

Oxovanadium(V) amine bisphenolates as epoxidation catalysts

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Abstract

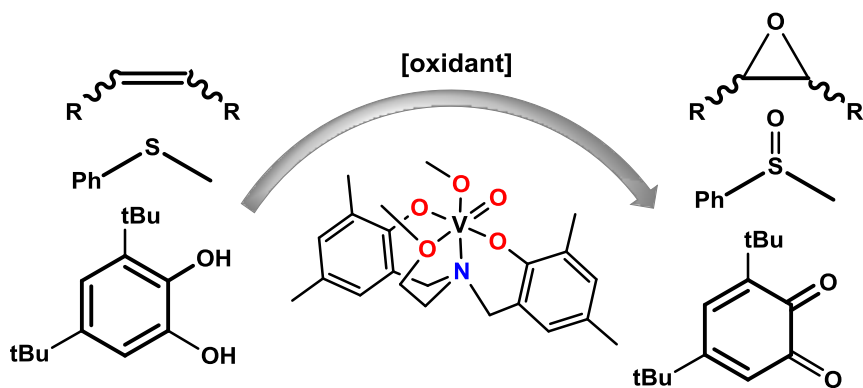
Airstable oxovanadium(V) complexes with tetradentate amine bisphenol ligands were made by the reaction of $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ and ligand precursors in MeOH solutions. Isolated compounds were studied as catechol oxidase models as well as catalysts for epoxidation and sulfoxidation reactions. All compounds can catalyse such oxidation reactions without notable structure-activity correlations. The ^{51}V NMR studies indicate that the complexes turn to the number of different species during the catalytic experiments.

Keywords

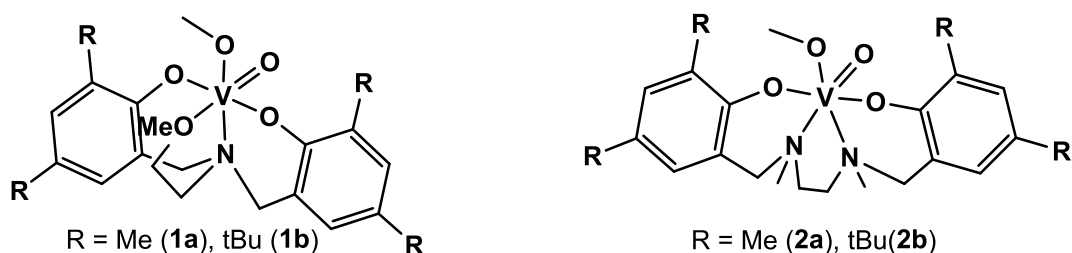
Vanadium; catalysis; biomimetic; oxo transfer

Graphical abstract

Oxovanadium(V) complexes with tetradentate amine bisphenols catalyse epoxidation and sulfoxidation reactions. They also act as models for catechol oxidase.



Oxovanadium(V) complexes can be used as catalysts for a number of organic oxidation reactions.[1] Moreover, they are generally considered as model compounds for vanadium-based oxidative enzymes.[2] Tetradentate amine bisphenols are a versatile group of organic ligands as they can form stable complexes with practically all transition metals.[3] Accordingly, a number of oxovanadium(V) amino bisphenolates are prepared[4-6] and used as catalysts for organic oxidation reactions, *e.g.* the oxidation of catechol to *o*-benzoquinone,[7] oxidation of dopamine,[8] oxidation of alcohols,[9] oxidation of aromatic hydrocarbons[10], sulfoxidations[11] and coupling CO₂ with epoxides[12]. In some cases, the vanadium compounds are reported to be hydrolytically unstable and possibly decompose under turn-over conditions.[4,7,10] In the present study, we used four oxovanadium complexes with tetrapodal and linear tetradentate amine bisphenols (Scheme 1) as catalysts for epoxidation, sulfoxidation and catechol oxidation reactions. The stabilities of the catalyst precursors were studied by ⁵¹V NMR analyses. Complexes **1a** and **1b** were made of VOSO₄·xH₂O and free ligands, H₂L^{Me} and H₂L^{tBu}, respectively, in MeOH solutions applying the procedure published by Debnath et al. for the preparation of **2a** and **2b**.^[10]¹



Scheme 1. The catalyst complexes used in this study.

The ¹H NMR and ¹³C NMR of **1a** and **1b** indicate the presence of several components. At room temperature, ⁵¹V NMR show two components for **1a** in 3:2 ratio whereas for **1b** the ⁵¹V NMR spectrum indicates a C_s symmetric major component (by a *ca.* 70% population) as well as three minor components. Such solution behaviour of oxovanadium(V) complexes with tetrapodal amine bisphenolate ligands is well known.[5,11,13] Electronic absorption spectra of complexes **1a** and **1b** in CHCl₃ show multiple bands in the UV and visible regions. The highest energy bands at 285 nm

¹ In a typical reaction procedure 1.0 mmol of both the free ligands (H₂L^{Me} or H₂L^{tBu}) and VOSO₄ · 5 H₂O were added in 10 ml of AR-grade MeOH at room temperature, whereupon dark solutions formed. To these solutions was then added 2.1 equivalents of triethyl amine and the solutions were stirred and heated at reflux for three hours. Subsequently the reaction mixtures were allowed to slowly cool to room temperature before they were left to stand at –20°C. In a few days dark to black crystals had formed and they were separated and washed with ice-cold methanol to obtain complexes in 50 -70 % yields. See Supplementary material for the spectroscopic data for **1a** and **1b**.

result from ligand $\pi \rightarrow \pi^*$ transitions, whereas other intense bands at ca. 350 nm are due to LMCT transitions. The methoxide groups in **1a** are lost during the electrospray ionization mass spectrometric analyses, whereas the MS data show monomeric $[\text{VO}(\text{L}^{\text{Me}})]^+$ ($m/z = 408$) as well as oxygen-bridged dimeric species $[\text{VO}(\text{L}^{\text{Me}})\text{-O-VO}(\text{L}^{\text{Me}})+\text{H}]^+$ ($m/z = 833$) $[\text{VO}(\text{L}^{\text{Me}})\text{-O-VO}(\text{L}^{\text{Me}})+\text{Na}]^+$ ($m/z = 855$). The MS for **1b** shows a signal for monomeric complex $[\text{VO}(\text{L}^{\text{tBu}})(\text{OMe})+\text{Na}]^+$ ($m/z = 630$).

The molecular structure of **1b** was studied by X-ray crystallography (Figure 1), which verified that there are two similar but crystallographically different molecules in an asymmetric unit.² The vanadium(V) ion has a distorted octahedral coordination sphere in which the equatorial positions are occupied by the two phenolate oxygen atoms, the oxygen atom from the side-arm ether and the terminal oxido ligand. The nitrogen donor of the ligand backbone and methoxide oxygen donor are in the apical positions. The bonding parameters are typical for oxovanadium(V) amine bisphenolates.[4,5,7-11,14]

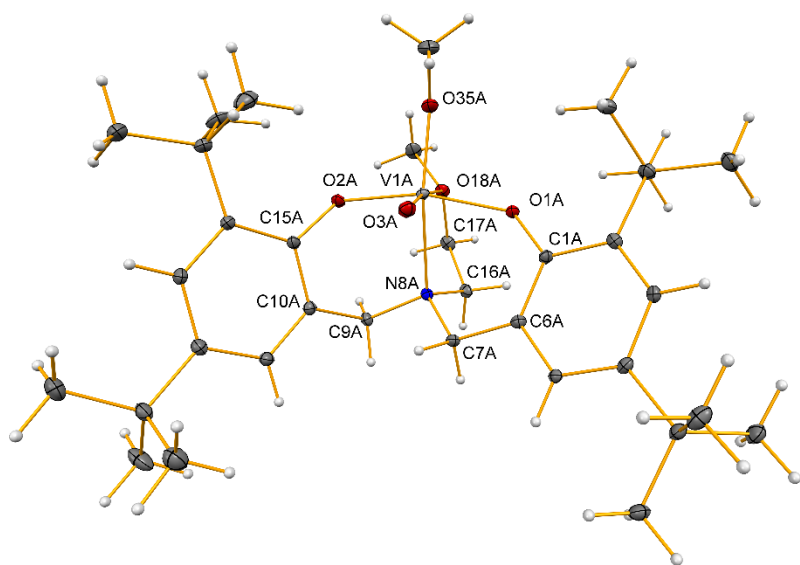


Figure 1. Molecular structure of **1b**. Only one of the two molecules in the asymmetric unit is shown. Selected distances (Å) and angles (°): V1A-O1A: 1.8864(14); V1A-O2A: 1.8968(15); V1A-O3A: 1.5932(16); V1A-O18A: 2.2761(16); V1A-O35A: 1.7973(15); V1A-N8A: 2.2624(18); O1A-V1A-O2A: 157.25(7); O3A-V1A-O18A: 171.33(7); O35A-V1A-N8A: 159.23(7).

Catechol oxidase activities of the complexes were studied using 3,5-di-*tert*-butylcatechol (**S4**) as a model compound. The reactions were run under atmospheric oxygen in CHCl_3 solutions having

² CCDC 1569236 contains the supplementary crystallographic data for **1b**.

substrate concentrations of 0.5 - 5.0 mmol and 1 -10 mol-% catalyst loadings. The oxidation product of 3,5-di-*tert*-butylcatechol, 3,5-di-*tert*-butyl-*o*-benzoquinone, has a distinctive absorbance at 383 nm, therefore the reaction was easily followed by UV-spectroscopy detecting the increase in the absorbance using a 5 min interval. The original blue colour of the reaction mixtures turned rapidly green, apparently upon the coordination of the catecholate ion to the vanadyl centre.[7] The strong, broad absorption band at *ca.* 680 nm, is characteristic for a charge transfer in vanadium catecholate complexes. In our experiments, this absorption firstly increased in intensity and then started to decrease slowly, while the band at 383 nm continued to increase with time. We may assume that the formed vanadium catecholate complex undergoes an intramolecular redox process and then releases the formed *o*-benzoquinone ligand. Re-oxidation of the reduced vanadium species by O₂ restarts the catalytic cycle. The reaction rates and the substrate concentrations were fitted to the Michaelis–Menten equation, $V_o = V_{max} [S] / ([S] + K_m)$, using Origin 2015 software to determine K_m . The Michaelis–Menten like kinetic parameters *i.e.* the maximum rate V_{max} , the Michaelis constant K_M and the catalytic rate k_{cat} were rather similar for all studied compounds (Table 1).

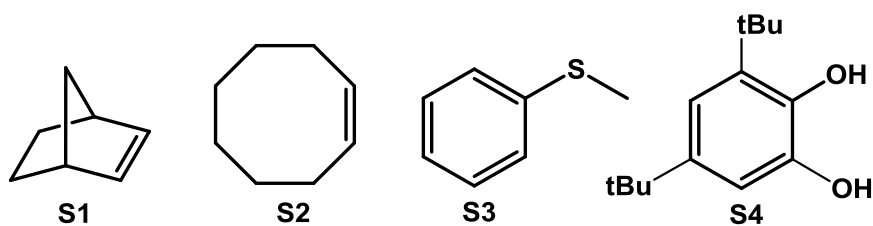
Table 1. Catechol oxidase activity

	1a	1b	2a	2b
V_{max} ($\times 10^{-6}$ M min ⁻¹)	9.65	10.1	8.43	10.4
K_M (mM)	0.45	1.15	1.17	1.07
k_{cat} (h ⁻¹)	11.6	12.2	10.1	12.5

In the preliminary epoxidation experiments, all complexes were tested as catalysts for the epoxidation of norbornene (**S1**) with *tert*-BuOOH. The reactions were run in CDCl₃ solutions at 50 °C using a [substrate]: [oxidant]: [catalyst] ratio of 100:200:1 (Table 1).³ Complexes **1a** and **1b** with tetrapodal ligands showed moderate activity whereas complexes **2a** and **2b** with more rigid linear ligands showed only a slight activity. The highest conversion was obtained by **1a**, so it was selected as a model catalyst for further studies. The epoxidations of **S1** and *cis*-cyclooctene (**S2**) were run in CDCl₃ and MeCN-*d*₃ solutions at 50 °C whereas the sulfoxidation of thioanisole (**S3**) was studied at 25 °C. The reaction solvent seems to have some effect on the reaction course since the epoxidation reactions of **S1** and **S2** were found to be remarkable faster in a CDCl₃ solution compared with the

³ In a typical experiment, *ca.* 2 mg of a catalyst precursor and 35 mg of norbornene were dissolved in 0.6 ml of CDCl₃ and 90 µl of *tert*-BuOOH was added (80-% in water). The reaction was followed by ¹H NMR at 50 °C for 2 hours. In the reaction, the alkene multiplet at 6.0 ppm was turned to the epoxide multiplet at 3.1 ppm.

reaction rate in MeCN solution. The sulfoxidation reaction had an opposite solvent effect as the reaction was faster in a MeCN solution.



Scheme 2. The substrates used in the oxidation studies.

Table 1. Epoxidation of norbornene with *tert*-BuOOH using oxovanadium catalysts.

	1a	1b	2a	2b
TOF/h ^{-1a}	66	42	6	18
Conv-% ^b	62	49	29	23
Yield-% ^b	37	30	26	20

^a TOF calculated after 10 min reaction. ^b by NMR on the reaction mixture after 2 hours

Table 2. Epoxidations and sulfoxidation with *tert*-BuOOH using catalyst **1a**.

	S1	S2	S3
CHCl₃			
TOF/h ^{-1a}	66	72	48
Conv-% ^b	62	77	37
Yield-% ^b	37	67	37
MeCN			
TOF/ h ^{-1a}	18	6	276
Conv-% ^b	13	26	93
Yield-% ^b	12	25	79

[substrate] : [oxidant] : [catalyst] = 100:200:1 ^a TOF calculated after 10 min reaction. ^b by NMR on the reaction mixture after 2 hours.

The colour of the reaction solution turned from yellow to green during the oxidation reactions, which indicates some decomposition of the complexes. The catalyst solutions in CDCl_3 were analysed by ^{51}V NMR at room temperature prior to the injection of the oxidant. The spectra of complexes **1a** and **1b** with tripodal ligands indicate the presence of one major component as well as one minor component whereas the complexes **2a** and **2b** with linear tetradentate ligands show signals for single components only. However, after the oxidation took place all solutions turned into mixtures of several components, probably due to the formation of dimeric species or some simple inorganic vanadates.[8]

In conclusion, we have used oxovanadium(V) complexes with tetradentate aminophenol ligands as catalysts for epoxidation and sulfoxidation reactions and studied their activity in a catechol oxidase model reaction. All compounds can catalyse such oxidation reactions and there are no remarkable structure-activity correlations. The ^{51}V NMR studies indicate that the complexes decompose to a number of different species during the catalytic experiments.

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