



Pyridoxal based ONS and ONO vanadium(V) complexes: Structural analysis and catalytic application in organic solvent free epoxidation



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ABSTRACT

A series of dinuclear and mononuclear oxovanadium(V) complexes containing tridentate Schiff base ligands derived from pyridoxal and appropriate thiosemicarbazide or hydrazide are reported. The compounds were characterised by elemental analysis, thermogravimetric analysis, IR and NMR spectroscopy. The molecular structure of the dioxido-vanadium(V) complex $[\text{VO}_2(\text{HL}^5)] \cdot \text{MeOH} \cdot \text{H}_2\text{O}$ ($\text{H}_2\text{L}^5 =$ pyridoxal benzhydrazido ligand), determined by X-ray crystallography, reveals an unexpected distorted trigonal bipyramidal arrangement of the VO_2 moiety. A DFT study of this molecule and of the related $[\text{VO}_2(\text{H}_2\text{L}^5)]$ complex of V^{IV} reveals a moderate effect of the oxidation state change on the bond distances and angles, pointing to solvation as the cause of the structural distortion. All complexes were tested as (pre) catalysts for olefin epoxidation by aqueous *tert*-butylhydroperoxide (TBHP) under solvent-free conditions. Low vanadium loadings (0.05% vs. olefin) resulted in good cyclooctene conversions and TOFs. The lifetime of one catalyst was explored through repeated runs with recovery/recycling. DFT calculations have also addressed the olefin epoxidation mechanism, which reveals the possible direct O atom transfer from the activated *tert*-butoxido ($t\text{BuOO}^-$) ligand, without the need to generate a peroxido (O_2^{2-}) ligand.

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1. Introduction

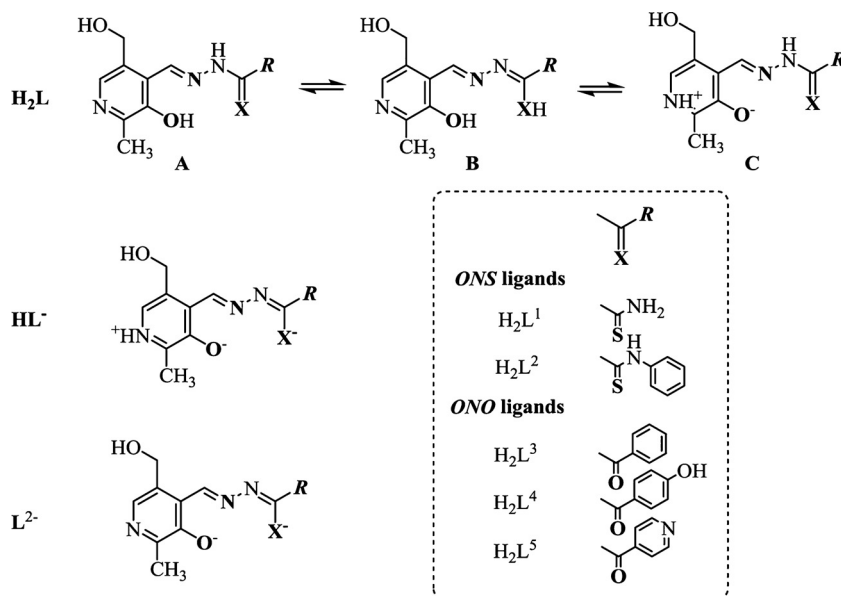
Vanadium has growing impact in coordination chemistry because of its biological and catalytic properties [1]. It can exist in a wide range of oxidation states from $-III$ to $+V$ [2]. The rich chemistry of oxidovanadium(V) is due to its ability to adopt three different structural motifs: (i) $[\text{VO}]^{3+}$, (ii) $[\text{VO}_2]^+$ and (iii) $[\text{V}_2\text{O}_3]^{4+}$ [3]. The combination of the pyridoxal moiety with thiosemicarbazides and hydrazides provides interesting chemical and biological activity for the resulting condensation products. It is known that the neutral form of such ligands, H_2L , exists in three tautomeric forms A–C (Scheme 1), of which the third one is zwitterionic. The singly and doubly deprotonated forms HL^- and L^{2-} have also been described and it has been demonstrated that their tridentate coordination involves the limiting forms shown in Scheme 1 [4]. Oxido vana-

dium metal complexes with Schiff base chelating ligands have been reported [5] in which O, N donor ligands have the tendency to stabilize vanadium in its highest oxidation state.

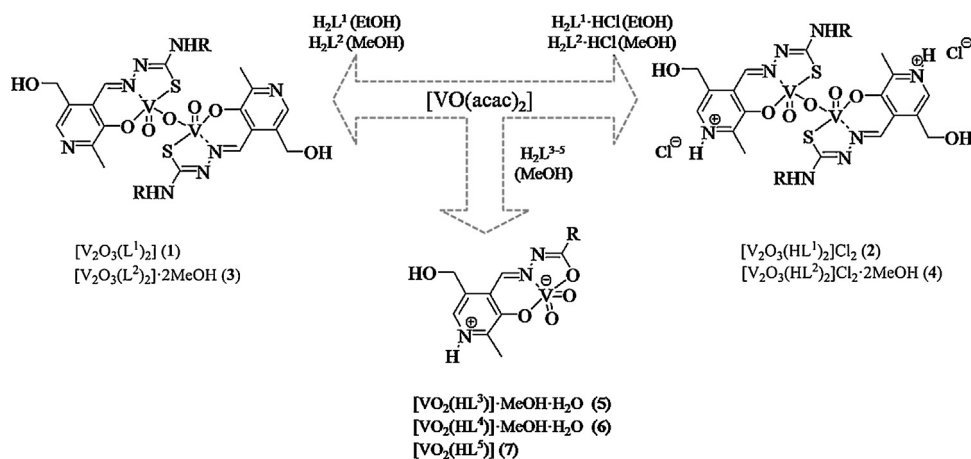
Coordination complexes of oxidovanadium(V) $[\text{VO}]^{3+}$ and $[\text{VO}_2]^+$ are well known as (pre) catalysts for oxidation reactions of different substrates [6] as well as in sulfoxidation processes [7], but only few studies concern olefin epoxidation [8]. Epoxides are important intermediates for the synthesis of several commercial products [9]. Traditional catalytic processes use organic solvents, which cause safety and pollution problems due to flammability, toxicity and volatility [10]. Avoiding solvents is the crucial point for “greening” the epoxidation processes. Following the principle “the best solvent is no solvent” [11], an organic solvent-free process is emerging as the most appropriate choice, since it is environmentally friendlier, less hazardous and characterized by lower running costs [10–12]. Taking into account economic and environmental viewpoints, great efforts are invested in catalyst recovery and recycling [8,13]. Although the catalytic efficiency is usually significantly decreased in repeated runs, the opposite trend (activity increase in subsequent runs) may also be observed [14].

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Scheme 1. ONS and ONO donors ligands used for the preparation of vanadium^V complexes. The ligand tautomerism is also illustrated in the scheme.



Scheme 2. Proposed compositions of V^V complexes.

We present herein the preparation and spectroscopic characterisation of mononuclear and dinuclear vanadium (V) complexes derived from the ligands H₂L¹–H₂L⁵ (Scheme 1), of general formula [V₂O₃(L¹)₂], [V₂O₃(HL¹)₂]Cl₂, [V₂O₃(L²)₂]·2MeOH, [V₂O₃(HL²)₂]Cl₂·2MeOH, [VO₂(HL^{3,4})]·MeOH·H₂O, and [VO₂(HL⁵)] (Scheme 2). All isolated species were used as (pre) catalysts for the organic solvent-free epoxidation of *cis*-cyclooctene using the same procedure of our previously published studies with the vanadium complex [V₂O₃(SAP)₂] (SAP = salicylideneaminophenolato) [8][8c], with the Keggin polyoxometalate [PMo₁₂O₄₀]³⁻ [15], with the molybdenum complex [MoO₂(SAP)₂] [16], and in particular with tridentate pyridoxal derivatives of dioxidomolybdenum(VI) [17]. In these epoxidations, the oxidant is *tert*-butylhydroperoxide (TBHP) administered as an aqueous solution, water not acting as a reaction solvent. Moreover, the lifetime of [VO₂(HL⁴)]·MeOH·H₂O catalyst was explored through repeated runs with recovery/recycling. The olefin epoxidation mechanism has also been addressed by DFT calculations.

2. Experimental

2.1. Materials and methods

Pyridoxal hydrochloride, thiosemicarbazides, hydrazides, isoniazide, [VO(acac)₂], aqueous TBHP (70%), cyclooctene and acetophenone (Aldrich) were commercially available and used as received. Solvents (MeOH, EtOH, Et₂O) were reagent grade. All ligands were prepared according to literature procedures [18,19]. Infrared spectra were recorded on KBr pellets at room temperature with a Mattson Genesis II FTIR spectrometer. Thermogravimetric analyses were performed with a thermal analyzer SDT-Q600. The samples were placed into platinum crucibles and heated at 10 K min⁻¹ in reconstituted air flow from 25 °C to 600 °C. ¹H NMR spectra were recorded at 200.1 MHz on a Bruker Avance DPX-200 spectrometer. ⁵¹V NMR spectra were recorded at 131.6 MHz on a Bruker Avance 500 spectrometer. Elemental analyses (C, H, N) were performed by

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