although the geometry of the disordered ethanol molecule is relatively inaccurate, the observed O4···O7 distance of 2.788 Å is indicative of rather strong hydrogen bonding.

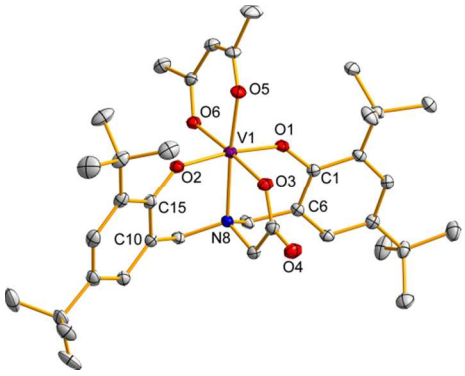


Fig. 1. The molecular structure of **1**. A solvent molecule and hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°] in **1**-**3**.

Complex **1**			
V1-O1	1.8054(17)	O1-V1-O2	170.96(8)
V1-O2	1.7921(17)	O3-V1-O6	176.77(8)
V1-O3	1.9851(18)	O5-V1-O6	90.13(7)
V1-O5	1.9415(18)	O5-V1-N8	173.90(8)
V1-O6	2.0019(18)	V1-O1-C1	142.36(16)
V1-N8	2.190(2)	V1-O2-C15	142.12(15)
Complex **2**			
V1-O1	1.6059(11)	O1-V1-N8	174.56(5)
V1-O2	1.8170(11)	O2-V1-O3	113.02(5)
V1-O3	1.7993(11)	O2-V1-O4	122.07(5)
V1-O4	1.8046(11)	O3-V1-O4	117.81(5)
V1-N8	2.3479(11)	V1-O2-C1	140.21(10)
		V1-O3-C15	142.27(10)
Complex **3**			
V1-O1	1. 597(3)	O1-V1-N8	99.61(15)
V1-O2	1.861(3)	O2-V1-O3	158.36(14)
V1-O3	1.895(3)	O2-V1-O4	78.14(13)
V1-O4	2.237(3)	O3-V1-O4	85.56(13)
V1-O5	1.817(3)	O5-V1-N8	153.10(15)
V1-N8	2.230(4)	V1-O2-C1	128.5(3)
		V1-O3-C15	118.1(3)
		V1-O5-C19	121.7(3)

Vanadium ethanolamine bisphenolates are known to crystallise either as pentacoordinated monomers or hexacoordinated dimeric units.[13] X-ray analyses revealed the monomeric structure of complex **2** with a VNO_4 coordination sphere around the central atom (Figure 2) as the ligand has coordinated through two phenolate oxygens as well as the oxygen and nitrogen donors of the aminoalcohol group. The equatorial positions are occupied by the phenolate and alcoholate oxygens whereas the oxo group and the neutral nitrogen donor coordinate in the axial positions with an O1-V1-N8 angle of 174.56°. The structure is relatively similar to those reported earlier for corresponding vanadium aminobisphenolates.[14] The geometric parameter $\tau = (\beta - \alpha)/60$, where β and α are the two largest L-M-L angles, describes a coordination sphere of five coordinated atoms. It has a value of 1 if the structure is pentagonal bipyramidal and 0 if it is square pyramidal.[22] For **2** ($\alpha_{O2\text{-}V1\text{-}O4}$ = 122.07, $\beta_{O1\text{-}V1\text{-}N8}$ = 174.56) the value τ = 0.87, which indicates a slightly distorted pentagonal bipyramidal geometry.

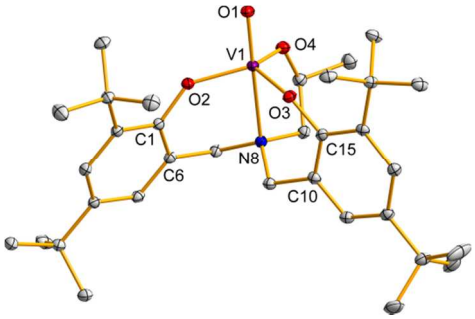


Fig. 2. The molecular structure of **2**. Hydrogen atoms are omitted for clarity

Complex **3** is formed of mononuclear molecules in which the organic ligand is coordinated to the V=O moiety as a pentadentate trianion to form a distorted octahedral coordination sphere. The terminal oxo group in the axial position is located *trans* to the ether oxygen in the ligand side-arm with a O1-V1-O5 angle of 174.25°. Two phenolate oxygen atoms, alkoxide oxygen and a neutral nitrogen donor form the equatorial plane. The phenolate groups are *trans* with the O2-V1-O3 angle of 158.36°.

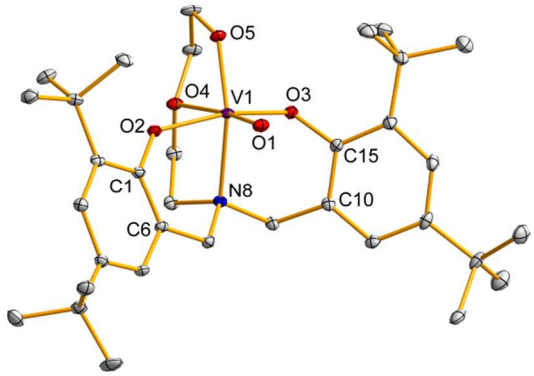


Fig. 3. The molecular structure of **3**. Hydrogen atoms are omitted for clarity

Catalyst studies

The catalytic activities of synthesised vanadium complexes for the epoxidation of *cis*-cyclooctene were studied using 1.5 equivalents of *tert*-BuOOH as an oxidant and 2 mol-% catalyst loadings (see Table 2). The test reactions were run under ambient atmosphere in $CDCl_3$ solutions while the reaction course was monitored by ^{1}H NMR. The studied complexes had practically no catalytic activity at room temperature. At 50 °C, complex **1** was still inactive but oxovanadium(V) complexes **2**, **3** and $[V_2O_2(L^{2'})_2]$ show some activity after an initiation period of around 30 minutes. The activities were still low (TOF = 10 h^{-1} for **2**, 18 h^{-1} for **3** and 13 h^{-1} for $[V_2O_2(L^{2'})_2]$, respectively) with all catalysts. Nevertheless, the reactions were selective and total conversions of the alkene to the epoxide were gained in 24 hour reactions without oxidant decomposition.

Table 2. Catalytic activities of **1** - **3** and $[V_2O_2(L^{2'})_2]$ (2 mol-% of catalyst) for epoxidation of *cis*-cyclooctene with 1.5 equivalents of *tert*-BuOOH at 50 °C.

catalyst	$t_{1/2}$ [min][a]	conversion [%][b]	TON[c]	TOF [h^{-1}][d]
1	--	~1	--	--
2	340	100	15	10
3	200	100	27	18
$[V_2O_2(L^{2'})_2]$	250	100	20	13

[a] Time required for a 50% degrease of the initial concentration of alkene.

[b] Yield of product measured by ^{1}H NMR after 24 h.

[c] TON calculated after 90 min of reaction as (mol product)·(mol catalyst)$^{-1}$

[d] TOF calculated after 90 min of reaction as (mol product)·(mol catalyst)$^{-1}$·1t/h)$^{-1}$

Experimental

Materials and methods

All syntheses and manipulations were done under ambient atmosphere. Solvents (HPCL grade) were used as received. $VO(acac)_2$ was prepared as described in the literature.[23] Ligand precursors H_3L^1 and H_3L^2 were synthesised applying slight modifications of published procedures.[24,25] All other chemicals were reagent grade, available commercially and used as received. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) and tetrabutylammonium perchlorate (Bu_4NClO_4) were dried and used as a supporting electrolyte for recording cyclic voltammograms of the complexes. Elemental analyses were performed using a Vario El III elemental analyzer.

Synthesis of H_3L^3. A mixture of 2,4-di-tert-butylphenoxide (2.06 g, 10 mmol), paraformaldehyde (0.30 g, 10 mmol) and 2-(2-aminoethoxy)ethan-1-ol (0.53 g, 5 mmol) were stirred and heated (110 – 120 °C) in a round-bottomed flask for two hours. The cooled reaction mixture was mixed with 20 ml of ethanol to obtain 2.54 g (47 %) of aminoalcohol bisphenol. ^{1}H and ^{13}C NMR spectra were identical with those published earlier.[26]

[V(acac)(L^1)] 1: 135 mg (0.51 mmol) of $VO(acac)_2$ and 260 mg (0.51 mmol) of H_3L^1 were mixed with 8 ml of ethanol to form a dark mixture. The open reaction vessel was kept at room temperature for 5 hours, sealed and then kept in a refrigerator for 4 days. Dark brown crystals of complex **1** were separated in a 188 mg (57 %) yield. Anal. Calcd. (%) for $C_{37}H_{53}NO_6V$ (658.77 g/mol): C, 67.46; H, 8.11; N, 2.13. Found: C, 67.76; H, 8.09; N, 2.28.

[VO(L^2)] 2: *Method A*. 135 mg (0.51 mmol) of $VO(acac)_2$ and 255 mg (0.50 mmol) of H_3L^2 were dissolved in 10 ml of ethanol by gentle heating. The open reaction vessel was kept at room temperature for 5 hours, sealed and then the dark red solution was kept at -18 °C for 4 days to obtain 135 mg (47 %) of **2** as dark red crystals. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.27 (1 H, d, *J* 2.4, 3-H), 7.23 (1 H, d, *J* 2.4, 13-H), 7.08 (1 H, d, *J* 2.4, 5-H), 6.89 (1 H, d, *J* 2.4, 11-H), 5.20 (1 H, m, 17-H), 4.37 (1 H, d, *J* 12.7, 7-Hα), 3.77 (1 H, d, *J* 14.0, 9-Hβ), 3.18 (1 H, d, *J* 14.0, 9-Hα), 3.15 (1 H, d, *J* 12.7, 7-Hβ), 2.60 (1 H, dd, *J* 12.3, 11.0, 16-Hα), 2.48 (1 H, dd, *J* 12.3, 3.7, 16-Hβ), 1.53 (9 H, s, 2-*t*Bu), 1.51 (9 H, s, 14-*t*Bu), 1.30 (9 H, s, 4-*t*Bu), 1.26 (9 H, s, 12-*t*Bu), 1.19 (3 H, d, *J* 6.1, 17-Me). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 165.2 (C1), 164.5 (C15), 145.4 (C12), 144.6 (C4), 136.0 (C14), 135.7 (C2), 125.0 (C6), 124.8 (C10), 124.7 (C11), 124.5 (C5), 122.9 (C3), 122.7 (C13), 82.0 (C17), 59.6 (C16), 57.0 (C7), 56.9 (C9), 35.2 (2 C, 2-*C*$(CH_3)_3$ and 14-*C*$(CH_3)_3$), 34.52, 34.50 (4-*C*$(CH_3)_3$ and 12-*C*$(CH_3)_3$), 31.6 (4-C(*C*$H_3)_3$), 31.5 (12-C(*C*$H_3)_3$), 29.9, 29.8 (2-C(*C*$H_3)_3$ and 14-C(*C*$H_3)_3$), 21.4 (17-Me). ^{51}V NMR (132 MHz, $CDCl_3$, TMS): δ -397.0 (br s, FWHM 308 Hz). Anal. Calcd. (%) for $C_{33}H_{50}NO_4V$ (575.71 g/mol): C, 68.85; H, 8.75; N, 2.43. Found: C, 68.66; H, 8.59; N, 2.29.

Method B: 178 mg (0.35 mmol) of H_3L^2, 131 mg of $VOSO_4{\cdot}5H_2O$ (0.52 mmol) and 0.1 ml of triethylamine were dissolved in 10 ml of MeOH. The mixture was stirred in an open vessel for 18 hours. Complex **2** was isolated by filtration as a dark green crystalline solid in a 72 % yield based on the ligand (144 mg).

Method C: 255 mg (0.50 mmol) of H_3L^2 was dissolved in 10 ml of acetonitrile by gentle heating. The solution was allowed to cool to room temperature and 120 µl of $VO(OPr)_3$ (124 mg, 0.51 mmol) was added. The dark red solution was kept at -18 °C for 4 days to yield 245 mg (85 %) of dark red crystals of **2**.

[VO(L^3)] 3: *Method A*. 115 mg (0.43 mmol) of $VO(acac)_2$ and 217 mg (0.40 mmol) of H_3L^3 were dissolved in 5 ml of acetonitrile. The formed dark solution was allowed to react with atmospheric oxygen for 3 hours and the sealed reaction vessel was kept overnight at room temperature to obtain **3** as dark green precipitate in a 120 mg (56 %) yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.30 (2 H, d, *J* 2.3, 3-H/13-H), 7.00 (2 H, d, *J* 2.4, 5-H/11-H), 5.16 (2 H, t, *J* 5.3, 19-H_2), 4.30 (2 H, t, *J* 5.3, 18-H_2), 4.18 (2 H, d, *J* 13.9, 7-Hβ/9-Hβ), 3.98 (2 H, d, *J* 13.9, 7-Hα/9-Hα), 3.97 (2 H, t, *J* 5.7, 17-H_2), 3.12 (2 H, t, *J* 5.7, 16-H_2), 1.48 (18 H, s, 2-*t*Bu/14-*t*Bu), 1.29 (18 H, s, 4-*t*Bu/12-*t*Bu). ^{13}C NMR (101 MHz, $CDCl_3$, TMS): δ 163.1 (C1/C15), 141.1 (C4/C12), 134.8 (C2/C14), 123.5 (C3/C13), 122.5 (C5/C11), 121.0 (C6/C10), 76.5 (C19), 72.8 (C18), 65.6 (C17), 62.6 (C7/C9), 58.6 (C16), 35.1 (2-*C*$(CH_3)_3$/14-*C*$(CH_3)_3$), 34.3 (4-*C*$(CH_3)_3$/12-*C*$(CH_3)_3$), 31.8 (4-C(*C*$H_3)_3$/12-C(*C*$H_3)_3$), 30.3 (2-C(*C*$H_3)_3$/14-C(*C*$H_3)_3$). ^{51}V NMR (105 MHz, $CDCl_3$, TMS): δ -409.5 (br s, FWHM 240 Hz). Anal. Calcd. (%) for $C_{34}H_{52}NO_5V$ (605.72 g/mol): C, 67.42; H, 8.65; N, 2.31. Found: C, 67.15; H, 8.57; N, 2.09.

Method B: 184 mg (0.34 mmol) of H_3L^3, 93 mg of $VOSO_4{\cdot}5H_2O$ (0.37 mmol) and 0.1 ml of triethylamine were dissolved in 10 ml of MeOH. The mixture was stirred in an open vessel for 18 hours. Complex **3** was isolated by filtration as a dark green crystalline solid in a 79 % yield based on the ligand (163 mg).

Method C: 70 µl of $VO(OPr)_3$ (73 mg, 0.30 mmol) was added to the stirred solution of H_3L^3 (0.31 mmol, 170 mg) in 5 ml of anhydrous dichloromethane. The dark solution was evaporated and the remaining solid was recrystallized from 5 ml of hot acetonitrile. 170 mg (93 %) of green plates were isolated by filtration.

Catalyst studies

Catalytic experiments were run in deuterated chloroform solutions while the reactions were monitored by ^{1}H NMR spectroscopy. Solutions of tBuOOH (0.3 ml, 0.3M) and *cis*-cyclooctene (0.3 ml, 0.2 M + 0.1 M of $C_2H_4Cl_2$ as an internal standard) were added in a 5 mm NMR tube. The catalyst solution (12 µl, 0.2 M,) was added and the NMR tube was subsequently placed in the NMR probe. The reaction rates were estimated upon the integrated intensities of substrate and product spectra, as the alkene multiplet at 5.6 ppm was turned to the epoxide multiplet at 2.9 ppm.

Cyclic voltammetry

The cyclic voltammetric experiments (CVs) were done in a three-electrode one-compartment cell connected to an Autolab (PGSTAT101) potentiostat. CVs were recorded at ambient temperature using a platinum working electrode with 1 mm Ø. The Pt electrode was polished with diamond paste (0.25 to 1 μm, Struers A/s) and rinsed with deionized water before use. A Ag/AgCl wire was used as the quasi-reference electrode, calibrated vs. ferrocene (Fe/Fe^{+}) ($E_{1/2}(Fe/Fe^{+})$ = 0.43 V) and all potentials mentioned are vs. this Ag/AgCl electrode. A coiled Pt wire (1 mm Ø) was used as counter electrode. Samples were dissolved in MeCN containing 0.1 M of (Bu_4NBF_4) or ($Bu_4N)ClO_4$ as the supporting electrolyte. The voltammograms were recorded between 0 to +1.8 V and/or 0 to -1.8 V during 3 consecutive cycles using 50-200 mV/s as scan rate.

X-ray crystallography.

Table 2. Summary of crystallographic data for **1-3** at 123 K.

Complex	**1**	**2**	**3**
Formula	$C_{39}H_{59}NO_7V$	$C_{35}H_{53}N_2O_4V$	$C_{34}H_{52}NO_5V$
M_r	704.81	616.73	605.70
Crystal system	orthorhombic	monoclinic	monoclinic
Space group (no.)	*Pna*2$_1$(33)	*P*2$_1$/*n* (14)	*P*2$_1$/*n* (14)
a/Å	18.2255(6)	12.5241(4)	10.8297(3)
b/Å	13.2449(9)	14.3021(4)	10.4967(4)
c/Å	16.4934(5)	19.6163(10)	29.3356(10)
α/°	90.00	90.00	90.00
β/°	90.00	100.670(4)	93.008(3)
δ/°	90.00	90.00	90.00
V/Å^3	3981.4(3)	3452.9(2)	3330.1(2)
Z	4	4	4
μ(Cu-K$_\alpha$)/mm^{-1}	1.176[a]	2.693	2.797
Obs. reflections	8915	16497	15921
R_{int}	0.0300	0.0244	0.0368
Parameters	504	393	404
R1[a]	0.0544 (0.0408)	0.0373(0.0343)	0.0882(0.0765)
wR2[a]	0.0871 (0.0810)	0.0881(0.0859)	0.2104(0.2262)
Goodness of fit	1.023	1.019	1.109
Peak, hole /*e Å*$^{-3}$	0.192/-0.271	0.224/-0.455	0.866/-0.466

[a] MoK$_\alpha$ radiation
[b] $R1 = \Sigma \mid |Fo| - |Fc| \mid \; / \; \Sigma \, |Fo|$
[c] values in parentheses for reflections with I > 2.0σ(I)
[d] $wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] \; / \; \Sigma [w(F_o^2)^2] \}^{1/2}$ and
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP)]$, where $P = (2F_c^2 + F_o^2)/3$

Single crystals of **1** were isolated from the ethanolic reaction mixture whereas complexes **2** and **3** were crystallized from acetonitrile. Complex **S4** crystallised from the methanolic reaction mixture. Crystallographic data for complexes **1** and **S4** were collected at 123K with a Nonius-Kappa diffractometer equipped with CCD area-detector using Mo-Kα radiation (λ = 0.71073 Å). SADABS absorption correction was applied to the data of **1** and **S4**.[27] For **2** and **3**, the data collection (123 K) was made with Agilent SuperNova dual wavelength diffractometer equipped with Atlas CCD area detector using Cu-Kα radiation (λ = 1.54184 Å) and CrysAlisPro program package.[28] The analytical numeric absorption correction using a multifaceted crystal was performed as implemented in CrysAlisPro program.[28] The structures were solved by direct methods using SIR97[29] and SHELXS-97[30] programs and full-matrix, least-squares refinements on F^2 were performed using the SHELXL-97[30], Olex2[31] or WinGX[32] program packages. All figures were drawn with Diamond 3.[33] CCDC 977973-977976 contain the supplementary crystallographic data for **1-3** and **S4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+ 44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

NMR spectroscopy

The ^1H, ^{13}C and ^{51}V NMR spectra were recorded with Bruker Avance 400 (^1H: 399.75 MHz, ^{13}C: 100.52 MHz, ^{51}V: 105.15 MHz) and Bruker Avance 500 (^1H: 500.13 MHz, ^{13}C: 125.76 MHz, ^{51}V: 131.55 MHz) NMR spectrometers in deuterated chloroform ($CDCl_3$) solutions at 25 °C (298 K). The spectrometers were equipped with a broad-band observe probe (Bruker BBO-5 mm-Zgrad). The proton and carbon chemical shifts were referenced to internal TMS (tetramethylsilane; δ_{TMS} = 0.00 ppm). The 0 ppm vanadium reference frequency was calculated from the TMS ^1H frequency by using the unified chemical shift scale by IUPAC ($\Xi(^{51}V, VOCl_3) = 26.302948$).[34] The 1D ^1H and ^{51}V NMR spectra were measured with a single-pulse–acquire sequence (flip angles 30° and 90°, and recycle delays 5.6 s and 0.3 s, respectively). The 1D ^{13}C NMR spectra (flip angle 45°, recycle delay 2.9 s) were measured with broadband ^1H decoupling (waltz16). The gradient-selected $^1H\{^1H\}$ COSY spectra were recorded in double-quantum filtered mode. $^1H\{^1H\}$ NOE spectra were acquired with the 1D DPFGSE-NOE or 2D NOESY sequence by using a mixing time of 0.3 s. The $^1H\{^{13}C\}$ HSQC (with multiplicity editing) and HMBC experiments were optimized for $^1J_{CH}$ = 145 Hz and J_{CH}(long-range) = 8–10 Hz. The chemical shift assignment corresponds to the crystallographer's atom numbering shown in Figs. 2 and 3; the suffixes α and β distinguish between diastereotopic hydrogens as discussed in the text. The *J* values are given in Hz.

Conclusions

$VO(acac)_2$ reacts with a glycine bisphenol H_3L^1 to form a monomeric complex [V(acac)(L^1)] **1**. Albeit the reaction was carried out under oxidative conditions (air or oxygen atmosphere) the oxidation state of the metal ion remains as V(IV). The CV of **1** shows a reversible one-electron process at $E_{1/2}$ = +1.18. However, under similar conditions, 2-propanolamine bisphenol H_3L^2 and aminoethoxyethanol bisphenol H_3L^3 react with $VO(acac)_2$, $VOSO_4$ or $VO(OPr)_3$ to form oxovanadium(V) complexes [$VO(L^2)$] **2** and [$VO(L^3)$] **3**,

respectively. In complex **1**, the central vanadium ion has a distorted octahedral coordination sphere formed by two oxygen donors from acetyl acetonato ligand as well as one nitrogen atom and three oxygen donors from the glycine bisphenolate. Mononuclear complex **2** has a slightly distorted pentagonal bipyramidal coordination sphere around the central atom as the ligand has coordinated to the V=O group through three oxygens and one nitrogen donor of the organic ligand. Complex **3** is formed of mononuclear molecules in which the organic ligand is coordinated to the V=O moiety as a pentadentate trianion to form a distorted octahedral coordination sphere. Complexes **2** and **3** show moderate activity in the epoxidation *cis*-cyclooctene by *tert*-butyl peroxide.

Acknowledgements

Ilkka Palmunen is greatly acknowledged for performing the CV experiments. This work was supported by COST Action CM1003 "Biological oxidation reactions - mechanisms and design of new catalysts"

Notes and references

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† See supplementary material.

± Synthesis and structure of compound $[V_2O_2(L^{2'})_2]$ are described in reference 13 but CV and catalytic activity were measured during this study.

Electronic Supplementary Information (ESI) available: synthesis and characterisation of **S4**.

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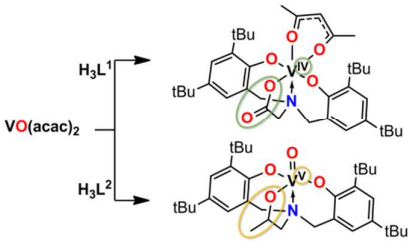
Table of contents entry:



Amine bisphenols react with $VO(acac)_2$ to yield V(IV) or V(V) complexes depending on the additional hydroxyl donor in the ligand side-arm.