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**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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*Dedicated to Arnie Rheingold, in recognition of a longlife service to the Inorganic Chemistry community.*

## **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.

## **Keywords**

Vanadium, vanadyl complexes, Schiff base ligands, epoxidation, homogeneous catalysis

## Introduction

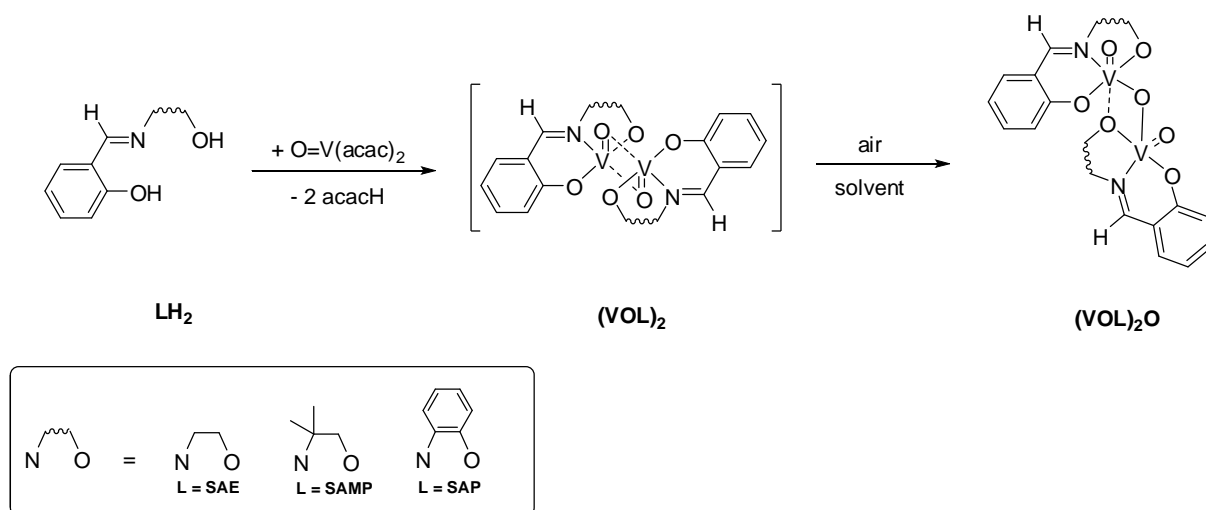
High-oxidation state metal oxido complexes are among the most interesting oxidation catalysts [1,2]. Among them, vanadium complexes are used in processes of industrial interest [3,4] and are present in several biological systems [5], for instance in bromoperoxidase [6,7]. The advantage of vanadium species 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 [9,10,11,12]. In particular, we have reported that the dioxomolybdic complexes  $[\text{MoO}_2\text{L}]_2$  and  $\text{MoO}_2\text{L}(\text{MeOH})$  (L= tridentate Schiff base ligand) catalyze the epoxidation of cyclooctene by aqueous TBHP with better selectivities than the reference compound  $\text{MoO}_2(\text{acac})_2$  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 behaviour 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  $[\text{V}_2\text{O}_3]^{2+}$  core and tridentate ONO ligands have apparently been scarcely explored in catalysis. Some articles relate highly enantioselective oxidative couplings of 2-naphthols [14,15,16,17], 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.

## Results and discussion

### *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).



**Scheme 1** – Synthetic procedure for the synthesis of  $(\text{VOL})_2\text{O}$  complexes.

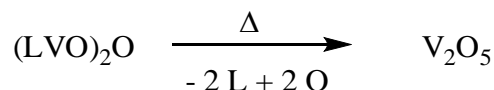
In the first reaction step,  $\text{V}(\text{O})(\text{acac})_2$  and one equivalent of the tridentate  $\text{LH}_2$  ligand lead to a  $[\text{V}^{\text{IV}}(\text{O})\text{L}]_2$  intermediate complex as described elsewhere for a procedure carried out under anaerobic conditions [20,21]. Transformation into the corresponding dinuclear  $[\text{LV}(\text{O})]_2\text{O}$  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  $980 \text{ cm}^{-1}$ , attributable to  $\text{V}=\text{O}$  vibrations, one broad band around  $760 \text{ cm}^{-1}$  for the  $\text{V}-\text{O}-\text{V}$  moiety, as well as the imino vibration around  $1630 \text{ cm}^{-1}$  (see Table 1) [22,23,24 25,26].

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

Compound	$\text{V}=\text{O}$	$\text{V}-\text{O}-\text{V}$	$\text{CH}=\text{N}$
$[(\text{SAE})\text{VO}]_2\text{O}$ ( <b>1</b> )	979	756	1630
$[(\text{SAMP})\text{VO}]_2\text{O}$ ( <b>2</b> )	977	757	1628
$[(\text{SAP})\text{VO}]_2\text{O}$ ( <b>3</b> )	990	753	1602

The thermal behaviour in the  $20\text{-}650^\circ\text{C}$  range is similar to those observed with  $[\text{MoO}_2\text{L}]_2$  complexes [10]. Ligand loss and concurrent oxygen uptake occur to yield the final vanadium oxide  $\text{V}_2\text{O}_5$  (see Scheme 2 and Table 2). The thermograms of the three compounds are shown in the Supporting Information.



**Scheme 2** – General scheme of the thermal degradation behaviour

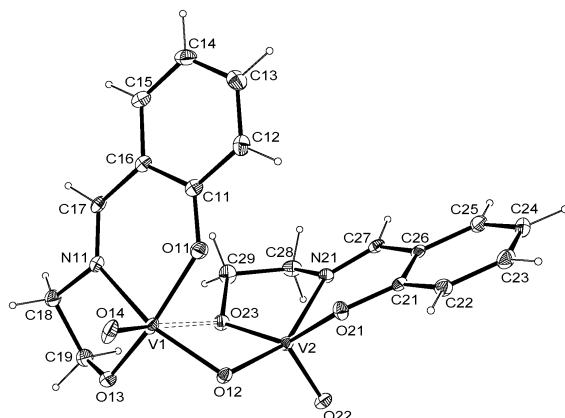
**Table 2.** Experimental and theoretical mass losses observed in TG analysis for complexes 1-3 within the range 20-650°C.

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

#### *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 Figure 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-oxethyl)-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 ( $> 2.8 \text{ \AA}$ ), making the coordination geometry around V(2) more typical of a square pyramid, but the geometry is strongly distorted in both cases [displacements from the mean plane of atoms O(12), O(21), O(23) and N(21): V(2), 0.469(1)  $\text{\AA}$ ; O(11), 2.322(2)  $\text{\AA}$ ; displacements from the mean plane of atoms O(11), O(12), O(13) and N(11): V(1), 0.365(1)  $\text{\AA}$ ; O(23), 2.015(2)  $\text{\AA}$ ].



**Figure 1** - Molecular structure of  $[\text{VO}(\text{SAE})]_2\text{O}$ , **1**

**Table 3.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **1**.

Bond	Distance	Bond	Distance
V(1)-O(14)	1.590(2)	V(2)-O(22)	1.597(2)
V(1)-O(13)	1.811(2)	V(2)-O(12)	1.770(2)
V(1)-O(12)	1.866(2)	V(2)-O(21)	1.840(2)
V(1)-O(11)	1.899(2)	V(2)-O(22)	1.893(2)
V(1)-N(11)	2.101(2)	V(2)-N(21)	2.112(2)
V(1)-O(23)	2.401(2)	V(1)-V(2)	2.9422(7)

Bonds	Angle	Bonds	Angle
O(14)-V(1)-O(13)	100.43(11)	O(22)-V(2)-O(12)	107.21(10)
O(14)-V(1)-O(12)	102.90(10)	O(22)-V(2)-O(21)	104.52(10)
O(13)-V(1)-O(12)	100.67(9)	O(12)-V(2)-O(21)	99.98(9)
O(14)-V(1)-O(11)	98.39(11)	O(22)-V(2)-O(23)	108.72(10)
O(13)-V(1)-O(11)	155.99(10)	O(12)-V(2)-O(23)	84.94(9)
O(12)-V(1)-O(11)	89.45(9)	O(21)-V(2)-O(23)	143.24(9)
O(14)-V(1)-N(11)	101.97(10)	O(22)-V(2)-N(21)	96.43(10)
O(13)-V(1)-N(11)	78.25(9)	O(12)-V(2)-N(21)	154.06(9)
O(12)-V(1)-N(11)	154.86(9)	O(21)-V(2)-N(21)	83.83(9)

O(11)-V(1)-N(11)	83.39(9)	O(23)-V(2)-N(21)	77.35(9)
O(14)-V(1)-O(23)	172.04(9)	O(22)-V(2)-V(1)	132.54(8)
O(13)-V(1)-O(22)	83.98(9)	O(12)-V(2)-V(1)	37.10(6)
O(12)-V(1)-O(23)	69.61(7)	O(21)-V(2)-V(1)	110.85(7)
O(11)-V(1)-O(23)	79.21(8)	O(23)-V(2)-V(1)	54.45(6)
N(11)-V(1)-O(22)	85.36(8)	N(21)-V(2)-V(1)	117.54(7)
O(1)-V(1)-V(2)	132.14(8)	O(11)-V(1)-V(2)	69.15(6)
O(12)-V(1)-V(2)	107.62(7)	N(11)-V(1)-V(2)	120.99(7)
O(3)-V(1)-V(2)	34.90(6)	O(23)-V(1)-V(2)	39.90(5)

### *DFT calculations for complex 1*

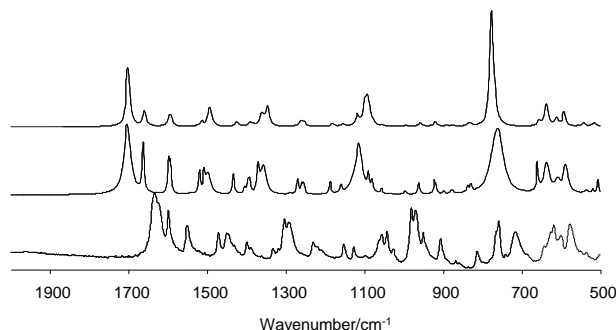
The structure of **1** was optimized by DFT using the experimentally determined structure as input and included the calculation of the normal mode frequencies on the geometry minimum. The agreement between experimental and calculated structure is excellent (see Table 4). Note that the computed V=O bonds are shorter relative to the experiment, whereas the V-N and the loose V...O bonds are longer. The use of a better basis set for the V atom yields a slightly better agreement for the covalent V-O bonds but a greater disagreement for the loose V...O bond. A comparison between computed and observed IR absorptions is shown in Figure 2. The three most relevant vibrations are those associated with the C=N, V=O and asymmetric V-O-V stretching motions. As expected, all computed frequencies are slightly shifted to higher frequencies relative to those observed experimentally (see Figure 2). The use of the better basis set for the V atom causes little changes to the calculated spectrum. Greater shifts are noted for the vibrations of doubly bonded moieties, whereas a closer agreement is found for the V-O-V vibration. The same trend has been observed for higher nuclearity tungsten and molybdenum polyoxometalates [30]. This phenomenon is probably related to the greater discrepancy between calculated and observed bond distances for the bonds of higher multiplicity.

**Table 4.** Comparison of experimental and theoretical bond lengths (Å) for compound **1**.

	Observed	Calculated (B3LYP/6-31g)	Calculated B3LYP/6-31g + SDD for V
V1-O11	1.899(2)	1.908	1.892
V1-O12	1.866(2)	1.810	1.801
V1-O13	1.811(2)	1.811	1.809
V1-O14	1.590(2)	1.564	1.570
V1-N11	2.101(2)	2.167	2.165
V1-O23	2.401(2)	2.662	2.847
V2-O12	1.770(2)	1.759	1.767



V2-O21	1.840(2)	1.840	1.851
V2-O22	1.597(2)	1.568	1.574
V2-O23	1.893(2)	1.880	1.861
V2-N21	2.112(2)	2.160	2.162



**Figure 2** - Comparison between experimental and calculated vibrational spectra of compound **1**: bottom: experimental; middle: computed with the 6-31g basis set for all atoms; top: computed with the SDD basis set for the V atom.

*Epoxidation of cyclooctene with TBHP in water using [VO(SAP)]<sub>2</sub>O complex.*

Complex **3** has been tested as cyclooctene epoxidation pre-catalyst using aqueous TBHP or aqueous H<sub>2</sub>O<sub>2</sub> (30% wt) as oxidant, without organic solvents, at 80°C (**3**/oxidant/cyclooctene = 1/200/100). Under these conditions, 94% of the cyclooctene was converted in 5.5 h with an epoxide selectivity of 83% when using TBHP as oxidant, whereas no reaction occurred with H<sub>2</sub>O<sub>2</sub>. This may be related to the inability of the H<sub>2</sub>O<sub>2</sub> reagent to mix with the organic substrate phase. A control experiment carried out under the same condition with the equivalent amount of H<sub>2</sub>SAP ligand instead of complex **3** gave no conversion, confirming the catalytic role of the vanadium atom. In another control reaction, the oxidation was carried out under the same conditions with the precursor complex VO(acac)<sub>2</sub>, without the SAP ligand. The conversion was still quite high (74% after 5.5 h), but the selectivity was completely different (only 13% of epoxide). This result confirmed the important role of the ligand SAP associated to vanadium. Finally, the same experiment was carried out in the presence of TEMPO in order to test whether radicals may be involved, yielding identical results. Compared to previous studies, carried out in solution of organic solvents ranging from aromatic to chlorinated ones, the activity is very good as well as the selectivity. Bellemin *et al.* indicated a conversion of just 50% of 1-hexene to the corresponding using TBHP and the [(2,6-Bis((-)-menthyl)pyridine)VO]<sub>2</sub>O dimeric complex [19] as pre-catalyst, the nature of which is similar to that of compound **3**. Other contributions

relate the epoxidation of cyclooctene with V(IV) complexes in a  $N_2O_2$  tetradentate coordination environment. A few of these systems displayed moderate cyclooctene epoxidation activity with TBHP in acetonitrile (88-96% selectivity but only 46-75 % conversion in 6 h and at reflux [31]. The solvent influence (dichloromethane, acetonitrile or chloroform) was investigated, the highest conversion (94%) being obtained with  $VO\{salnptn(3-OMe)_2\}$  and  $VO\{hnaphnptn\}$  in chloroform after 6 h [32]. Similar complexes have been used in combination with greener oxidants, i.e. dioxygen, again for cyclooctene epoxidation by THBP, leading to conversion (selectivity) in the range 25-91 % (30-60%) in acetonitrile or in DMF [33,34]. Another  $[VOL]_2$  complex containing vanadium(V) atoms and NNO Schiff base ligands has shown good epoxidation activity (94% after 4 h) but in chloroform [35]. Although all these systems are catalytically efficient, organic solvents were needed in the experimental procedures. We have shown here for the first time that a vanadyl complex is also catalytically efficient in the absence of organic solvent and by using an aqueous oxidant.

## Conclusion

The synthesis of bis(vanadyl) complexes of general formula  $[VO(L)]_2O$  with tridentate ligands (L= SAE, SAMP, SAMP) has been revisited here. The synthetic procedure makes use of easily accessible ligands. The crystallographic structure of  $[VO(SAE)]_2O$  has been determined here for the first time. Compound  $[VO(SAP)]_2O$  exhibited good catalytic activity in cyclooctene epoxidation using aqueous TBHP as oxidant and no organic solvent. These results are of interest for the development of greener oxidation protocols. Further mechanistic and experimental studies under solvent-free conditions are in progress and will be described in due course.

## Experimental section

Compound  $VO(acac)_2$  (Aldrich), MeOH and acetonitrile (Aldrich, technical grade) were used as received. The ligands  $SAEH_2$ ,  $SAMPH_2$  and  $SAPH_2$  were synthesized using previously described methods [10]. Infrared spectra were recorded on KBr pellets at room temperature with a Mattson Genesis II FTIR spectrometer. Thermogravimetric analyses were performed with a SETARAM TGA 92-16.18 thermal analyzer. The samples were placed into nickel/platinum alloy crucibles and heated at  $0.83\text{ K}\cdot\text{s}^{-1}$  in reconstituted air flow from  $20^\circ\text{C}$  to

650°C. An empty crucible was used as a reference.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR measurements were carried out with a Bruker Avance DPX 200 spectrometer.

*Synthesis of [VO(SAE)]<sub>2</sub>O (1).* This procedure follows previously reported protocols using ethanol instead of dichloromethane [20] or acetone [36]. In a 100 mL flask, SAEH<sub>2</sub> (497.6 mg, 3.01 mmol) was dissolved in methanol (10 mL) and a MeOH solution of VO(acac)<sub>2</sub> (795.6 mg, 3.00 mmol, in 15 mL) was then added dropwise. The mixture was then refluxed for four hours. Volatiles were eliminated by evaporation and the pasty brown residue was recrystallized from hot acetonitrile to afford dark crystals suitable for X-ray crystallography, which were finally washed with a minimum of diethyl ether (yield 330 mg, 48.6 %).  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>): 3.66 (m, 2H), 3.76 (m, 2H), 4.72 (s, 2H), 6.4-8.0 (m, 4H), 8.44 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO-*d*<sub>6</sub>): 59.0 (CH<sub>2</sub>N), 67.8 (CH<sub>2</sub>O), 118.4 (C<sub>Ar</sub>), 120.4 (C<sub>Ar</sub>), 120.5 (C<sub>Ar</sub>), 135.4 (C<sub>Ar</sub>), 136.3 (C<sub>Ar</sub>), 165.4 (C<sub>Ar</sub>-O) 168.7 (CH=N). UV-Vis (DMSO; nm (ε in mol<sup>-1</sup> L cm<sup>-1</sup>)): 262 nm (32000), 355 (8500). TGA: Exp (theor) mass loss of 61.4% (61.8) – 2 (L-O).

*Synthesis of [VO(SAMP)]<sub>2</sub>O, (2).* This procedure follows previously reported protocols using ethanol instead of dichloromethane [20] or acetone [36]. To a solution of SAMPH<sub>2</sub> (583 mg, 3.02 mmol) in methanol (10 mL) was added a methanol solution of VO(acac)<sub>2</sub> (796 mg, 3.00 mmol, in 15 ml). The mixture was then refluxed for four hours. The solution was then concentrated under vacuum to a dark pasty residue. Addition of acetonitrile led to a red-blood solution, which yielded a few crystals upon standing for three days. The partial evaporation of the solution led to a solid has been separated from the solution by filtration and washed with diethylether. The solid was recrystallized by dissolution in the minimum amount of acetonitrile and dark crystals suitable for X-ray crystallography were obtained after slow evaporation (yield 0.520 g, 68 %).  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>) 1.00-1.80 (m, 6H), 4.51 (s, 2H), 6.4-8.0 (m, 8H), 8.89 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO-*d*<sub>6</sub>): 26.6, 76.4, 89.1, 118.1, 120.6, 121.5, 135.2, 137.2, 163.4, 163.9. UV-Vis (DMSO; nm (ε in mol<sup>-1</sup> L cm<sup>-1</sup>)): 264 nm (39000), 356 (7900). TGA: Exp (theor) mass loss of 66.2% (65.8) – 2 (L-O).

*Synthesis of [VO(SAP)]<sub>2</sub>O (3).* This procedure follows previously reported protocols using ethanol instead of dichloromethane [20] or acetone [36]. To a solution of SAPH<sub>2</sub> (641.7 mg, 3.0mmol) in MeOH (10 mL) was added dropwise a MeOH solution of VO(acac)<sub>2</sub> (795.6 mg, 2.36 mmol, in 15 mL). The resulting mixture was refluxed for four hours and left cooling at room temperature, leading to crystals after one night. The rest of the pastry solution was slowly evaporated, washed with diethyl ether. (Yield 715 mg 84%).  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>): 6.4-8.0 (m, 8H), 9.40 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (DMSO-*d*<sub>6</sub>): 118.2, 120.7, 123.3, 130.6, 133.6,

137.7, 149.9, 161.9, 193.1. UV-Vis (DMF; nm ( $\epsilon$  in mol<sup>-1</sup> L cm<sup>-1</sup>)) 275 nm (46000), 382 (15500) 427 (20500). TGA: Exp (theor) mass loss 68.3% (68.2) – 2 (L-O).

*Catalytic tests.* In a round flask was added **3** (52.4 mg, 0.091 mmol), dodecane (internal reference, 42.0 mg, 0.246 mmol) and cyclooctene (1.07 g, 9.68 mmol). The magnetically stirred mixture was heated to 80°C and the reaction was started by the addition of aqueous TBHP (2.5 mL, 70% wt, 18.06 mmol). Stirring was stopped after 5.5 h, leading to the appearance of two phases. A 0.1 ml sample of the organic phase was withdrawn, mixed with Et<sub>2</sub>O (2 mL) and a small quantity of MnO<sub>2</sub> to destroy the residual peroxide. The mixture was then filtered through silica and analyzed by GC equipped with FID. GC parameters were quantified with authentic samples of products prior to the analysis. Conversion of *cis*-cyclooct-1-ene and the formation of the cyclooctene oxide were calculated from calculation curves ( $r^2= 0.999$ ) relatively to dodecane prior to the reaction. Other reactions were carried out in an NMR tube and analyzed by <sup>1</sup>H NMR using acetophenone as internal standard.

*X-ray crystallography.* Single crystals of compounds **1** and **2** were mounted under inert perfluoropolyether on the tip of a glass fibre and cooled in the cryostream of a Bruker APEXII-II diffractometer. Data were collected using the monochromatic MoK $\alpha$  radiation ( $\lambda= 0.71073$ ). The structures were solved by direct methods (SIR97) [37] and refined by least-squares procedures on  $F^2$  using SHELXL-97 [38]. All H atoms attached to carbon were introduced in idealised positions and treated as riding models in the calculations. The drawing of the molecule was realised with the help of ORTEP3 [39]. Crystal data and refinement parameters for **1** and **2** are shown in Table 5. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 775912. and CCDC 775913. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk))

Table 5 . Crystal data and structure refinement for **1**

	<i>1</i> – [VO(SAE)] <sub>2</sub> O	<i>2</i> – [VO(SAMP)] <sub>2</sub> O
Empirical formula	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>7</sub> V <sub>2</sub>	C <sub>22</sub> H <sub>26</sub> N <sub>2</sub> O <sub>7</sub> V <sub>2</sub>
Formula weight	476.22	532.33
Temperature (K)	110(2)	293(2)
Wavelength (Å)(MoK $\alpha$ )	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /n	C2/c
Unit cell dimensions	a = 6.6299(3) Å b = 16.9926(8) Å	a = 33.758(2) b = 7.1777(6)

	$c = 16.7975(7) \text{ \AA}$ $\alpha = \gamma = 90^\circ, \beta = 99.474(2)^\circ$	$c = 19.4965(15)$ $\alpha = \gamma = 90^\circ, \beta = 99.363(5)$
Volume	$1866.58(14) \text{ \AA}^3$	$4661.2(6) \text{ \AA}^3$
Z	4	8
Density (calculated)	$1.695 \text{ Mg/m}^3$	$1.517 \text{ Mg/m}^3$
Absorption coefficient	$1.047 \text{ mm}^{-1}$	$0.847 \text{ mm}^{-1}$
F(000)	968	2192
Crystal size	$0.17 \times 0.05 \times 0.04 \text{ mm}^3$	$0.131 \times 0.066 \times 0.03 \text{ mm}^3$
$\theta$ range for data collection	$1.72$ to $25.23^\circ$ .	$2.12$ to $26.06$
Index ranges	$-7 \leq h \leq 7$ , $-20 \leq k \leq 20$ , $-20 \leq l \leq 20$	$-39 \leq h \leq 37$ $-8 \leq k \leq 8$ $-24 \leq l \leq 24$
Reflections collected	28864	19486
Independent reflections	3355 [R(int) = 0.0583]	4365 [R(int) = 0.1091]
Completeness to $\theta$	99.6 %	94.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data / restraints / parameters	3355 / 0 / 262	4365 / 0 / 302
Goodness-of-fit on $F^2$	1.029	1.012
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0355 wR2 = 0.0736	R1 = 0.0492 wR2 = 0.0996
R indices (all data)	R1 = 0.0548 wR2 = 0.0823	R1 = 0.0927 wR2 = 0.1184
Largest diff. peak and hole ( $e.\text{\AA}^{-3}$ )	0.490 and -0.383	0.352 and -0.356

*Computational details.* The geometry of  $[\text{VO}(\text{SAE})]_2\text{O}$  was optimized without any symmetry constraint with the Gaussian 03 program suite [40]. The calculations used the standard B3LYP three-parameter functional [41,42,43] in conjunction with the 6-31G\*\* basis set, either for all atoms, or for the light atoms (O, N, C, H) plus the SDD set for the V atom, which includes a pseudopotential, augmented by an f polarization function with the optimized [44] 1.715 coefficient. The optimized geometry was confirmed to be a local minimum by the frequencies analysis. The calculated IR spectrum shown in Figure 2 was generated from the DFT-generated frequencies and intensities by applying Lorentzian functions and adjusting the line width to best fit the experimental spectra.

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