

# Oxo-bridged bis oxo-vanadium(V) complexes with tridentate Schiff base ligands (VOL)<sub>2</sub>O (L = SAE, SAMP, SAP): Synthesis, structure and epoxidation catalysis under solvent-free conditions

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## ABSTRACT

The dinuclear V(V) complexes (VOL)<sub>2</sub>O (L = SAE (**1**), SAMP (**2**), SAP (**3**)) have been synthesized from VO(acac)<sub>2</sub> and the corresponding tridentate ligands LH<sub>2</sub> in methanol under reflux conditions and subsequent air oxidation in organic solvent. They have been characterized by IR and NMR spectroscopy, by thermogravimetric analysis, and by single crystal X-ray diffraction for **1** and **2**. DFT calculations were carried out for a better understanding of the vibrational pattern, principally the V–O related vibrations. Complex [VO(SAP)]<sub>2</sub>O (**3**) catalyzes the epoxidation of cyclooctene by TBHP in water in the absence of any added solvent with good selectivity.

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## 1. Introduction

High-oxidation state metal oxido complexes are among the most interesting oxidation catalysts [1,2]. Among them, vanadium complexes are used in processes of industrial interest [3,4] and are present in several biological systems [5], for instance in bromoperoxidase [6,7]. The advantage of vanadium species is their ability to activate smooth oxidants. Indeed, a variety of (ep)oxidation reactions with smooth oxidants, including dioxygen, have been reported with use of “V(O)L(OR)” complexes [8]. We have recently become interested in oxidative processes catalyzed by oxomolybdenum complexes [9–12]. In particular, we have reported that the dioxomolybdc complexes [MoO<sub>2</sub>L]<sub>2</sub> and MoO<sub>2</sub>L(MeOH) (L = tridentate Schiff base ligand) catalyze the epoxidation of cyclooctene by aqueous TBHP with better selectivities than the reference compound MoO<sub>2</sub>(acac)<sub>2</sub> under the same experimental conditions [12]. However, we found that some of these systems

are limited by hydrolytic stability. We have therefore set out to examine the behavior of the related oxovanadium(V) systems.

Mimoun has already reported on the excellent catalytic activity of mononuclear oxovanadium(V) complexes containing tridentate ligands, outlining the role played by peroxy-substituted intermediates [13]. Dinuclear complexes with a [V<sub>2</sub>O<sub>3</sub>]<sup>2+</sup> core and tridentate ONO ligands have apparently been scarcely explored in catalysis. Some articles relate highly enantioselective oxidative couplings of 2-naphthols [14–17], others epoxidation or sulfoxidation catalysis [18,19], but the majority of experiments have been performed using organic chlorinated solvents. We have then decided to use these species under solvent-free conditions.

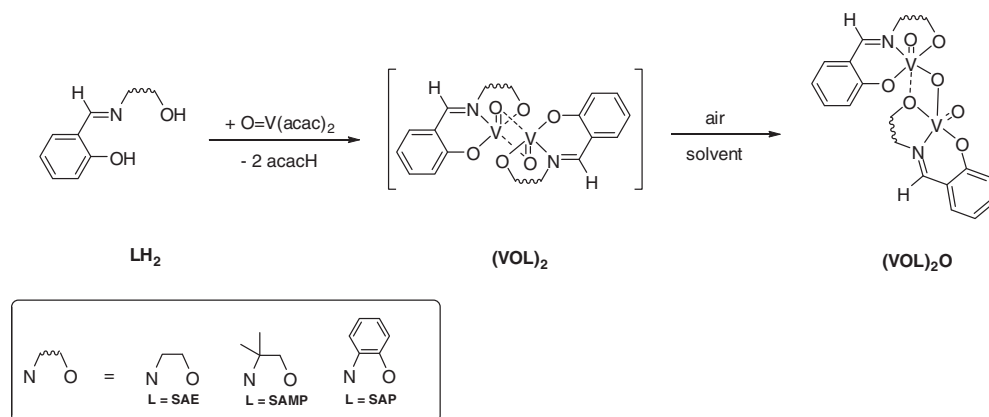
## 2. Results and discussion

### 2.1. Synthesis and characterization of (VOL)<sub>2</sub>O complexes

The LH<sub>2</sub> ligands salicylideneaminoethanol (SAEH<sub>2</sub>), salicylideneaminomethylpropanol (SAMPH<sub>2</sub>) and salicylideneaminophenol, (SAPH<sub>2</sub>) have been obtained as described recently using salicylaldehyde and the corresponding aminoalcohols in water [10]. The syntheses of the dinuclear vanadium complexes occur in a “one pot” procedure, through two consecutive reactions steps (see Scheme 1).

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**Scheme 1.** Synthetic procedure for the synthesis of (VOL)<sub>2</sub>O complexes.

In the first reaction step, V(O)(acac)<sub>2</sub> and one equivalent of the tridentate LH<sub>2</sub> ligand lead to a [V<sup>IV</sup>(O)L]<sub>2</sub> intermediate complex as described elsewhere for a procedure carried out under anaerobic conditions [20,21]. Transformation into the corresponding dinuclear [LV(O)]<sub>2</sub>O complex occurred by simple air oxidation. The compounds gave dark solids, in sufficiently good crystalline state for **1** and **2** to perform an X-ray structural determination (see below).

The IR spectra of these species show absorption bands around 980 cm<sup>-1</sup>, attributable to V=O vibrations, one broad band around 760 cm<sup>-1</sup> for the V–O–V moiety, as well as the imino vibration around 1630 cm<sup>-1</sup> (see Table 1) [22–26].

The thermal behavior in the 20–650 °C range is similar to those observed with [MoO<sub>2</sub>L]<sub>2</sub> complexes [10]. Ligand loss and concurrent oxygen uptake occur to yield the final vanadium oxide V<sub>2</sub>O<sub>5</sub> (see Scheme 2 and Table 2). The thermograms of the three compounds are shown in the Supporting Information.

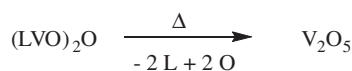
## 2.2. X-ray characterization of (VOL)<sub>2</sub>O complexes

Single crystals suitable for X-ray analysis could be obtained for compounds **1** and **2**. The structure of compound **2** (and also that of **3**) had already been reported in the literature [20], but was determined at a higher level of precision in our case, certainly due to the

low-temperature measurement. A view of the molecular geometry is shown in Fig. 1, with selected distances and angles listed in Table 3. The molecular unit is composed of two [(SAE)V=O] moieties asymmetrically linked together through the bridging O(3) atom [V–O bond lengths of 1.770(2) and 1.866(2) Å for V(2)–O(3) and V(1)–O(3), respectively]. The V=O bonds lengths are in the range 1.59–1.60 Å, conform to those found in the literature for related terminal V<sup>V</sup>=O bonds. Each vanadium atom is located at the center of a O<sub>3</sub>N base in a square pyramidal geometry, a terminal oxido ligand being situated at the top of the pyramid. The structures of **1**, **2**, and that previously reported for **3** [20], are very close to each other in terms of length of the covalent and coordinative bonds and coordination geometries (bond angles). An interesting feature that has been observed earlier in other related structures is the presence of a loose intramolecular O...V interaction between an oxygen atom of one [OV(SAE)] unit and the vanadium center of the second [OV(SAE)] unit (V(1)–O(23), 2.401(2) Å). This distance is at the short end of the range observed for this class of compounds, the shortest being 2.380(2) Å for compound **2** (our low-temperature structure; 2.404(2) Å in the literature report [20]). Others are 2.403(9) Å for compound **3** [27], 2.459 Å for [(ONpAE)-VO]<sub>2</sub>O [ONpAE = *N*-(2-oxyethyl)-2-oxidonaphthaliden-iminato] [22] and the longest one is 2.684 Å for [(SABH)VO]<sub>2</sub>O SABH = salicylaldehydebenzoylhydrazonato [28]. However, the dioxane adduct of compound **3** does not show this type of interaction [29]. The V(2)...O(11) distance is even longer (>2.8 Å), making the coordination geometry around V(2) more typical of a square pyramid, but the geometry is strongly distorted in both cases

**Table 1**  
Main IR vibration for compounds **1–3**.

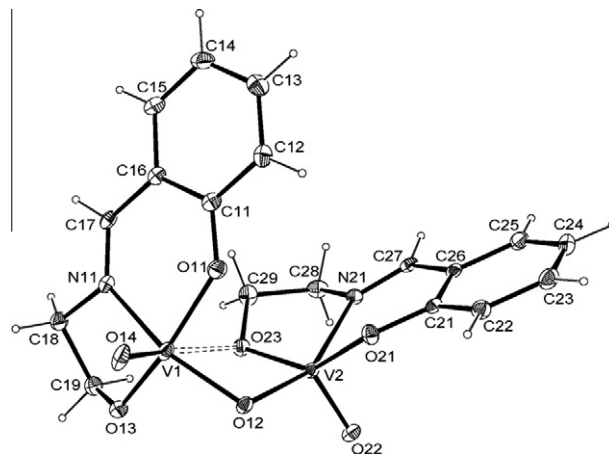
| Compound                               | V=O | V–O–V | CH=N |
|--|-----|-------|------|
| [(SAE)VO] <sub>2</sub> O ( <b>1</b> )  | 979 | 756   | 1630 |
| [(SAMP)VO] <sub>2</sub> O ( <b>2</b> ) | 977 | 757   | 1628 |
| [(SAP)VO] <sub>2</sub> O ( <b>3</b> )  | 990 | 753   | 1602 |



**Scheme 2.** General scheme of the thermal degradation behavior.

**Table 2**  
Experimental and theoretical mass losses observed in TG analysis for complexes **1–3** within the range 20–650 °C.

| Compound                               | Experimental loss | Theoretical |
|--|-------------------|-------------|
| [(SAE)VO] <sub>2</sub> O ( <b>1</b> )  | 61.4              | 61.8        |
| [(SAMP)VO] <sub>2</sub> O ( <b>2</b> ) | 66.2              | 65.8        |
| [(SAP)VO] <sub>2</sub> O ( <b>3</b> )  | 68.3              | 68.2        |



**Fig. 1.** Molecular structure of [VO(SAE)]<sub>2</sub>O, **1**.

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