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# Synthesis, characterization and crystal structure determination of a new vanadium(IV) Schiff base complex (VOL<sub>2</sub>) and investigation of its catalytic activity in the epoxidation of cyclooctene

Gholamhossein Grivani<sup>a,\*</sup>, Vida Tahmasebi<sup>a</sup>, Aliakbar Dehno Khalaji<sup>b</sup>, Karla Feifarová<sup>c</sup>, Michal Dušek<sup>c</sup>

<sup>a</sup> School of Chemistry, Damghan University, Damghan 36715-364, Iran

<sup>b</sup> Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran <sup>c</sup> Institute of Physics ASCR, v.v.i., Na Slovance 2, 182 21 Praha 8, Czech Republic

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#### ABSTRACT

The vanadium(IV) Schiff base complex VOL<sub>2</sub>,  $L = 2-{(E)-[2-chloroethyl)imino]methyl}-6-methoxy phenol,$ has been synthesized by the reaction of a methanolic solution of VO(acac)<sub>2</sub> with a methanolic solution of the Schiff base ligand, and it has been characterized using single-crystal X-ray crystallography, elemental analysis (CHN) and FT-IR spectroscopy. The crystal structure determination of this complex shows a deformed tetragonal pyramidal N<sub>2</sub>O<sub>3</sub> coordination sphere of the vanadium center. The Schiff base ligand acts as a bidentate ligand with the two phenolato oxygen atoms and the two imine nitrogen atoms in trans positions. Non-classical inter- and intra-molecular hydrogen bonds of the type C-H···O have been found in the structure, the latter connecting the monomeric VOL<sub>2</sub> units. The catalytic activity of the VOL<sub>2</sub> Schiff base complex in the epoxidation of cyclooctene was investigated using different reaction parameters, such as solvent effect, oxidant, alkene/oxidant ratio and the catalyst amount. The results showed that with a catalytic amount of the VOL<sub>2</sub> Schiff base complex and a 1:3 ratio of the cyclooctene/TBHP, the cyclooctene was effectively and selectively converted into the corresponding epoxide with CHCl<sub>3</sub> as the solvent.

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#### 1. Introduction

Schiff bases are versatile ligands that can bind to metal ions and form metal complexes with interesting properties [1–11]. These complexes have high stability, interesting and important properties in different oxidation states and their coordination chemistry has been extraordinarily developed in different aspects [12-14]. Recently many researchers have been concentrating on the coordination chemistry of vanadium complexes [15-18] with wellestablished different chemical and biological functions. Vanadium plays a central role in a variety of biochemical processes, such as haloperoxidation [19-23], nitrogen fixation [24,25], phosphorylation [26], glycogen metabolism [27-29], insulin mimicking [30-33] and in anti-parasitic agents [34]. In addition, high-valent vanadium complexes have been considered as new versatile catalytic reagents for a wide range of oxidation reactions [35,36], like oxidation of olefines and alcohols [37-41], benzene/alkylaromatic compounds [42,43] and sulfides [44-46]. Recently we have characterized two new O, N Schiff base ligands derived from salicylaldehyde with 2-bromo ethyl ammonium hydrobromide and 2-chloro ethyl ammonium hydrochloride, and have investigated the catalytic activities of their vanadyl complexes in the epoxidation of alkenes [47,48]. In a continuation of our work in this area, here we describe the synthesis, characterization, crystal structure determination and catalytic activity of the  $VOL_2$  Schiff base complex (L = 2-{(E)-[2-chloroethyl)imino]methyl}-6-methoxy phenol) (Scheme 1).

## 2. Experimental

All reagents and solvents for the synthesis and analysis were commercially available and purchased from Merck, and were used as received without further purification. Infrared spectra were recorded using KBr disks on a FT-IR Perkin Elmer RXI spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer and the results agreed with the calculated values. The <sup>1</sup>H NMR spectrum of the ligand was measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All GC yields based on the starting materials were obtained by using a Varian CP-3800 instrument with a silicon-DC 200 column.

2.1. Synthesis of the 2-{(E)-[2-chloroethyl)imino]methyl}-6-methoxy phenol (L)

In a 250 ml round bottom flask containing 100 ml of absolute methanol were added 10 mmol of 3-methoxy-2-hydroxybenzalde-



<sup>\*</sup> Corresponding author. Tel./fax: +98 232 5235431. E-mail address: grivani@du.ac.ir (G. Grivani).



Scheme 1. Preparation procedures for the new bidentate O,N Schiff base ligand L and its vanadyl Schiff base complex.

hyde and 10 mmol of 2-chloroethyl ammonium hydrochloride. Then 10 mmol of NaOH, dissolved in 5 ml H<sub>2</sub>O, were added to the above solution and the contents were refluxed for 4 h. After cooling to room temperature, the reaction mixture was added to 100 ml of water at 0 °C in a beaker, and then kept in an ice bath for 1 h. The yellow crystals that formed were filtered off, washed with slightly cold water and dried in an oven. M.p.: 68 °C. *Anal.* Calc. for C<sub>10</sub>H<sub>12</sub>ClNO: C, 55.87; H, 5.58; N, 6.53. Found: C, 56.20; H, 5.62; N, 6.55%. IR (KBr pellet, cm<sup>-1</sup>): 3150–3300 (b, O–H, phenolic), 2780–2870 and 2890–3000 (w, C–H aliphatic and aromatic), 1634 (s, C=N), 1471, 1439 (m, C=C), 734 (m, C–Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  (ppm)): 13.41 (1H, O–H), 8.36 (1H, H–C=N)), 6.95 (1H, phenyl–H), 6.91 (1H, phenyl–H), 6.82 (1H, phenyl–H), 3.90 (2H, –CH<sub>2</sub>Cl) (3H, –OMe), 3.78 (2H, –N–CH<sub>2</sub>–).

## 2.2. Synthesis of VO(L)<sub>2</sub>

In a 100 ml round bottom flask, 5 mmol of L was dissolved in 40 ml of MeOH and to this solution was added 2.5 mmol of VO(acac)<sub>2</sub> dissolved in 20 ml of MeOH. The contents of the flask were then refluxed with stirring for 2 h. After evaporating the solvent, the remaining reaction mixture was crystallized in a solvent mixture of MeOH/CHCl<sub>3</sub> (1/1, v/v). The greenish crystals that formed were filtered off, washed with n-hexane and dried in an oven. M.p.: 194 °C. Anal. Calc. for  $C_{20}H_{22}Cl_2N_2O_5V$ : C, 48.10; H, 4.23; N, 5.62. Found: C, 48.78; H, 4.47; N, 5.69% IR (KBr pellet, cm<sup>-1</sup>): 2780–2870 and 2890–3000 (w, C—H aliphatic and aromatic), 1622 (s, C=N), 1540, 1473 (m, C=C), 738 (m, C-Cl), 984 (s, V=O).

#### 2.3. X-ray structure determination

A single crystal of dimensions 0.32 mm × 0.23 mm × 0.11 mm was chosen for the X-ray diffraction study. Crystallographic measurements were carried out at 120 mmK with a four circle CCD diffractometer, Gemini of Oxford diffraction, Ltd., with mirror-collimated Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å), using the area detector Atlas. The crystal structure was solved by direct methods with the program SIR2002 [49] and refined with the JANA2006 program package [50] by the full-matrix least-squares technique on  $F^2$ . The molecular structure plots were prepared by ORTEP III [51]. Hydrogen atoms were mostly discernible in the difference Fourier maps and could be refined to a reasonable geometry. According to common practice, they were nevertheless kept in ideal positions during the refinement. In this structure no H atoms are bounded to nitrogen. The isotropic atomic displacement parameters of all hydrogen atoms were evaluated as  $1.2U_{eq}$  of the parent atom. Crystallographic data, details of the data collection and structure solution and refinements are listed in Table 1.

#### 2.4. General procedure of the epoxidation reaction

In a 10 ml round bottom flask equipped with a magnetic stirring bar, 0.5 mmol of the alkene was reacted with different amounts of the oxidant and the vanadyl Schiff base complex in 5 ml of solvent, by refluxing the reaction mixture. The progress of the reaction was monitored by GLC.

## 3. Results and discussion

## 3.1. Synthesis and characterization

Scheme 1 shows the preparation procedures for the bidentate Schiff base ligand L and its VOL<sub>2</sub> Schiff base complex. The Schiff

 Table 1

 Crystallographic data and structure refinement for VOL2.

Empirical formula	$C_{20}H_{22}Cl_2N_2O_5V_1$
Formula weight	492.3
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.2198 (6)
b (Å)	12.0634 (7)
<i>c</i> (Å)	16.6407 (10)
β (°)	108.434 (5)
$V(Å^3)$	2136.7 (2)
Ζ	4
$\mu$ (mm <sup>-1</sup> )	6.49
T <sub>min</sub>	0.557
T <sub>max</sub>	1
Measured reflections	16499
Independent reflections	3797
Reflection with $I > 3\sigma(I)$	3238
R <sub>int</sub>	0.035
S	1.48
$R[F^2 > 2\sigma(F^2)]$	0.027
$wR(F^2)$	0.063
Parameters	272
$\Delta ho_{ m max}$ (e Å $^{-3}$ )	0.21
$\Delta  ho_{ m min}$ (e Å <sup>-3</sup> )	-0.20
Crystal size (mm <sup>3</sup> )	$0.32\times0.23\times0.11$

base ligand L was prepared by the simple reaction of OMe-salicyaldehyde with an equimolar amount of 2-chloroethyl ammonium hydrochloride in the presence of NaOH in methanol as a solvent under reflux conditions. In the subsequent reaction of the prepared Schiff base ligand L and VO(acac)<sub>2</sub> in a molar ratio of 2:1 in methanol under reflux conditions, the vanadyl Schiff base complex was prepared. The Schiff base ligand L and its vanadyl Schiff base complex were characterized by CHN analysis, FT-IR and <sup>1</sup>H NMR spectra. The structure of the vanadium(IV) Schiff base complex, VOL<sub>2</sub>, was determined by single crystal X-ray analysis, while the FT-IR spectra of L and VOL<sub>2</sub> provided data regarding the nature of their functional groups. The FT-IR spectrum of the Schiff base ligand L shows a broad band in the region 3150-3300 cm<sup>-1</sup>, indicating the presence of the phenolic O–H group. This band is absent in the FT-IR spectrum of the vanadium(IV) Schiff base complex VOL<sub>2</sub>, indicating the coordination of the ligand via phenolato group. The fundamental stretching mode of the azomethine moiety,  $v_{C=N}$ , for the free ligand appeared at 1634 cm<sup>-1</sup>, and this is shifted to a lower frequency by 22 cm<sup>-1</sup>, appearing at 1612 cm<sup>-1</sup>, in the FT-IR spectrum of the vanadium(IV) Schiff base complex VOL<sub>2</sub>. This change is attributed to the involvement of the azomethine nitrogen of the Schiff base ligand (L) in coordination to the vanadium(IV) center. VOL<sub>2</sub> complexes generally show  $v_{V=0}$  around 860 cm<sup>-1</sup> for polynuclear linear chain structures (V=0...V=0...) and have an orange color, but they show  $v_{V=0}$  around 970 cm<sup>-1</sup> for the monomeric form with a green color in the solution and solid state [52,53]. Thus the sharp band at 984 cm<sup>-1</sup> in the FT-IR spectrum of the VOL<sub>2</sub> Schiff base complex is attributed to the V=O vibrations, indicating the monomeric form of the L<sub>2</sub>V=O Schiff base complex in the solid state, as confirmed by single crystal X-ray diffraction (Fig. 1).

## 3.2. Crystal and molecular structure of the VOL<sub>2</sub>

An ORTEP view of the VOL<sub>2</sub> Schiff base complex with the atoms numbering scheme is given in Fig. 1. Table 2 lists selected bond lengths and angles. In this complex, the Schiff base ligands are anionic and N,O-bidentate. Vanadium(IV) is coordinated by two nitrogen and two oxygen atoms of two independent ligands in the basal plane and by one oxygen atom in the apical position. The square pyramidal geometry around the vanadium(IV) ion in this complex is distorted because of the different bond distances and angles. The largest angular distortion from an ideal square pyramidal geometry (90 and 180°) occurs in the angles O1-V1-C2 [110.58(6)°], O1-V1-O4 [112.36(7)°], O2-V1-O4 [137.06(6)°] and N1-V1-N2 [157.03(6)°]. The V=O, V–O and V–N distances (Table 2) are similar to those found in other vanadium(IV) complexes with bidentate Schiff base ligands [47,48].

In this complex, the two ligands are planar and the angle between the planes of the two V-O-C-C-C-N rings is 24.980(32)°. This complex shows intramolecular C-H $\cdots$ O hydrogen bonding (Fig. 1, Table 3), as well as non-classical C-H $\cdots$ O intermolecular hydrogen bonds linking the monomeric units to each other (Fig. 2, Table 3).

#### 3.3. Catalytic activity

In order to investigate the catalytic activity of the vanadium(IV) Schiff base complex (VOL<sub>2</sub>) in epoxidation reactions, cyclooctene was used as a model substrate and different reaction parameters, such as solvent, oxidant, alkene/oxidant ratio and the amount of the catalyst, were optimized. Fig. 3 illustrates the results of the epoxidation of cyclooctene in the presence of tert-butyl hydroperoxide (TBHP) as an oxidant with a catalytic amount of the vanadium(IV) Schiff base complex (VOL<sub>2</sub>) in different solvents. The trend of the observed solvent effect was  $CHCl_3 > CH_3CN > CCl_4 > CH_2Cl_2 > MeOH > CH_3CN/H_2O > THF$ . It seems that in aprotic solvents, such as CHCl<sub>3</sub>, CH<sub>3</sub>CN and CCl<sub>4</sub>, a high epoxidation yield is observed. Rayati et al. also investigated the catalytic activities of two vanadium(IV) Schiff base complexes in the cyclooctene epoxidation reaction with TBHP using chloroform, acetonitrile and dichloromethane as solvents and they obtained the highest conversion (94-95%) with chloroform [54]. Martins and co-workers studied the epoxidation of cyclooctene using a diamine bis(phenolate)



Fig. 1. An ORTEP view of VOL<sub>2</sub> showing 50% probability displacement ellipsoids and the atom-numbering. Dashed lines indicate intramolecular C-H···O hydrogen bonds.

 Table 2

 Selected bond distances (Å) and angles (°) for VOL2.

	·····	,	
V1-01	1.5950(13)	02-C1	1.3253(18)
V1-02	1.9082(13)	04-C11	1.3193(19)
V1-04	1.9056(12)	N1-C8	1.294(2)
V1-N1	2.1019(15)	N1-C9	1.471(3)
V1-N2	2.1026(15)	N2-C18	1.290(2)
N2-C19	1.470(3)		
01-V1-02	110.58(6)	01-V1-04	112.36(7)
01-V1-N1	101.91(6)	01-V1-N2	101.06(6)
02-V1-04	137.06(6)	02-V1-N1	86.11(6)
02-V1-N2	85.74(6)	04-V1-N1	85.38(6)
04-V1-N2	86.05(6)	N1-V1-N2	157.03(6)
V1-02-C1	125.85(13)	V1-04-C11	128.26(12)
V1-N1-C8	121.76(13)	V1-N1-C9	121.83(10)
V1-N2-C18	122.97(14)	V1-N2-C19	119.62(10)
C18-N2-C19	117.08(15)	02-C1-C2	122.83(17)
02-C1-C6	118.24(17)	04-C11-C12	123.10(17)
04-C11-C16	118.34(16)	C12-C11-C16	118.52(15)

 Table 3

 Geometric parameters of hydrogen bonds for VOL2.

D—H···A	Distance (Å)			D-H…A (°)
	D—H	$H{\cdots}A$	$D{\cdots}A$	
C9—H9a…O1 C9—H9b…O5 C2—H20a…O1 C8—H8…O1	0.960 0.960 0.960 0.960	2.528 2.855 2.872 2.509	3.365 3.558 3.499 3.226	145.649 130.793 123.828 131.471

vanadium complex in the presence of the TBHP and  $H_2O_2$  in CHCl<sub>3</sub> and CH<sub>3</sub>CN [55]. Their results show that the activity of the vana-

dium complexes in the epoxidation of cyclooctene in the presence of TBHP in CHCl<sub>3</sub> is much higher than in the presence of H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN. Thus our results are consistent with the previous observations. By addition of H<sub>2</sub>O (as a protic solvent) to CH<sub>3</sub>CN, the conversion was decreased dramatically (Fig. 3). In another controlled experiment, in order to further confirm the effect of the coordination ability of the solvent on the yield of the epoxide, we tested the influence of the addition of imidazole. As can be seen in Fig. 4, the yield of the epoxidation of cyclooctene by the vanadium(IV) Schiff base complex (VOL<sub>2</sub>) in CHCl<sub>3</sub> in the presence of TBHP decreased significantly on addition of imidazole. Therefore the observed low conversion in MeOH, CH<sub>3</sub>CN/H<sub>2</sub>O and THF in Fig. 3 can be related to the high coordination ability of these solvents to the metal center. Thus, as the coordination ability of the solvent is increased, the activity of the titled complex is decreased. We also tested different reaction media to obtain a suitable oxidant media for the epoxidation of cyclooctene (Table 4). The results show that a high conversion is only obtained in the presence of TBHP in CHCl<sub>3</sub>. This may be related to the ability of TBHP and the inability of H<sub>2</sub>O<sub>2</sub> and NaIO<sub>4</sub> to mix with the organic substrate phase. Figs 5 and 6 show respectively the cyclooctene/oxidant ratio and the effect of the amount of catalyst in the epoxidation reaction of cyclooctene by the Schiff base complex (VOL<sub>2</sub>). According to these plots, a 1:3 ratio of cvclooctene/oxidant and 0.014 mmol of the catalyst can be chosen as the optimal amounts providing the highest epoxide yields.

In our previous researches we investigated the epoxidation of cyclooctene by vanadium(IV) Schiff base complexes derived from salicylaldehyde and 2-halo ethyl amine (Br, Cl) [47,48]. We found that the trend of the solvent effect on the epoxidation of cyclooctene by the related vanadium(IV) Schiff base complexes in the presence of TBHP, is changed by using 2-chloro ethyl amine instead



Fig. 2. Packing arrangement and hydrogen bonding for VOL<sub>2</sub>.



**Fig. 3.** The catalytic epoxidation of cyclooctene in different solvents in the presence of TBHP by the vanadyl Schiff base complex VOL<sub>2</sub>. Reaction conditions: 5 ml solvent, 0.5 mmol cyclooctene, 1.5 mmol TBHP and 0.014 mmol VOL<sub>2</sub> complex.



**Fig. 4.** The catalytic epoxidation of cyclooctene in  $CHCl_3$  in the presence of TBHP by the vanadyl Schiff base complex  $VOL_2$  without (No Im) and with imidazole addition (With Im). Reaction conditions: 5 ml solvent, 0.5 mmol cyclooctene, 1.5 mmol TBHP and 0.014 mmol VOL<sub>2</sub> complex and 0.014 mmol imidazole in the case of imidazole addition.

of 2-bromo ethyl amine. The found trend was  $CCl_4 > CHCl_3 > CH_3$ .  $CN > THF > MeOH > CH_3CN/H_2O$  for 2-bromo ethyl amine and  $CHCl_3 > CCl_4 > CH_3CN > CH_2Cl_2 > CH_3CN/H_2O > THF > MeOH$  for 2-chloro ethyl amine. In this research we used the substituted salicylaldehyde (3-methoxy salicylaldehyde) and 2-chloro ethyl amine, and we observed the trend  $CHCl_3 > CH_3CN > CCl_4 > CH_2$ .  $Cl_2 > MeOH > CH_3CN/H_2O > THF$  for the solvent effect on the epoxidation of cyclooctene by  $VOL_2$  in the presence of TBHP. A comparison of the observed solvent effect for the titled complex in this work and the related complex in Ref. [48] can be useful. The two vanadium(IV) Schiff base complexes are different in the

#### Table 4

Epoxidation of cyclooctene in different reaction media by the vanadium Schiff base complex  $\mathrm{VOL}_{2^*}^a$ 

Solvent	Oxidant	Time (min)	Conversion (%)
CHCl <sub>3</sub>	TBHP	114	86
CHCl <sub>3</sub>	$H_2O_2$	114	7
CH <sub>3</sub> CN/H <sub>2</sub> O(3:2)	NaIO <sub>4</sub>	114	13
THF	$H_2O_2$	114	3
CH <sub>3</sub> CN	$H_2O_2$	114	4
MeOH	$H_2O_2$	114	no reaction
CCl <sub>4</sub>	$H_2O_2$	114	no reaction
CH <sub>3</sub> CN/H <sub>2</sub> O(3:2)	$H_2O_2$	114	no reaction

 $^{\rm a}\,$  Reaction conditions: 5 ml solvent, 0.5 mmol cyclooctene, 1.5 mmol oxidant and 0.014 mmol VOL\_2 complex.



**Fig. 5.** The effect of the alkene/oxidant ratio in the epoxidation of cyclooctene with CHCl<sub>3</sub> as the solvent by the vanadyl Schiff base complex VOL<sub>2</sub>. Reaction conditions: 5 ml solvent, 0.5 mmol cyclooctene, 2 mmol, 1.5 mmol, 1 mmol and 0.6 mmol for 1:4, 1:3, 1:2 and 1: 1.2 ratios, respectively TBHP and 0.014 mmol VOL<sub>2</sub> complex.

methoxy group on the salicyliden moiety. Thus the variations in the observed trend for the solvent effect in comparison to the related trend in Ref. [48] can be attributed to the electron donating properties of the methoxy group of the salicyliden moiety. The effect of different pendant groups and different substituted salicylidens in vanadium(IV) Schiff base complexes on the solvent effect of the cyclooctene epoxidation reaction are under investigation by our research group. Very recently the mechanistic aspects of the catalytic epoxidation of alkenes by vanadium(IV) complexes were reviewed by Conte et al. [56]. Our obtained results on the epoxidation of cyclooctene by the vanadium(IV) Schiff base complex (VOL<sub>2</sub>) confirm the proposed mechanism for the epoxidation of cyclooctene by vanadium(IV) complexes, see Scheme 2 [56]. The formation of peroxyvanadium(V) species in the epoxidation route for alkenes has been established [57]. This can be examined by titration of a solution of the vanadium(IV) Schiff base complex with TBHP. Fig 7 shows the changes of the UV-Vis spectra of a solution of the vanadium(IV) Schiff base complex (VOL<sub>2</sub>) during titration with TBHP. The intensity of the bands at 375 and 285 nm was reduced, along with the gradual appearance of two new bands at 330 and 265 nm. At the end of the titration the bands at 375 and 285 nm disappeared. At the same time, the bands appearing at 610 and 550 nm, due to d-d transitions of  $[V^{VOL_2}]$ , slowly disappeared upon addition of TBHP. In agreement with



**Fig. 6.** The effect of the amount of the vanadyl Schiff base complex  $VOL_2$  in the epoxidation of cyclooctene with  $CHCl_3$  as the solvent in the presence of TBHP. Reaction conditions: 5 ml solvent, 0.5 mmol cyclooctene, 1.5 mmol TBHP and 0.01, 0.014 and 0.02 mmol  $VOL_2$  complex.



Scheme 2. The proposed mechanism for the epoxidation of cyclooctene by VOL<sub>2</sub>.



**Fig. 7.** The UV–Vis spectral changes observed during the titration of the V<sup>IV</sup>OL<sub>2</sub> Schiff base complex with TBHP. The spectra were recorded after successive additions of 1  $\mu$ l of TBHP to 5 ml a ca. 10<sup>-4</sup> M solution of V<sup>IV</sup>OL<sub>2</sub> in chloroform.

the literature [58-60], these spectral changes and the presence of two isosbestic points at 355 and 310 nm suggest the oxidation of vanadium(IV) and the interaction of the formed vanadium(V) complex with TBHP to give oxoperoxovanadium(V) species. Thus the active center in the epoxidation of cyclooctene by the vanadium(IV) Schiff base complex (VOL<sub>2</sub>) in the presence of TBHP is the vanadium(V). The observed trend in Fig. 3 shows that a high epoxide yield is obtained in solvents with a low coordination ability. In this case TBHP, containing a hard coordinating atom (O), links to the hard vanadium(V) center without any restriction by the solvent molecules. In solvents with high coordination ability, the solvent molecules compete with TBHP and coordinate to the vanadium center, thus retarding the coordination of the TBHP, causing a lower epoxide yield. This is tested by addition of the highly coordinating molecule imidazole during the epoxidation of cyclooctene under optimized conditions, where upon the epoxide vield was lowered on addition of imidazole as a highly coordinating molecule (Fig. 4). Thus our results agree with this mechanism.

### 4. Conclusion

In conclusion, we have readily synthesized a new vanadium(IV) Schiff base complex (VOL<sub>2</sub>). The catalytic activity of the VOL<sub>2</sub> complex was investigated in the epoxidation of cyclooctene. The reaction conditions were optimized and the results showed that the VOL<sub>2</sub> complex can be used as a highly active and selective homogeneous catalyst in the epoxidation of cyclooctene. In addition some mechanistic aspects of the cyclooctene epoxidation by the vanadium(IV) Schiff base complex VOL<sub>2</sub> were investigated.

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#### Appendix A. Supplementary data

CCDC 890891 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

#### References

- [1] N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk, Chem. Rev. 107 (2007) 46.
- [2] W. Radecka-Paryzek, V. Patroniak, J. Lisowski, Coord. Chem. Rev. 249 (2005)
- 2156.
  [3] G. Filomeni, G. Cerchiaro, A.M.C. Ferreira, A. Martino, J.Z. Pedersen, G. Rotilio, M.R. Ciriolo, J. Biol. Chem. 282 (2007) 12010.
- 4] L. Laxmi, K. Praveen, A.K. Singhai, Indian J. Cancer 44 (2007) 62.
- [5] J. Lv, T. Liu, S. Cai, X. Wang, L. Liu, Y. Wang, J. Inorg. Biochem. 100 (2006) 1888.
- [6] L. Shi, H.-M. Ge, S.-H. Tan, H.-Q. Li, Y.-C. Song, H.-L. Zhu, R.X. Tan, Eur. J. Med.
- Chem. 42 (2007) 558.
- [7] H. Naeimi, M. Moradian, Can. J. Chem. 84 (2006) 1575.
- [8] K.C. Gupta, A.K. Sutar, J. Macromol. Sci., Part A: Pure Appl. Chem. 44 (2007) 1171.
- [9] C. Adhikary, R. Bera, B. Dutta, S. Jama, G. Bocelli, A. Cantoni, S. Chandhuri, S. Koner, Polyhedran 27 (2008) 1556.
- [10] J. Wen, J. Zhao, X. Dong, T. You, J. Mol. Catal. A: Chem. 245 (2006) 242.
- [11] A.H. Kianfar, S. Mohebbi, J. Iran. Chem. Soc. 4 (2007) 215.
- [12] Z. Cimerman, S. Miljanic, N. Galic, Croat. Chem. Acta 73 (1) (2000) 81.
- [13] A. Elmali, M. Kabak, Y. Elerman, J. Mol. Struct. 484 (1999) 229.
- [14] K.B. Gudasi, S.A. Patil, R.S. Vadari, R.B. Shenoy, M.S. Patil, Transition Met. Chem. 30 (2005) 1014.
- [15] M.-J. Xie, X.-D. Yang, W.-P. Liu, S.-P. Yan, Z.-H. Meng, J. Inorg. Biochem. 104 (2010) 851.
- [16] L.-Z. Li, Z.-H. Guo, Q.-F. Zhang, T. Xu, D.-Q. Wang, Inorg. Chem. Commun. 13 (2010) 1166.

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- [17] D. de Rio, A. Galindo, J. Tejedo, F.J. Bedoya, A. Lenco, C. Mealli, Inorg. Chem. Commun. 3 (2000) 32.
- [18] H. Sigel, A. Sigel (Eds.), Metal Ions in Biological Systems: Vanadium and its Role in Life, vol. 31, Marcel Dekker, New York, 1995.
- [19] C.J. Schneider, J.E. Penner-Hahn, V.L. Pecoraro, J. Am. Chem. Soc. 130 (2008) 2712.
- [20] C. Wikete, P. Wu, G. Zampetlla, L.D. Gioia, G. Licini, D. Rehder, Inorg. Chem. 46 (2007) 196.
- [21] H. Sakurai, H. Sano, T. Takino, H. Yasui, J. Inorg. Biochem. 80 (2000) 99.
- [22] W. Plass, Coord. Chem. Rev. 255 (2011) 2378.
- [23] D. Wischang, O. Brücher, J. Hartung, Coord. Chem. Rev. 255 (2011) 2204.
- [24] T.S. Smith, C.A. Root, J.W. Kampf, P.G. Rasmussen, V.L. Pecoraro, J. Am. Chem. Soc. 122 (2000) 767.
- [25] E. Kiss, A. Benyei, T. Kiss, Polyhedron 22 (2003) 27.
- [26] C.R. Cornman, E.P. Zovinka, M.H. Meixner, Inorg. Chem. 34 (1995) 5099.
- [27] D.C. Crans, R.L. Bunch, L.A. Theisen, J. Am. Chem. Soc. 111 (1989) 7597.
- [28] D.C. Crans, J.J. Smee, E. Gaidamauskas, L.Q. Yang, Chem. Rev. 104 (2004) 849.
   [29] J.H. McNeill, V.G. Yuen, H.R. Hoveyda, C. Orvig, J. Med. Chem. 35 (1992) 1489.
- [30] K.H. Thompson, J.H. McNeill, C. Orvig, Chem. Rev. 99 (1999) 2561.
- [31] A.J. Tasiopoulos, A.N. Troganis, A. Evangelou, C.P. Raptopoulou, A. Terzis, Y. Deligiannakis, T.A. Kabanos, Chem. Eur. J. 5 (1999) 910.
- [32] A.A. Nejo, G.A. Kolawole, A.R. Opoku, C. Muller, J. Wolowska, J. Coord. Chem. 62 (2009) 3411.
- [33] A.A. Nejo, G.A. Kolawole, A.R. Opoku, J. Wolowska, P. O'Brien, Inorg. Chim. Acta 362 (2009) 3993.
- [34] D. Gambino, Coord. Chem. Rev. 255 (2011) 2193.
- [35] J.A.L. da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, Coord. Chem. Rev. 255 (2011) 2232.
- [36] G. Licini, V. Conte, A. Coletti, M. Miriam, C. Zonta, Coord. Chem. Rev. 255 (2011) 2345.
- [37] V. Conte, F. Di Furia, G. Licini, Appl. Catal., A: Gen. 157 (1997) 335.
- [38] S. Mohebbi, D.M. Boghaei, A.H. Sarvestani, Appl. Catal., A: Gen. 278 (2005) 263.

- [39] W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino, H. Yamamoto, Angew. Chem., Int. Ed. Engl. 44 (2005) 4389.
- [40] J.H. Hwang, M. Abu-Omar, Tetrahedron Lett. 40 (1999) 8313.
- [41] M. Bagherzadeh, M. Amini, J. Coord. Chem. 63 (2010) 3849.
- [42] E. Battistel, R. Tassinari, M. Fornaroli, L. Bonoldi, J. Mol. Catal. A: Chem. 202 (2003) 107.
- [43] G.B. Shul'pin, G. Suss-Fink, J. Chem. Soc., Perkin Trans. 2 (1995) 1459.
- [44] A. Barbarini, R. Maggi, M. Muratori, G. Sartori, R. Sartorio, Tetrahedron: Asymmetry 15 (2004) 2467.
- [45] T.S. Smith II, V.L. Pecoraro, Inorg. Chem. 41 (2002) 6754.
- [46] R. Ando, T. Yagyu, M. Maeda, Inorg. Chim. Acta 357 (2004) 2237.
- [47] G. Grivani, A.D. Khalaji, V. Tahmasebi, K. Gotoh, H. Ishida, Polyhedron 31 (2012) 265.
- [48] G. Grivani, G. Bruno, H.A. Rudbari, A.D. Khalaji, P. Pourteimouri, Inorg. Chem. Commun. 18 (2012) 15.
- [49] M.C. Burla, M. Camalli, B. Carrozzini, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 36 (2003) 1103.
- [50] V. Petricek, M. Dusek, L. Palatinus, Jana2006. Structure Determination Software Programs, Institute of Physics, Praha, Czech Republic, 2008.
- [51] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
- [52] R. Ando, S. Mori, M. Hayashi, T. Yagyu, M. Maeda, Inorg. Chim. Acta 357 (2004) 1177.
- [53] C.J. Chang, J.A. Labinger, H.B. Gray, Inorg. Chem. 36 (1997) 5927.
- [54] S. Rayati, M. Koliaei, F. Ashouri, S. Mohebbi, A. Wojtczak, A. Kozakiewicz, Appl. Catal. A: Gen. 346 (2008) 65.
- [55] F. Madeira, S. Barroso, S. Namorado, P.M. Reis, B. Royo, A.M. Martins, Inorg. Chim. Acta 383 (2012) 152.
- [56] V. Conte, A. Coletti, B. Floris, G. Licini, C. Zonta, Coord. Chem. Rev. 255 (2011) 2165.
- [57] M.R. Maurya, A. Arya, P. Adao, J.C. Pessoa, Appl. Catal. A: Gen. 351 (2008) 239.
- [58] M.R. Maurya, S. Sikarwar, M. Kumar, Catal. Commun. 8 (2007) 2017.
- [59] M.R. Maury, A. Kumar, J. Mol. Catal. A: Chem. 250 (2006) 190.
- [60] M.R. Maurya, A.K. Chandrakar, S. Chand, J. Mol. Catal. A: Chem. 270 (2007) 225.