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# Hemicryptophane–oxidovanadium(V) complexes: Lead of a new class of efficient supramolecular catalysts

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ABSTRACT

Hemicryptophane–oxidovanadium(V) complexes **1** and **2** were tested in the oxidation of sulfide to sulfoxide. They were found to be efficient supramolecular catalysts in the oxidation of thioanisol with yields up to 95%. Furthermore, turnover up to 180 was obtained by decreasing the amount of catalyst to 0.5% molar. A direct comparison between hemicryptophane complexes **1** and **2** and the model complex **3**, which lacks a cavity, was made. The cage structure in **1** and **2** strongly enhanced the catalytic activity, and higher yields were obtained with **1** or **2** than with the model compound **3**. Kinetic constants for the oxidation of thioanisol were estimated up to sixfold higher with the hemicryptophane complexes than with the model complex **3**.



## 1. Introduction

Haloperoxidases such as the chloroperoxidase from the mold *Curvularia inaequalis* are able to catalyze the oxidation of sulfide to sulfoxide [1]. In these enzymes the vanadate core is covalently bound to the Nε of a proximal histidine, and the vanadium atom is in a trigonal-bipyramidal environment [2–4]. Due to the catalytic activity of the peroxidase in sulfoxidation, model reactions were developed in which vanadium-based catalysts were employed to oxidize sulfide [5–11]. These vanadium complexes usually contain Schiff base ligands, heida ($H_2$heida = N-(2-hydroxyethyl)iminodiacetic acid), trialcool, aminobi-, or tri-alcoolate ligands. The latter were designed to mimic the coordination environment of the vanadate-dependent haloperoxidase with respect to both the nature of the donor set and the coordination geometry [9–11].

More generally, the use of transition metal complexes to mimic the catalytic activity of enzymes has been extensively investigated over the past 30 years. Simultaneously, supramolecular chemistry has grown into a major scientific field. Advances in synthesis, spectroscopic analysis, and computing have allowed the studies of even more sophisticated and complex supramolecular objects. Thus, research has been conducted to combine the knowledge obtained from supramolecular chemistry and from transition metal catalysis to construct supramolecular catalysts [12–21]. Molecules containing a cavity for substrate encapsulation and a metal center for catalytic activity have been reported and can be classified as host–guest catalysts. Two main types of supramolecular catalysts have been widely studied, namely: cyclodextrin- and calixarene-based systems. Transition metal complexes attached to a cyclodextrin scaffold have become increasingly popular [22,23]. In some cases, a well-improved reaction rate was observed when compared to the reaction carried out with the complex that lacks a cavity [24,25]. In the same way, the use of calixarenes in metal-based catalysis has received much attention, leading to similar effects [26]. Nevertheless, most synthetic systems have turned out to be inactive, and no example of such supramolecular catalysts has led to commercial applications [15,21]. Thus, the discovery of new classes of supramolecular systems including a transition metal and their ability to display catalytic activity remain a challenge.

We have already reported the synthesis of hemicryptophane–oxidovanadium(V) complexes **1** and **2** (Fig. 1), which contain a $C_3$-symmetrical cyclotriveratrylene (CTV) moiety with *P* or *M* configuration, providing both a shaping unit and a lipophilic chiral cavity, as well as a chiral $C_3$-symmetrical vanadium complex with potential catalytic activity [27,28]. The vanatrane moiety models specific features of vanadate-dependent haloperoxidase, such as the trigonal-bipyramidal $O_4N$ coordination of vanadium(V) and the chiral environment of the active site. We thus investigated the catalytic activity of these hemicryptophane complexes in the sulfoxidation reaction, since, according to Sanders classification, it belongs to transfer reactions, which should be ideal for demonstrating catalysis and turnover with supramolecular systems [15]. Herein we report that these complexes are indeed efficient supramolecular catalysts: excellent yields and selectivities were observed in the oxidation of sulfide to sulfoxide and a turnover up to 180 was obtained. Furthermore, a direct comparison between these complexes and a model complex, which lacks a cavity, was

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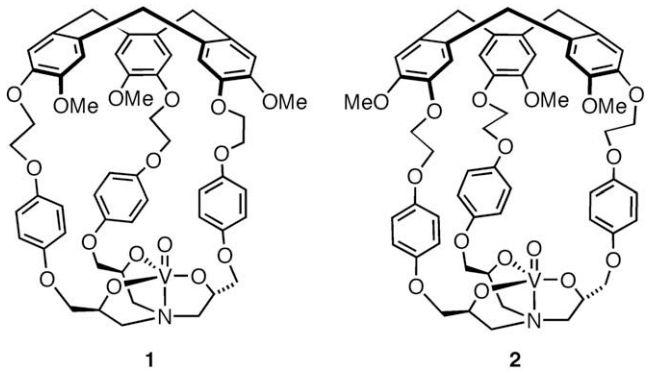


**Fig. 1.** Hemicryptophane–oxidovanadium(V) complexes **1** and **2**.

made. A sixfold reaction rate increase was found with the supramolecular catalyst compared to the model.

## 2. Experimental

### 2.1. Materials and methods

$^{1}H$ $^{13}C$ and $^{51}V$ NMR spectra were recorded at 500.1 or 200.13 MHz ($^{1}H$), 50.3 MHz ($^{13}C$), and 131.54 MHz ($^{51}V$), with Bruker DPX 500 or DPX 200 spectrometers. Chemical shifts are referenced to TMS ($^{1}H$ and $^{13}C$) and $VOCl_3$ ($^{51}V$). HPLC analyses were performed on an Agilent-1100 apparatus (binary pump, autosampler, column, thermostat, and diode array detector) using Chiralpack IC (0.46 × 25 cm) column. Cumyl hydroperoxide (Fluka, 80% in cumene) and *t*-butyl hydroperoxide (Aldrich, 5 M in nonane) were stored at 0 °C. Thioanisol (Acros), Benzylphenyl sulfide (Acros), benzophenone (Acros), and $VO(OiPr)_3$ (Aldrich) were used as received from the supplier.

### 2.2. Preparation of the model complex **3**

#### 2.2.1. Synthesis of the epoxide **5**

A solution of *p*-methoxyphenol **4** (1.315 g, 10.6 mmol) in DMF (8 mL) was added to NaH (625 mg, 14.5 mmol) (55% suspension in oil) and was washed with hexane. After stirring under argon for 30 min, a solution of *S*-(−)-glycidyl nosylate (2.5 g, 9.65 mmol) in DMF (8 mL) was added. The mixture was stirred at room temperature under argon for 25 h. Then the reaction was quenched by adding water (100 mL) and the resulting mixture was extracted with $CH_2Cl_2$ (3 × 100 mL). The organic phase was washed with a 1 M NaOH solution (100 mL) and brine (100 mL), dried over sodium sulfate, filtrated, and evaporated. After column chromatography was performed over silica gel (petroleum ether/ether, 1/1), 1.3 g (68%) of **5** was obtained as a white solid. $^{1}H$ NMR ($CDCl_3$, 200.13 MHz): $\delta$ ppm 7.39 (d, 2H, $J$ = 8.7 Hz), 6.82 (d, 2H, $J$ = 8.7 Hz), 4.16 (m, 1H), 3.92 (m, 1H), 3.73 (s, 3H), 3.36 (m, 1H), 2.93 (m, 1H), 2.75 (m, 1H). $^{13}C$ NMR ($CDCl_3$, 50.3 MHz): $\delta$ ppm 44.3, 49.9, 55.8, 69.0, 115.2, 130.1, 158.3. HRMS calcd. for $C_{10}H_{12}O_3$: 180.0786, found: 180.0788.

#### 2.2.2. Synthesis of the trialkanolamine ligand **6**

A solution of **5** (1.1 g, 6.1 mmol) in methanol (11 mL) was added to a solution of 7N $NH_3$ in methanol (0.4 mL, 2.8 mmol). After stirring for 4 days at room temperature, the solvent was stripped off. After column chromatography was performed over silica gel (ether/ethanol, 98/2), 0.55 g (90%) of **6** was obtained as a white solid. $^{1}H$ NMR ($CDCl_3$, 200.13 MHz): $\delta$ ppm 6.81 (s, 4H), 4.89 (s, 1H), 4.23 (m, 1H), 3.91 (m, 2H), 3.75 (s, 3H), 2.83–2.60 (m, 2H), $^{13}C$ NMR ($CDCl_3$, 50.3 MHz): $\delta$ ppm 154.3, 153.1, 115.8, 114.9, 71.0, 67.5, 59.3, 56.0. HRMS calcd. for $C_{10}H_{12}O_3$: 558.2703, found: 558.2706.

#### 2.2.3. Synthesis of model complex **3**

A solution of **6** (218 mg, 0.403 mmol) in THF (8 mL) was added dropwise to a solution of vanadium(V) oxytriisopropoxide (87 μL) in THF (8 mL). After stirring at room temperature for 1 h, the solution was concentrated. Crystallization from toluene solution afforded 210 mg (87%) of **3** as a yellow solid. $^{1}H$ NMR ($CDCl_3$, 200.13 MHz): $\delta$ ppm 6.82 (s, 4H), 5.20 (m, 1H), 4.06 (dd, $J$ = 4.3 Hz, $J$ = 8.8 Hz, 1H), 3.91 (m, 2H), 3.77 (s, 3H), 3.39 (dd, $J$ = 12.8 Hz, 3.9 Hz 1H), 3.10 (t, $J$ = 10.9 Hz, 1H), $^{13}C$ NMR ($CDCl_3$, 50.3 MHz): $\delta$ ppm 154.5, 152.7, 115.9, 115.0, 83.2, 70.5, 57.6, 30.0. $^{51}V$ NMR ($CDCl_3$, 131.54 MHz)) $\delta$ ppm −392.6. HRMS calcd. for $C_{10}H_{12}O_3$: 622.1857, found: 622.1861.

### 2.3. Epoxidation procedure

Oxidation of thioanisol: thioanisol (3.4 mg, 0.275 mmol), oxidovanadium complex (0.0275 mmol), and benzophenone (4.6 mg, 0.23 mmol) as internal standards were dissolved in anhydrous dichloromethane (0.25 mL). The solution was then cooled to 0 °C. Cumyl hydroperoxide (5 μL, 0.275 mmol) or *tert*-butyl hydroperoxide (5 μL, 0.275 mmol) was then added under stirring.

Oxidation of benzylphenyl sulfide**:** benzylphenyl sulfide (5.5 mg, 0.275 mmol), oxidovanadium complex (0.0275 mmol), and benzophenone (4.6 mg, 0.23 mmol) as internal standards were dissolved in anhydrous dichloromethane (0.25 mL). The solution was then cooled to 0 °C. Cumyl hydroperoxide (5 μL, 0.275 mmol) or *tert*-butyl hydroperoxide (5 μL, 0.275 mmol) was then added under stirring.

## 3. Results and discussion

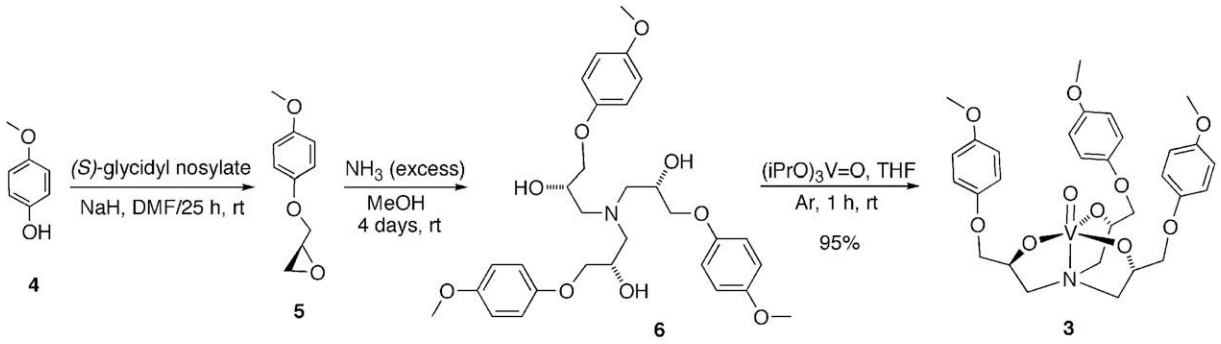
### 3.1. Synthesis of model complex **3**

We have previously reported the synthesis and structural study of complexes **1** and **2** (Fig. 1) [27,28]. The model complex **3** was synthesized in order to compare its catalytic activity with that of the hemicryptophane–oxidovanadium complexes. The enantiopure epoxide **5** was synthesized by a regioselective nucleophilic substitution reaction of *p*-methoxyphenol **4** on commercially available (*S*)-(−)-glycidyl nosylate (Scheme 1). It was previously shown by Sharpless that such nucleophilic displacement proceeded without racemization. Then, a solution of ammonia in methanol reacted with **5** to give the trialkanolamine precursor **6**. The $C_3$-symmetrical model complex **3** was finally obtained by reaction of **6** with one equivalent of vanadium(V) oxytriisopropoxide. The $^{1}H$ NMR spectrum was consistent with a structure with $C_3$ symmetry. Moreover, one signal in the range characteristic of five-coordinate vanadium complexes with an $O_4N$ donor set was observed in the $^{51}V$ NMR spectrum ($\delta$ = −392.6 ppm) [29]. According to the data reported earlier, this was attributed to a trigonal-bipyramidal vanadium complex with the N-amine trans to the oxo group [30].

### 3.2. Catalytic sulfoxidation

#### 3.2.1. Catalytic activities of **1** and **2**

The new supramolecular oxidovanadium(V) complex catalysts **1** and **2** were tested in the oxidation of sulfide using cumyl hydroperoxide (CHP) or *t*-butyl hydroperoxide (TBHP) as the oxygen source. The reactions were conducted with sulfides and oxidants at 0.01 M and with the catalyst at 0.001 M concentrations in dichloromethane at 0 °C. The results are summarized in Table 1. Both **1** and **2** are very efficient catalysts since high yields were




**Scheme 1.** Synthesis of model complex **3**.

obtained for the sulfoxidation of thioanisol using CHP as the oxygen source: 95% and 90%, respectively (entries 1 and 4, Table 1). High selectivities were also observed: 99:1 and 98:2 sulfoxide–sulfone ratios with catalysts **1** and **2,** respectively (entries 1 and 4, Table 1). The use of TBHP instead of CHP as the oxygen source slightly decreases the yield of the reaction: 72% *vs.* 95%, respectively, for catalyst **1** (entries 1 and 2, Table 1) and 85% *vs.* 90%, respectively, for catalyst **2** (entries 4 and 5, Table 1). When the amount of catalyst was reduced to 0.5% using CHP as the oxygen source (entries 3 and 6, Table 1), the yield for the sulfoxide was 90% for both **1** and **2** after 6 h at room temperature. These complexes can thus proceed with a turnover up to 180, making **1** and **2** the first members of a new family of supramolecular catalysts. Some host–guest systems combined with transition metal-based catalyst, able to achieve a high turnover, have been already reported in the literature. Nevertheless, most of the supramolecular systems designed to show a catalytic activity have turned out to be inactive probably due to their high rigidity, or have to be used in stoichiometric amount since the product of the reaction remains in the cavity preventing any catalytic cycle [15]. Thus these complexes belong to the unusual category of efficient supramolecular transition metal-based catalysts. High yields and excellent selectivities were also observed in the oxidation of benzylphenylsulfide using CHP as the oxygen source: 90% and 93% yields and 100% and 99% selectivities with catalysts **1** and **2,** respectively (entries 9 and 10, Table 1).

### 3.2.2. Influence of the $\Lambda/\Delta$ ratio on the catalytic activity of *1* and *2*

Despite the diastereomeric excess of the chiral catalysts used, the reaction afforded very low enantiomeric excesses (less than 10% in all cases, data not shown). We have previously reported that each of the optically pure hemicryptophane–oxidovanadium(V) complexes **1** and **2**, which differ by the *P* or *M* configuration of the CTV cap (formally *P*-(*S,S,S*)-**1** and *M*-(*S,S,S*)-**2**, respectively), exists in solution as a mixture of two diastereomeric conformers due to the $\Lambda$ and $\Delta$ forms of the vanatrane moiety: *P*-(*S,S,S*-$\Lambda$)-**1**/*P*-(*S,S,S*-$\Delta$)-**1** and *M*-(*S,S,S*-$\Lambda$)-**2**/*M*-(*S,S,S*-$\Delta$)-**2** (Fig. 2) [28]. In order to investigate the influence of the diastereomeric ratio of the complex on the catalytic activity, different ratios of *P*-(*S,S,S*-$\Lambda$)-**1** and *P*-(*S,S,S*-$\Delta$)-**1** (from 69% to 100%) and of *M*-(*S,S,S*-$\Lambda$)-**2** and *M*-(*S,S,S*-$\Delta$)-**2** (from 0% to 47%) were separately tested in catalysis using CHP as the oxygen source and thioanisol as the substrate (Table 2). Similar results were obtained in all cases, showing that the different diastereomeric catalysts present nearly the same activity. The enantiomeric excess of the sulfoxide changes very smoothly with the diastereomeric excess of the catalyst (less than 10% *ee* in each case). In particular, no improvement in the asymmetric induction could be observed by using diastereomerically pure *P*-(*S,S,S*-$\Lambda$)-**1.**

### 3.2.3. A direct comparison between hemicryptophanes *1*–*2* and the model *3*

A direct comparison between hemicryptophanes **1** and **2** and the model **3** was established in order to investigate the influence

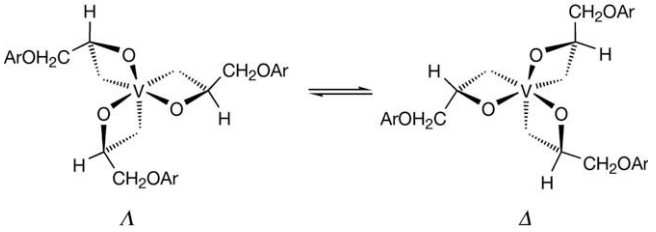



**Fig. 2.** View along the V–N transannular bond axis showing the diastereomeric staggered conformations $\Lambda$ and $\Delta$ of the vanatrane moiety.

**Table 1**
Oxidation of thioanisol and benzylphenyl sulfide with CHP or TBHP in the presence of catalysts **1**, **2,** and **3**.[a]

| Entry | Substrate | Catalyst | Oxygen source | Yield (%)[b] | Selectivity (%)[b] |
|---|---|---|---|---|---|
| 1 | Thioanisol | **1** | CHP | 95 | 98 |
| 2 | Thioanisol | **1** | TBHP | 72 | 96 |
| 3 | Thioanisol | **1**[c] | CHP | 90 | 96 |
| 4 | Thioanisol | **2** | CHP | 90 | 96 |
| 5 | Thioanisol | **2** | TBHP | 85 | 92 |
| 6 | Thioanisol | **2**[c] | CHP | 90 | 97 |
| 7 | Thioanisol | **3** | CHP | 28 | 98 |
| 8 | Thioanisol | **3** | TBHP | 46 | 95 |
| 9 | Benzylphenyl sulfide | **1** | CHP | 90 | 100 |
| 10 | Benzylphenyl sulfide | **2** | CHP | 93 | 99 |
| 11 | Benzylphenyl sulfide | **3** | CHP | 40 | 99 |

[a] Conditions: 10 mol% of catalyst, 1.0 equiv. of CHP or TBHP, $CH_2Cl_2$, 0 °C, 80 min.
[b] Yields and selectivity were determined by HPLC (CHIRALPACK IC, hexane–ethanol 80:20) with an internal standard (benzophenone).
[c] Conditions: 0.5 mol% of catalyst, room temperature, 6 h.

**Table 2**
Oxidation of thioanisol with CHP: influence of the $\Lambda/\Delta$ ratio on the catalytic activity of **1** and **2**.[a]

| Entry | Catalyst | $\Lambda/\Delta$ ratio | Yield (%)[b] | Selectivity (%)[b] |
|---|---|---|---|---|
| 1 | **1** | 100/0 | 94 | 95 |
| 2 | **1** | 100/18 | 95 | 98 |
| 3 | **2** | 100/35 | 85 | 97 |
| 4 | **2** | 100/50 | 83 | 99 |
| 5 | **2** | 100/100 | 82 | 99 |

[a] Conditions: 10 mol% of catalyst, 1.0 equiv. of CHP, $CH_2Cl_2$, 0 °C, 80 min.
[b] Yields and selectivities needed benzophenone as an internal standard and were determined by HPLC (CHIRALPACK IC, hexane–ethanol: 80:20).

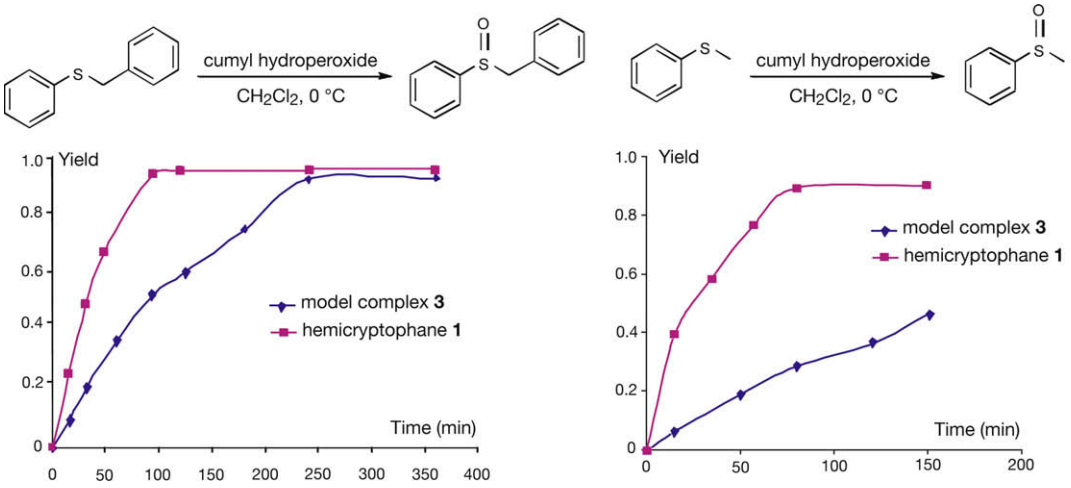



**Fig. 3.** Example of time course of oxygenation of thioanisol and benzylphenyl sulfide by cumyl hydroperoxide catalyzed by **1** and **3** (conditions: 10 mol% catalyst, 1.0 equiv. of CHP, $CH_2Cl_2$, 0 °C).

**Table 3**
Kinetic studies of the oxidation of sulfide with CHP in the presence of catalysts **1**, **2,** and **3**.[a]

| Entry | Substrate | Catalyst | TOF[b] × $10^{-3}$ ($s^{-1}$) | $k/k_3$[c] |
|---|---|---|---|---|
| 1 | Thioanisol | **3** | 0.58 | 1 |
| 2 | Thioanisol | **2** | 1.88 | 5.2 |
| 3 | Thioanisol | **1** | 1.98 | 6.3 |
| 4 | Benzylphenyl sulfide | **3** | 0.83 | 1 |
| 5 | Benzylphenyl sulfide | **2** | 1.94 | 2.8 |
| 6 | Benzylphenyl sulfide | **1** | 1.88 | 2.6 |

[a] Conditions: 10 mol% of catalyst, 1.0 equiv. of CHP, $CH_2Cl_2$, 0 °C.
[b] Turnover frequency is calculated by the expression of [product]/[catalyst] × 1/time after 80 min.
[c] $k/k_3$: ratio between the kinetic constant with the supramolecular catalyst **1** or **2** and the kinetic constant with the model catalyst **3**.

of the cyclotriveratrylene moiety on the catalytic reaction. It was found that both **1** and **2** were very efficient catalysts for the oxidation of thioanisol using CHP. Much better yields were obtained with **1** or **2** (95% and 90%, respectively) than with the model compound **3** (28%) under the same experimental conditions (entries 1, 4, and 7, Table 1). Similar results were obtained in the oxidation of benzylphenylsulfide (entries 9, 10, and 11, Table 1).

The time course for the sulfoxidation of thioanisol and benzylpenyl sulfide with catalysts **1**, **2,** and **3** using CHP as the oxygen source was monitored by HPLC (Fig. 3). The reaction times are clearly shorter with **1** or **2** than with the model compound **3.** The kinetic constants for the oxidation of thioanisol were estimated up to sixfold higher with the hemicryptophane complex **1** than with **3** (entry 3, Table 3). A similar but less pronounced effect was observed in the oxidation of benzylphenylsulfide (entries 5 and 6, Table 3). Therefore, the introduction of a CTV moiety strongly enhances the catalytic activity of the vanadium complexes. The improvement in the reaction rate may be due to the guest activation by molecular encapsulation. We have indeed previously reported the molecular mechanics model structure of the encapsulated methyl-*p*-tolyl sulfide inside the cavity of **2** [27]. It showed that the sulfide was trapped inside the molecular cavity of the vanadyl host. Moreover, it can be noticed that these hemicryptophane–oxidovanadium(V) complexes are rather flexible as observed in the solid state structure of **1** [28]. To decrease entropic cost many synthetic supramolecular systems were designed rigid, but most of them have turned out to be inactive. It has also been suggested that the quest for rigidity was a mistaken strategy and that supramolecular systems should be sufficiently flexible to allow responsiveness [15]. Thus the relative flexibility of complexes **1** and **2** could also account for their efficiency in catalytic oxidation.

The increase of the catalytic activity of host–guest complexes compared to that of the model catalysts, which lack a cavity, has been already described for other supramolecular systems, although such enhancements are not so usual. Furthermore, the number of supramolecular systems that display enhanced catalytic activities is low and is mainly restricted to metallo-cyclodextrins and calixarenes [23,26]. Hence, we have demonstrated that hemicryptophanes fall into this category and lead in the field of this new class of supramolecular catalysts.

## 4. Conclusion

In this work we have shown for the first time that hemicryptophane transition metal complexes are efficient supramolecular catalysts. Indeed, high yields in sulfoxidation reaction and turnover up to 180 were obtained using oxidovanadium(V) complexes **1** or **2**. The direct comparison with the model complex **3,** which lacks a cavity, emphasizes the role of the CTV moiety and hence the cage structure. Indeed, well-improved reaction rates were observed when **1** and **2** were used, in relation to the model complex **3**. There are only a small number of categories of supramolecular transition metal-based catalysts leading to both high turnover and enhancement of the catalytic activity compared to model molecules. Thus, the discovery of a new lead and a new class of supramolecular systems highlights the hemicryptophane-metal-based catalysis, and more general applications in various catalytic reactions are presently under consideration in our laboratory. For instance, the atrane structure is well known across the periodic table and has been widely studied [31–33] and metalatranes such as titanatrane have been successfully used in asymmetric catalysis [34]. Therefore, the introduction of a titanium atom in the atrane core of the hemicryptophane ligand may lead to efficient supramolecular catalysts for asymmetric synthesis.

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