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Oxidovanadium(V) amine bisphenolates as epoxidation, sulfoxidation and catechol oxidation catalysts

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Abstract

Air-stable oxidovanadium(V) complexes with tetradeutate amine bisphenolate ligands were made by the reaction of VOSO₄·xH₂O 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

Oxidovanadium(V) complexes with tetradeutate amine bisphenols catalyse epoxidation and sulfoxidation reactions. They also act as models for catechol oxidase.
Oxidovanadium(V) complexes can be used as catalysts for a number of organic oxidation reactions.[1-3] Moreover, they are generally considered as model compounds for vanadium-based oxidative enzymes.[4] Tetradecontate amine bisphenols are a versatile group of organic ligands as they can form stable complexes with practically all transition metals.[5] Accordingly, a number of oxidovanadium(V) amino bisphenolates are prepared[6-8] and used as catalysts for organic oxidation reactions, e.g. the oxidation of catechol to o-benzoquinone,[9] oxidation of dopamine,[10] oxidation of alcohols,[11] oxidation of aromatic hydrocarbons[12], sulfoxidations[13] and coupling CO₂ with epoxides[14]. In some cases, the vanadium compounds are reported to be hydrolytically unstable and possibly decompose under turn-over conditions.[6,9,12] In the present study, we used four oxidovanadium complexes with tetradecontal and linear tetradecontate 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, H₂LMe and H₂L⁴Bu, respectively, in MeOH solutions applying the procedure published by Debnath et al. for the preparation of 2a and 2b.[12]

![Scheme 1](image)

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 C₂ symmetric major component (by a ca. 70% population) as well as three minor components. Such solution behaviour of oxidovanadium(V) complexes with tetradecontal amine bisphenolate ligands is well known.[7,13,15] Electronic absorption spectra of complexes 1a

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¹ In a typical reaction procedure 1.0 mmol of both the free ligands (H₂LMe or H₂L⁴Bu) 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.
and 1b in CHCl₃ show multiple bands in the UV and visible regions. The highest energy bands at 285 nm result from ligand \( \pi \rightarrow \pi^* \) transitions, whereas other intense bands at ca. 350 nm are due to LMCT transitions. The methoxide group in 1a is lost during the electrospray ionization mass spectrometric analyses, whereas the MS data show monomeric \([\text{VO(}L^{\text{Me}}]\))⁺ \((m/z = 408)\) as well as oxido-bridged dimeric species \([\text{VO(}L^{\text{Me}}\text{-O-VO(}L^{\text{Me}}\text{)+H}]^+ \((m/z = 833)\) \([\text{VO(}L^{\text{Me}}\text{-O-VO(}L^{\text{Me}}\text{)+Na}]^+ \((m/z = 855)\). The MS for 1b shows a signal for monomeric complex \([\text{VO(}L^{\text{Bu}}\text{(OMe)+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 oxidovanadium(V) amine bisphenolates.[6,7,9-13,16]

![Molecular structure of 1b](image)

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).

² CCDC 1569236 contains the supplementary crystallographic data for 1b.
Catechol oxidase activities of the complexes were studied using 3,5-di-tert-butylcatechol (S1) as a model compound. The reactions were run under atmospheric oxygen in CHCl₃ solutions having 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 oxidovanadium(V) centre.[9] 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, \( V = \frac{V_{\text{max}}[S]}{[S]+K_M} \), using Origin 2015 software to determine \( K_M \). The Michaelis–Menten like kinetic parameters i.e. the maximum rate \( V_{\text{max}} \), the Michaelis constant \( K_M \) and the catalytic rate \( k_{\text{cat}} \) were rather similar for all studied compounds (Table 1). The reaction of 1b with catechol was followed by \(^{51}\)V NMR, which clearly indicated the formation of a new complex. The \(^{51}\)V NMR spectrum of 1b showed a chemical shift for the main component at -499 ppm, whereas the addition of two equivalents of S1 lead to the appearance of a new species with the chemical shift of -453 (Figure S3). In general, the coordination of catechols in a V(V) center can be verified by the low-field shifts in the \(^{51}\)V NMR spectra.[17]

|          | 1a   | 1b   | 2a   | 2b   |
|----------|------|------|------|------|
| \( V_{\text{max}} \) (x10⁻⁶ M min⁻¹) | 9.65 | 10.1 | 8.43 | 10.4 |
| \( K_M \) (mM)       | 0.45 | 1.15 | 1.17 | 1.07 |
| \( k_{\text{cat}} \) (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 (S2) 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). 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 norbornene (S2) and cis-cyclooctene (S3) were run in CDCl$_3$ and MeCN-d$_3$ solutions at 50 °C whereas the sulfoxidation of thioanisole (S4) was studied at 25 °C. The reaction solvent seems to have some effect on the reaction course since the epoxidation reactions of S2 and S3 were found to be remarkable faster in a CDCl$_3$ solution compared with the 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 oxidovanadium 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.

|       | S2 | S3 | S4 |
|-------|----|----|----|
| CHCl$_3$ |    |    |    |
| TOF/h$^{-1a}$ | 66 | 72 | 48 |

$^3$ In a typical experiment, ca. 2 mg of a catalyst precursor and 35 mg of norbornene were dissolved in 0.6 ml of CDCl$_3$ and 90 µl of tert-BuOOH was added (80-% in water). The reaction was followed by $^1$H 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.
|            | Conv-%<sup>b</sup> | Yield-%<sup>b</sup> | MeCN  |
|------------|-------------------|-------------------|-------|
|            | 62                | 77                | 37    |
|            | 37                | 67                | 37    |
| TOF/ h<sup>1a</sup> | 18                | 6                 | 276   |
|            | 13                | 26                | 93    |
| Yield-%<sup>b</sup> | 12                | 25                | 79    |

[substrate]:[oxidant]:[catalyst] = 100:200:1  
<sup>a</sup> TOF calculated after 10 min reaction. <sup>b</sup> 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 CDCl₃ were analysed by <sup>51</sup>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.[10]

In conclusion, we have used oxido vanadium(V) complexes with tetradentate aminephenol 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 <sup>51</sup>V NMR studies indicate that the complexes decompose to a number of different species during the catalytic experiments.

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Graphical abstract

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

- Air-stable oxidovanadium(V) complexes with tetradentate amine bisphenolate ligands were.
- All compounds can act as catechol oxidase models as well as catalysts for epoxidation and sulfoxidation.
- By $^{51}$V NMR, the complexes turn to the number of different species during the catalytic experiments.