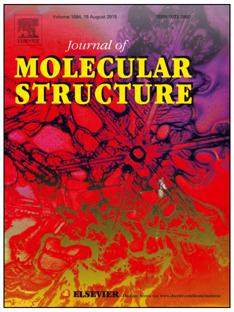

Synthesis, characterization, crystal structure determination and catalytic activity in epoxidation reaction of two new oxidovanadium(IV) Schiff base complexes

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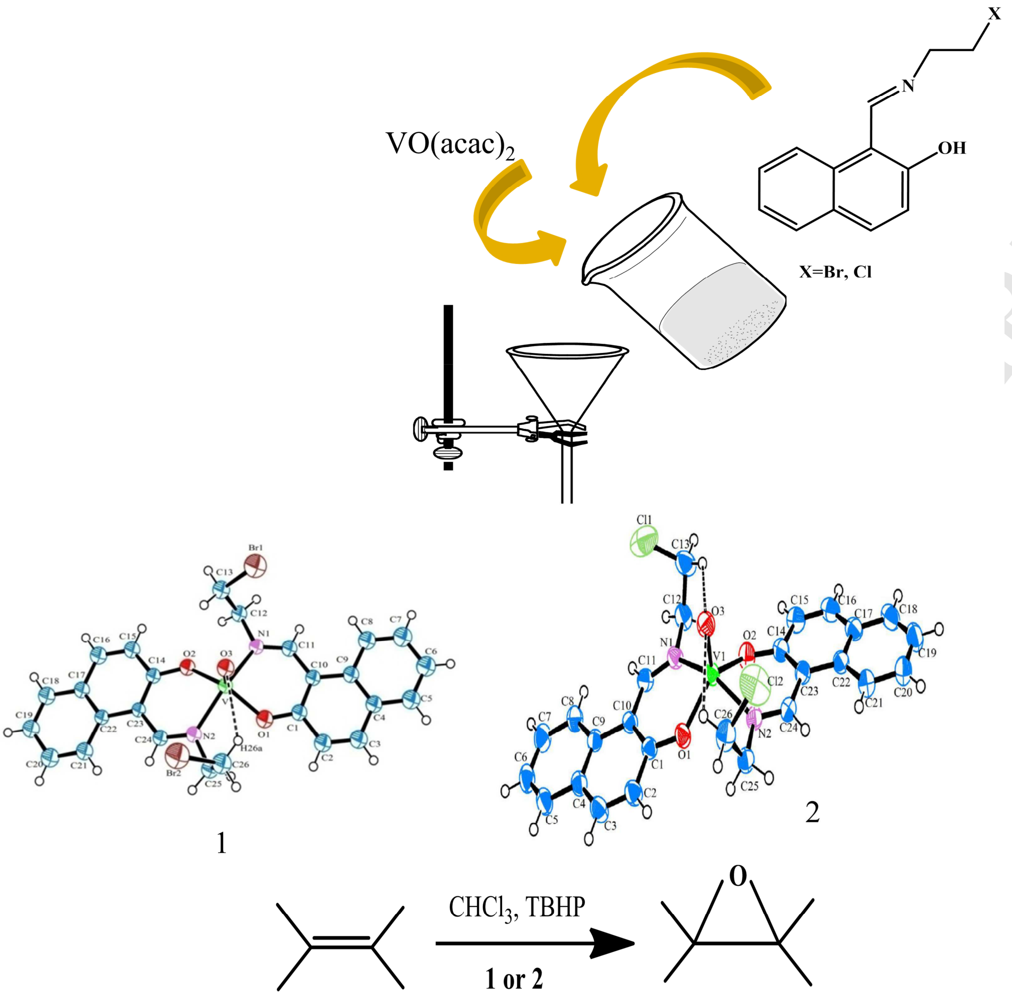
X
N
OH
VO(acac)$_2$
X=Br, Cl
1
2
CHCl$_3$, TBHP
1 or 2
O

Synthesis, characterization, crystal structure determination and catalytic activity in epoxidation reaction of two new oxidovanadium(IV) Schiff base complexes

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Abstract

The five coordinated vanadium(IV) Schiff base complexes of VO**L**^{1} (**1**) and VO**L**^{2} (**2**), H**L**^{1}=2-{(E)-[2-bromoethyl)imino]methyl}-2- naphthol, H**L**^{2}=2-{(E)-[2-chloroethyl)imino]methyl}-2-naphthol, have been synthesized and they were characterized by using single-crystal X-ray crystallography, elemental analysis (CHN) and FT-IR spectroscopy. Crystal structure determination of these complexes shows that the Schiff base ligands (**L**^{1} and **L**^{2}) act as bidentate ligands with two phenolato oxygen atoms and two imine nitrogen atoms in the *trans* geometry. The coordination geometry around the vanadium(IV) is distorted square pyramidal in which 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 catalytic activity of the

Schiff base complexes of **1** and **2** in the epoxidation of alkenes were investigated using different reaction parameters such as solvent effect, oxidant, alkene/oxidant ratio and the catalyst amount. The results showed that in the presence of TBHP as oxidant in 1: 4 and 1:3 ratio of the cyclooctene/oxidant ratio, high epoxide yield was obtained for **1** (76%) and **2** (80%) with TON(= mole of substrate /mole of catalyst) of 27 and 28.5, respectively, in epoxidation of cyclooctene.

Keywords: Oxidovanadium(IV) ; Schiff base; X-ray crystallography; Catalysis; Epoxidation;

Introduction

The Schiff base compounds, derived from condensation reaction of primary amines and aldehydes or ketones, are important class of ligands and played central role in the development of coordination chemistry [1-3] as they readily form stable complexes with most transition metals with interesting and important properties in different oxidation states [4-7]. Recently many researchers have been concentrating on the coordination chemistry of vanadium complexes. Interest in the coordination chemistry of vanadium complexes has grown enormously due to:(i) multifaceted biological activity observed in some low-order living systems like mushrooms[8-10], terrestrial fungi, algae [11, 12] and sea squirts [13]; (ii) involvement in active site of several enzymes such as vanadium-dependent nitrogenases, haloperoxidases [14, 15] as well as its involvement in phosphate metabolizing enzymes [16] and phosphomutases [17]; (iii) widely used as catalysts for many organic reactions[18-24]; (iv) exhibition of insulin mimesis by certain vanadium complexes [25–27] and, (v) exhibition anticancer properties by some oxidovanadium(IV) complexes [28, 29] as well as antibacterial and antimicrobial [30, 31] activity. Recently we reported the synthesis, characterization, crystal structure determination and catalytic activity of some oxidovanadium(IV) Schiff base complexes[32] derived from salicylaldehyde derivatives and 2-halo(chloro and bromo) ethyl amines [33–35]. In this research we describe the synthesis, characterization, crystal structure determination of two new oxidovanadium Schiff base complexes of **1** and **2** derived from 2-Hydroxy-naphthaldehyde and 2-bromo ethyl ammonium hydrobromide and 2-chloro ethyl ammonium hydrochloride, respectively. In addition the catalytic activity of synthesized vanadyl complexes in epoxidation of alkenes was investigated (scheme 1).

<Scheme 1>

Experimental

Materials

All reagents and solvents for synthesis and analysis were commercially available and purchased from Merck and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR PerkinElmer RXI spectrophotometer. Elemental analyses were carried out using a Heraeus CHN–O-Rapid analyzer. X-ray diffraction pattern of the freshly calcined sample was recorded in a Bruker AXS diffractometer D8 ADVANCE with Cu Ka radiation filtered by a nickel monochromator and operated at 40 kV and 30 mA. Diffraction pattern was recorded in the range of 2θ = 10–80 and the results agreed with calculated values. All GC yields base on starting materials were obtained by using Varian CP-3800 instrument with silicon-DC 200 column.

Synthesis of the 2-{(E)-[2-bromoethyl)imino]methyl}2- naphthol (HL^1)

To a 250 ml round bottom flask containing 100 ml absolute methanol were added 10 mmol 2-hydroxy-naphthaldehyde, 10 mmol of 2-bromo ammonium hydrobromide. Then 10 mmol of NaOH, dissolved in 5 ml of H_2O, was added to the above solution and the content was refluxed for 4 h. After evaporating the solvent by a rotary evaporator at 90 °C, the yellow precipitate was collected and washed with slightly cooled water and filtered (89%). The yellow crystals were obtained by the crystallization of precipitate in 1:1 mixture of chloroform and methanol. M.p.: 106°C. Anal. Calc. for $C_{13}H_{12}BrNO$: C, 56.63; H, 4.18; N,5.25 %. Found: C, 56.33; H, 3.97, N, 5.05 %. IR (KBr pellet, cm-1): 3300-3520 (b[1], O-H, phenolic), 2800-3070 (w[2], C-H aliphatic and aromatic), 1630 (s[3], C=N), 1490, 1538, (m[4], C=C).

Synthesis of the 2-{(E)-[2-chloroethyl)imino]methyl}2- naphthol (HL^2)

The Schiff base compound of H**L^2** was synthesized in similar to the preparation of the Schiff base compound of H**L^1** except 2-chloroethyl ammonium hydrochloride was used instead of 2-bromo ammonium hydrobromide (84%). M.p.: 104°C. Anal. Calc. for $C_{13}H_{12}ClNO$: C, 66.54; H, 5.04; N,6.03 %. Found: C, 67.09; H, 4.73, N, 6.02 %. IR (KBr pellet, cm^{-1}): 3300-3525 (b, O-H, phenolic), 2800-3060 (w, C-H aliphatic and aromatic), 1624 (s, C=N), 1430-1550, 1534(m, C=C).

Synthesis of the 1

---

[1] broad
[2] weak
[3] strong
[4] medium

In a 100 ml round bottom flask, 5 mmol of H**L**^{1} was dissolved in 40 ml of MeOH and to this solution was added 2.5 mmol of VO(acac)$_2$ dissolved in 20 ml of MeOH and the content was refluxed with stirring for 2 h. After evaporating of the solvent by a rotary evaporator at 90 °C, the content was crystallized in the solvent mixture of n-Hexane/CHCl$_3$ (1/1 *v/v*) Then the greenish crystals were filtered off and washed with n-hexane and dried in an oven (62%). M.p 270.^{o}C. *Anal*. Calc. for $C_{26}H_{20}Br_2N_2O_3V$: C, 50.40; H, 3.43; N, 4.67%. Found: C,50.42; H, 3.23; N, 4.52% IR (KBr pellet, cm^{-1}): 2880-3080, (w, C-H aliphatic and aromatic), 1610 (s, C=N), 1508, 1540 (m, C=C) and 970 (s, V=O).

Synthesis of the 2

The Schiff base complex of **2** was synthesized in similar to the preparation of the **1** Schiff base complex except 2-{(E)-[2-chloroethyl)imino]methyl}2- naphthol (H**L**^{2}) was used instead of 2-{(E)-[2-bromoethyl)imino]methyl}2- naphthol (H**L**^{1})(72%). M.p 265.^{o}C. *Anal*. Calc. for $C_{26}H_{20}Cl_2N_2O_3V$: C, 58.67; H, 3.99; N, 5.50%. Found: C,58.87; H, 3.77; N, 5.28% IR (KBr pellet, cm^{-1}): 2880-3080, (w, C-H aliphatic and aromatic), 1604 (s, C=N), 1508, 1540 (m, C=C) and 970 (s, V=O).

X-ray structure determination

Green single crystals with dimensions of 0.22 mm × 0.15 mm × 0.34 mm for **1** and the dimensions 0.35 mm × 0.18 mm × 0.40 mm for **2** were chosen for X-ray diffraction study. Crystallographic measurements were done at 296 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with mirrors-collimated Mo *K*α radiation ($\lambda = 0.71073$Å). The crystal structures were solved by direct methods with program SIR2002 [36] and refined with the Jana2006 program package [37] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by ORTEP III [38]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice they were nevertheless kept in ideal positions during the refinement. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

<Table 1>

General procedures of the epoxidation reaction

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

Results and discussion

Synthesis and Characterization

Scheme 1 shows the synthetic procedures of the bidentate Schiff base ligands of H**L^1**, H**L^2** and their vanadyl Schiff base complexes of **1** and **2**. The Schiff base ligands of H**L^1**, H**L^2** were prepared by the simple reaction of 2-hydroxy-naphthaldehyde with 2-bromo ammonium hyrobromide(H**L^1**) and 2-chloro ammonium hydrochloride (H**L^2**) in the presence of NaOH in the methanol as a solvent in the reflux conditions. Subsequently, by reaction of the synthesized Schiff base ligands (H**L^1**, H**L^2**) with $VO(acac)_2$ in the molar ratio of 2:1 in methanol in the reflux conditions, the vanadyl Schiff base complexes of **1** and **2**, were prepared. The two vanadyl Schiff base complexes of **1** and **2** are soluble in common organic solvents such as CH_3OH, $CHCl_3$ and $(CH_3)_2S{=}O$ (dimethyl sulfoxe) but insoluble in H_2O. The H**L**$^{\mathbf{1}}$**,** H**L**$^{\mathbf{2}}$ Schiff base ligands and their vanadyl Schiff base complexes were characterized by CHN analysis, FT-IR spectra. The structures of the oxovanadium(IV) Schiff base complexes of **1** and **2** were determined by single crystal X-ray analysis while the FT-IR spectra of H**L**$^{\mathbf{1}}$**,** H**L**$^{\mathbf{2}}$, **1** and **2** provided the data regarding to the nature of their functional groups. The FT-IR spectra of the Schiff base ligands (H**L**$^{\mathbf{1}}$**,** H**L**$^{\mathbf{2}}$) show a broad band in the region of 3300-3520 cm^{-1} indicating the presence of the phenolic O-H. This band is disappeared in the FT-IR spectrum of the **1** and **2** Schiff base complexes indicating the coordination of the ligand via phenolato dentate. The fundamental stretching mode of the azomethine moiety, $\nu_{C=N}$, for the free ligands(H**L**$^{\mathbf{1}}$**,** H**L**$^{\mathbf{2}}$) are appeared at 1630 cm^{-1} and 1624 cm^{-1} respectively which are shifted to the lower frequencies by 20 cm^{-1} and appeared at 1610 cm^{-1} in the FT-IR spectra of the **1** and **2** vanadium Schiff base complexes(S1 and S2 in Supplementary materials). These changes are attributed to the involvement of the azomethine nitrogen of the Schiff base ligands (H**L**$^{\mathbf{1}}$**,** H**L**$^{\mathbf{2}}$) in coordination to the vanadium(IV) center. The oxovanadium(IV) complexes generally show $\nu_{V=O}$ around 860 cm^{-1} for polynuclear linear chain structures ($V{=}O\cdots V{=}O\cdots$) with orange color but in solution they are green and around 970 cm^{-1} for monomeric form with green color in the solution and solid state [39, 40]. Thus the sharp band in 970 cm^{-1} in the FT-IR spectra of the oxidovanadium Schiff base complexes of **1** and **2**, attributed to the V=O vibration frequencies approves the monomeric form of (**L**$^{\mathbf{1}}$)$_2$V=O and (**L**$^{\mathbf{2}}$)$_2$V=O Schiff base complexes in the solid state as confirmed by the single crystal X-ray diffraction (Figs 1, 2). In comparison to similar complexes [33-35, 41,42], the two characteristic bands ($\nu_{C=N}$, $\nu_{V=O}$) in the synthesized ligands (H**L**$^{\mathbf{1}}$**,** H**L**$^{\mathbf{2}}$) and complexes (**1**, **2**) are located in the same region as it was seen in Table 2.

<Table 2>

Crystal and molecular structure

An ORTEP view of **1** and **2** Schiff base complexes with the atoms numbering scheme is given in Figs. 1 and 2, respectively. Tables 3 and 4 list the selected bond lengths and angles. In these complexes, 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 these complexes is distorted because of the different bond distances and angles. The largest angular distortion from an ideal square pyramidal geometry (90 & 180°) occurs in the angles of O3-V1-O1 [110.70(2), 110.75(6)], O3-V1-O2 [112.50 (7), 112.42(5)], O2-V1-O1 [136.80(2), 136.83(5)] and N1-V1-N2 [156.30(2), 156.30(5)] for **1** and **2** respectively. The V=O, V-O and V-N distances are similar to those found in other oxidovanadium(IV) complexes with bidentate Schiff base ligands [43-47].

<Figs. 1, 2> & <Tables 3, 4>

These complexes contain several intra- and inter-molecular non-classical hydrogen bonds of the type C–H…X (X = O, Br, Cl), as well as C–H···O intermolecular hydrogen bonds linking the monomeric units to each other (Figs. 3, 4 and Tables 5, 6).

<Figs. 3, 4> & <Table 5, 6>

Catalytic activity

In order to investigate the catalytic activity of the oxidovanadium Schiff base complexes of **1** and **2** in epoxidation reaction, the 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. 5 illustrates the results of the epoxidation of the cyclooctene in the presence of the tert-butyl hydroperoxide(TBHP) as an oxidant in different solvents with the catalytic amount of the oxidovanadium(IV) Schiff base complexes (**1** and **2**). 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 the aprotic solvents such as $CHCl_3$, CH_3CN and CCl_4 the high epoxidation yield is observed. By addition of the H_2O (as a protic solvent) to the CH_3CN the conversion was decreased dramatically (Fig. 5). We also tested the different reaction media to obtain the suitable oxidant media for epoxidation of the cyclooctene (Table 7). The results show that the high conversion is only obtained in the presence of the TBHP in $CHCl_3$. This may be related to the ability of the TBHP and inability of the H_2O_2 and $NaIO_4$ to mix with the organic substrate phase. Table 8 shows the cyclooctene/oxidant ratio and the effect of amount of the catalyst in epoxidation reaction of the cyclooctene by the Schiff base complexes of **1** and **2**. According to this table the 1:4 and 1:3 ratio of cyclooctene/oxidant and the 0.014 mmol of the catalysts can be chosen as the optimal amounts providing the highest epoxide yields for **1** and **2**, respectively. Table 9 shows the effect of catalyst concentration in epoxidation of cyclooctene in $CHCl_3$ as a solvent and in the presence of TBHP as an oxidant. The epoxidation reaction was carried out by using three amounts of catalysts of **1** and **2** (0.01, 0.014 and 0.02 mmol) with keeping of other conditions. According to this table it was clear that in the case of 0.014 mmol of both of catalysts the highest conversion were obtained. In this work, the stability of the vanadyl Schiff base complexes of **1** and **2** has not been studied in the optimum conditions. Thus the epoxidation of different alkenes were investigated in optimized conditions (0.014 mmol of catalysts, TBHP as an oxidant, 1:4 and 1:3 ratio of alkene/oxidant for **1** and **2** respectively and $CHCl_3$ as a solvent). The obtained results were showed in Table 10. As seen from these tables cyclic alkenes were more efficiently converted to their epoxides than linear alkenes and all alkenes selectively converted to their epoxides by **1** and **2**. In comparison, the activity of the vanadyl Schiff base complexes of **1** and **2** is lower than those vanadyl complexes that recently were reported [33, 41, 42]. Thus the naphtolate moiety have been decreased the activity of the vanadyl complexes respect to other substituted (H and OMe) salicylate moieties.

<Fig. 5 > & <Tables 7, 8, 9, 10>

Conclusion

In conclusion we readily synthesized two new oxovanadium(IV) Schiff base complexes and characterized them by spectroscopic methods as well as single crystal X-ray diffraction. The catalytic activity of the **1** and **2** complexes was investigated in the epoxidation of the alkenes. The reaction conditions were optimized and the results showed that the **1** and **2** complexes can be used as active and selective homogeneous catalysts in the epoxidation of alkenes. It seems that the naphtalate moiety decreases the activity of the vanadium center respect to the substituted salicylate (with H and OMe groups).

Appendix A. Supplementary

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Center. CCDC of 1440825 & 1440826 contains the supplementary crystallographic data for **1** and **2**. 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 or http:www.ccdc.cam.ac.uk.

Acknowledgements

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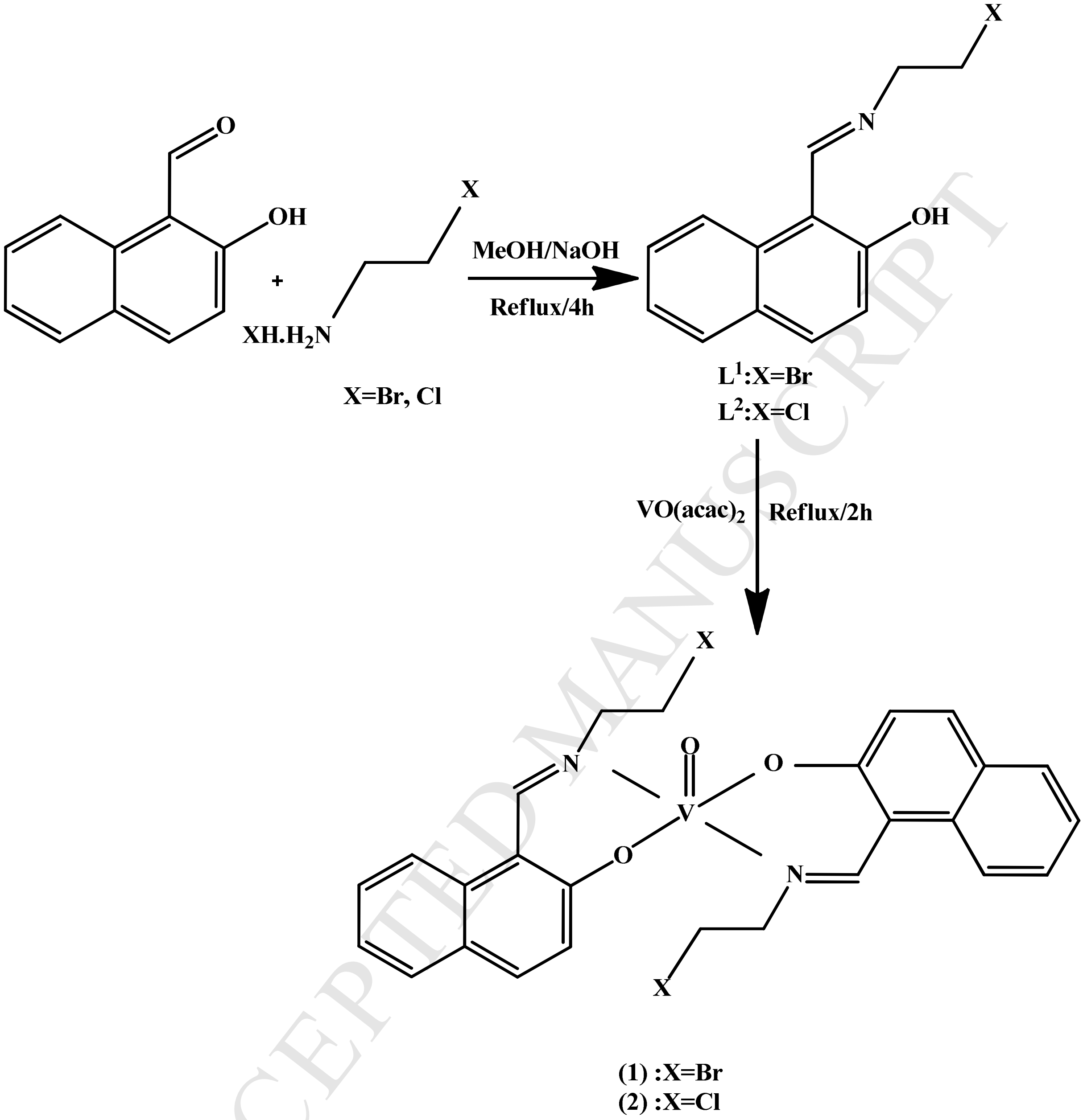
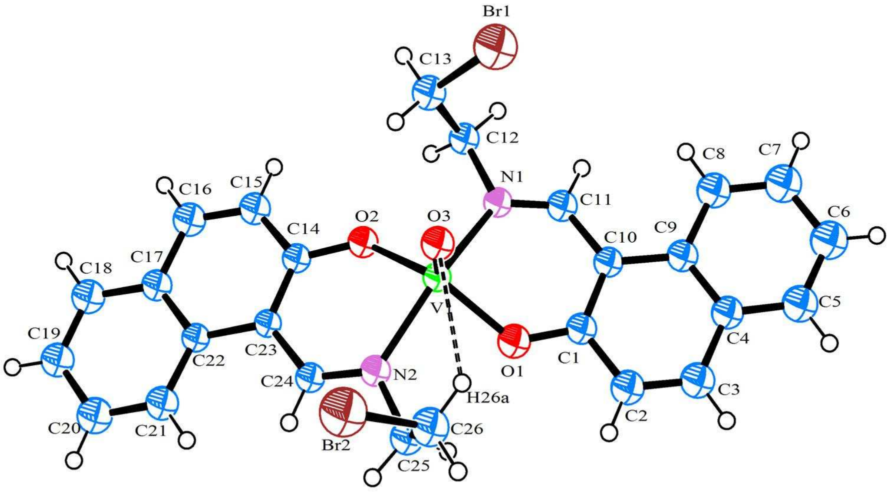


Scheme 1. Preparation procedure of the new bidentate O, N Schiff base ligands, H**L**^{1}, H**L**^{2}, and their vanadyl Schiff base complexes of **1** and **2**.



221

222 **Fig. 1.** An ORTEP view of the **1**, showing 50% probability displacement ellipsoids and the atom-numbering. Dashed lines indicate intramolecular C–H···O hydrogen bond.

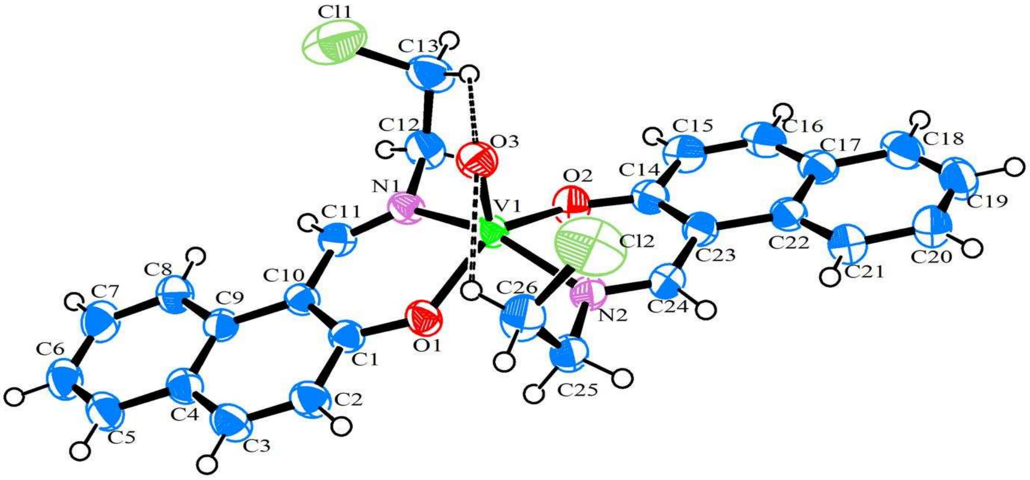


Fig. 2. An ORTEP view of the **2**, showing 50% probability displacement ellipsoids and the atom-numbering. Dashed lines indicate intramolecular C–H···O hydrogen bond.

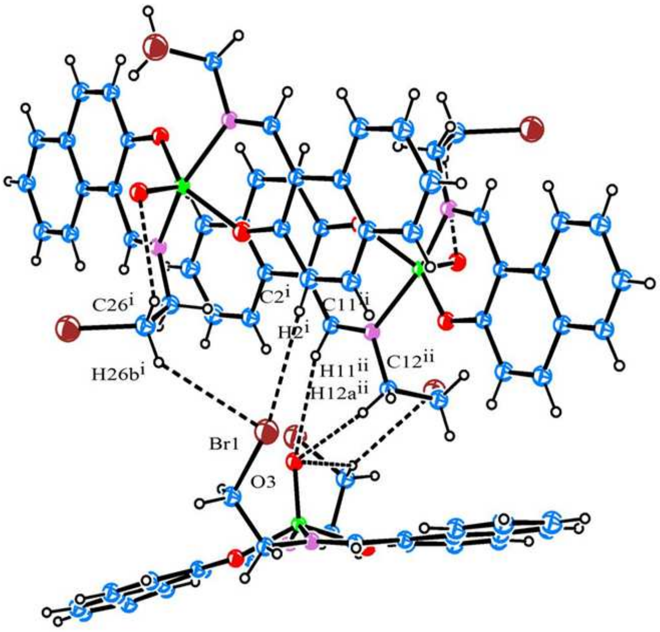


Fig. 3. Packing arrangement and hydrogen bonding for the **1**.

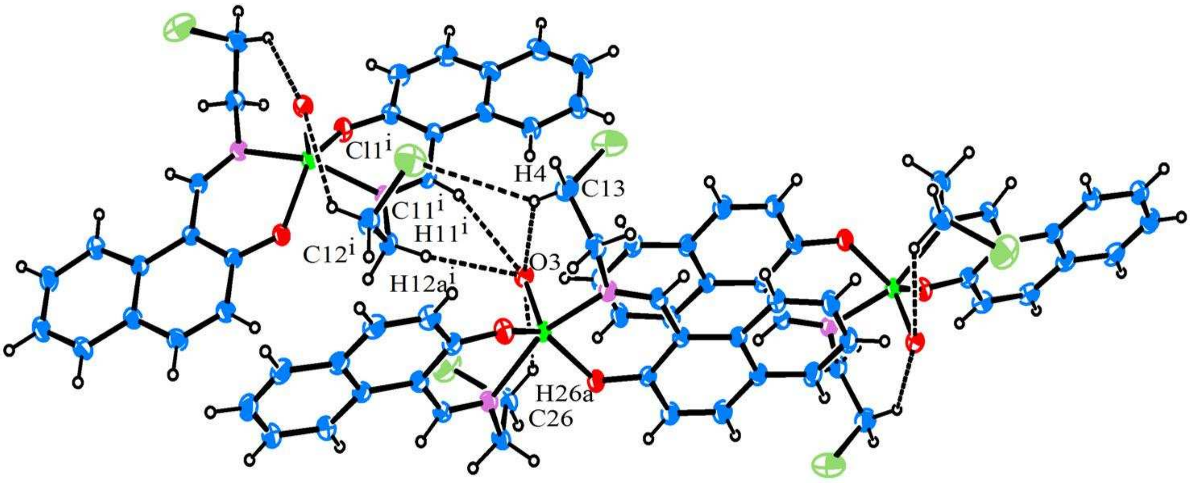


Fig. 4. Packing arrangement and hydrogen bonding for the **2**.

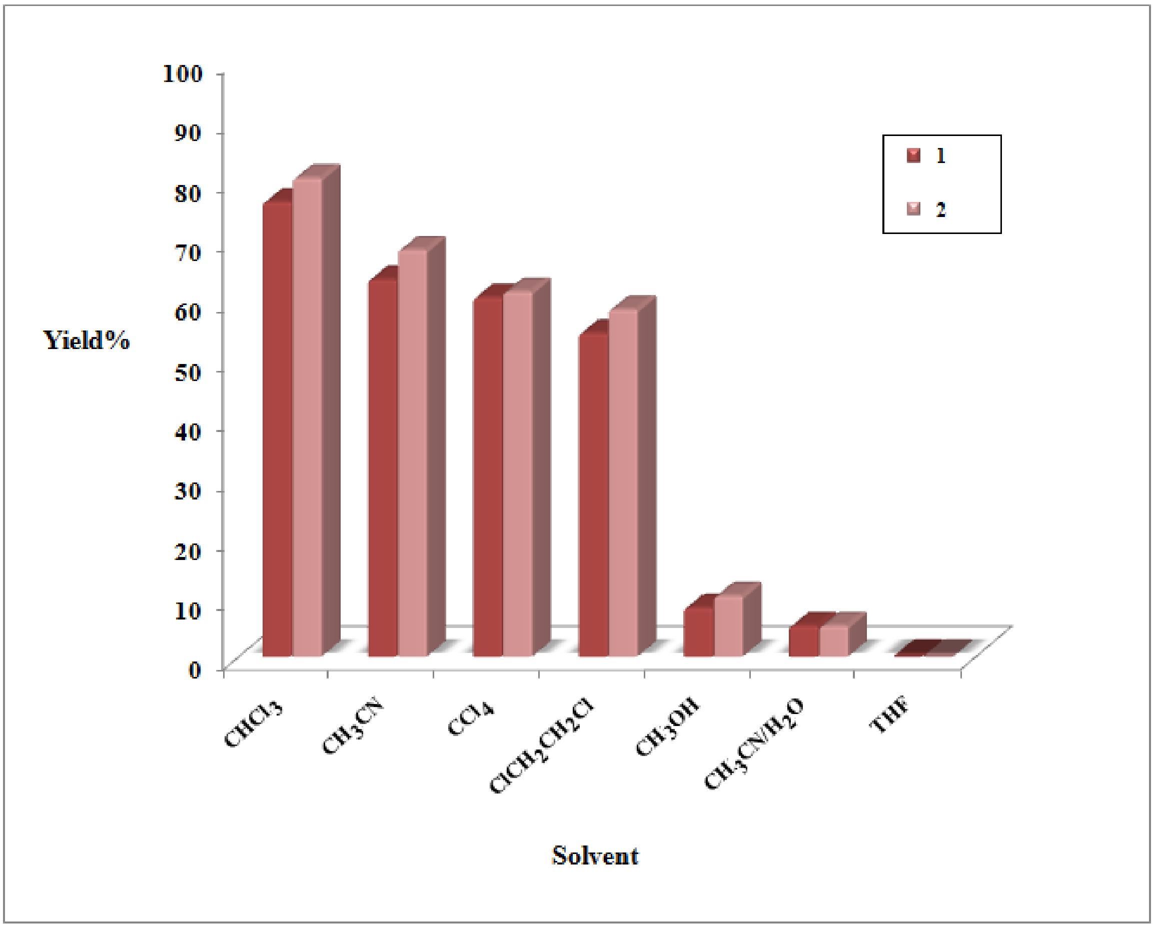


Fig 5. The catalytic epoxidation of the cyclooctene in different solvents in the presence of the TBHP by the **1** and **2** vanadyl Schiff base complexes. Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (1.5 mmol) TBHP and (0.014 mmol or 2.8× 10^{-3} M) catalyst; in neural PH .

Table 1. Crystallographic data and structure refinement for the **1** and **2**

	(1)	**(2)**
Empirical formula	$C_{26}H_{22}Br_2N_2O_3V$	$C_{26}H_{22}Cl_2N_2O_3V$
Formula weight	617.18	532.29
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	15.6158 (6)	15.5068 (4)
b (Å)	9.6941 (4)	9.7128 (3)
c (Å)	17.6582 (7)	17.6047 (4)
β(°)	115.616 (2)	115.919 (10)
V (Å^3)	2410.4 (2)	2384.8 (1)
Z	4	4
μ (mm^{-1})	3.76	0.67
R_{int}	0.053	0.040
S	1.01	1.02
F000	1220	1092
Dx(Mg m^{-3})	1.701	1.483
θ_{min} , θ_{max}	2.3, 28.00	2.60, 29.0
T (K)	296(2)	296 (2)
Independent reflections	5809	6334
Measured reflections	177339	95703
reflections with I>2σ(I)	4650	5141
Parameters	308	308
$R[F^2>2\sigma(F^2)]$	0.037	0.033
$wR(F^2)$	0.1233	0.097

$\Delta\rho_{max,}\, \Delta\rho_{min}$ ($e\text{Å}^{-3}$)	0.79, −0.78	0.49, −0.47
Index range	h;-23(23), k;-14(14), l;-26(26)	h;-21(21), k;-13(13), l;-24(24)

Table 2. The comparison of the two characteristic bands of $\nu_{C=N}$ and $\nu_{V=O}$ in the synthesized complexes(**1**, **2**) and similar vanadyl Schiff base complexes

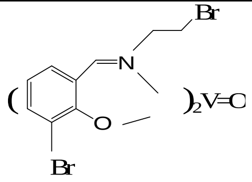
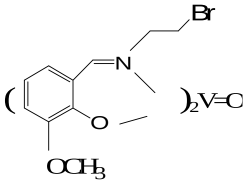
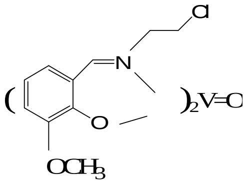
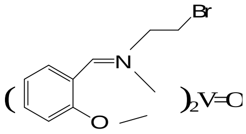
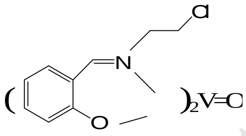
Complex	$\nu_{C=N}(cm^{-1})$		$\nu_{V=O}(cm^{-1})$	Ref
	Free Ligand	Complex		
	1636	1618	984	34
	1632	1612	982	33
	1634	1622	984	35
	1631	1620	993	41
	1640	1620	984	42
1	1630	1610	970	This research
2	1624	1604	970	This research

Table 3. Selected bond distances (Å) and angles (º) for the **1**.

V1-O1	1.913(5)	V1-N2	2.093(5)
V1-O2	1.893(5)	N1-C11	1.264(9)
V1-O3	1.600(5)	N1-C12	1.494(8)
V1-N1	2.113(5)	O1-C1	1.321(8)
O3-V1-O1	110.70(2)	O1-V1-O2	136.80(2)
O3-V1-N1	101.82(2)	N1-V1-N2	156.30(2)
O1-V1-N1	85.00(2)	V1-O1-C1	131.30(4)
C10-C11-N1	127.51(6)	V1-N1-C11	125.22(5)
C11-N1-C12	115.90(5)	C1-C10-C11	119.92(6)

Table 4. Selected bond distances (Å) and angles (º) for the **2**.

V1—O3	1.5965 (11)	V1—N2	2.1071 (12)
V1—O1	1.9051 (10)	N1—C11	1.2912 (19)
V1—O2	1.9163 (11)	N1—C12	1.4721 (19)
V1—N1	2.1005 (12)	O1—C1	1.3155 (16)
O3—V1—O1	112.42 (5)	O1-V1-O2	136.83 (5)
O3—V1—N1	101.66 (5)	N1-V1-N2	156.73 (5)
O1—V1—N1	85.63 (4)	V1-O1-C1	134.25 (9)
C10-C11-N1	127.77(6)	V1-N1-C11	125.74 (10)
C11-N1-C12	115.87 (12)	C1-C10-C11	120.46 (12)

Table 5. Geometric parameters of hydrogen bond for the **1**

D–H···A	Distance, Å			D–H···A, deg
	D–H	H···A	D···A	
C26-H26a···O3	0.971	2.632	3.339	129.95
C26^{i}-H26b^{i}···Br1	0.971	3.207	4.011	141.27
C2^{i}-H2^{i}··· Br1	0.930	3.085	3.980	162.17
C11^{ii}-H11^{ii}···O3	0.930	2.770	3.659	160.24
C12^{ii}-H12a^{ii}···O3	0.970	2.507	3.471	172.96

Table 6. Geometric parameters of hydrogen bond for the **2**

D–H· · · A	Distance, Å			D–H··A, deg
	D–H	H···A	D···A	
C26-H26a···O3	0.970	2.836	3.468	123.60
C13-H4··· O3	0.970	2.640	3.351	130.36
C13-H4···Cl1	0.970	3.158	3.925	137.23
C11^{i}-H11^{i}···O3	0.930	2.776	3.658	158.76
C12^{i}-H12a^{i}···O3	0.971	2.494	3.460	173.41

Table 7. Epoxidation of the cyclooctene in different reaction media by the oxovanadium Schiff base complexes, **1**[a] and **2**[a]

Solvent	Oxidant	Time(min)	Conversion(%)	
			(**1**)	(**2**)
$CHCl_3$	TBHP	140	76	80
$CHCl_3$	H_2O_2	140	6	12
CH_3CN/H_2O(3:2)	$NaIO_4$	140	8	12
THF	H_2O_2	140	3	6
CH_3CN	H_2O_2	140	3	6
MeOH	H_2O_2	140	No Reaction	No Reaction
CCl_4	H_2O_2	140	No Reaction	No Reaction
CH_3CN/H_2O(3:2)	H_2O_2	140	No Reaction	No Reaction

[a] Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (1.5 mmol) Oxidant and (0.014 mmol or 2.8×0^{-3}M) **1** and **2** complexes; in neutral PH.

Table 8. The effect of the alkene/oxidant ratio in the epoxidation of the cyclooctene in $CHCl_3$ as solvent by the vanadyl Schiff base complexes of **1** and **2**[a].

Time (min)	Yield%							
	Alkene/Oxidant 1:1.2		Alkene/Oxidant 1: 2		Alkene/Oxidant 1: 3		Alkene/Oxidant 1:4	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
10	12	17	8	12	9	12	10	13
20	20	25	15	25	17	21	20	26
30	25	32	23	31	26	34	25	34
40	33	40	28	34	36	42	38	47
50	38	42	32	36	45	52	48	58
60	40	45	35	40	51	56	51	63
70	43	48	45	45	58	62	56	69
80	48	52	49	48	63	67	61	73
90	51	54	56	56	65	72	68	76
100	54	57	61	58	68	75	72	80
110	58	59	65	65	70	76	75	80
120	59	60	67	67	72	77	78	81
130	60	62	68	68	74	79	79	81
140	60	62	70	71	76	80	81	81
150	60.5	63	71	72	76	80	81	80
160	60.5	63	70	72	76	80.5	81	78

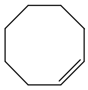
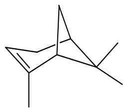
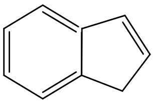
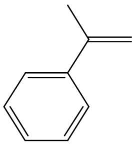
[a] Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (2 mmol, 1.5 mmol, 1 mmol and 0.6 mmol for 1:4, 1:3, 1:2 and 1: 1.2 ratios, respectively) TBHP and (0.014 mmol or 2.8×10^{-3} M) complex (**1**); in neural PH.

Table 9. The effect of the amounts of the vanadyl Schiff base complexes of **1** and **2** in epoxidation of the cyclooctene in $CHCl_3$ as solvent in the presence of the TBHP[a]

Time(min)	Yeild(%)					
	Amount of **1** catalyst (mmol)			Amount of **2** catalyst (mmol)		
	0.01	0.014	0.02	0.01	0.014	0.02
10	10	12	14	10	12	18
20	20	21	20	13	21	26
30	30	34	25	18	34	32
40	40	42	32	27	42	38
50	50	52	46	34	52	52
60	60	56	51	42	56	58
70	70	62	62	47	62	68
80	80	67	65	52	67	73
90	90	72	68	60	72	74
100	100	75	71	63	75	76
110	110	76	75	67	76	78
120	120	77	75	71	77	77
130	130	79	74	72	79	76
140	140	80	74.5	73	80	76.8
150	150	80	75	73.5	80	75.6
160	160	80.3	75	73	80.3	75

[a] Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (2 mmol) TBHP and (0.01, 0.014 and 0.02 mmol or 2×10^{-3}, 2.8×10^{-3} and 4×10^{-3} M) complex (**1**) in neutral PH.

Table 10. The epoxidation of alkenes in optimal conditions[a] in the presence of vanadyl Schiff base complexes of **1** and **2**

Alkene	Time(min)	%Conversion	
		(**1**)*	(**2**)**
	140	76	80
	300	35	38
	300	42	45
	140	70	74
	300	32	35
	320	25	30

[a] Reaction conditions: $CHCl_3$(5 ml), alkene (0.5 mmol), TBHP (2 mmol)*, (1.5 mmol)**, vanadium(IV) Schiff base catalyst (0.014 mmol or 2.8× 0^{-3}M); in neural PH.

References:

[1] N.E Borisova, M.D Reshetova, Y.A Ustynyuk, Chem. Rev. 103 (2007) 46-79.

[2] W. Radecka-Paryzek, V. Patroniak, J. Lisowski, Coord. Chem. Rev. 249 (2005) 2156-2175.

[3] J. Lv, T. Liu, S. Cai, X. Wang; L. Liu; Y. Wang, J. Inorg. Biochem. 100 (2006)1888-1896.

[4] A. Elmali, M. Kabak, Y. Elerman, J. Mol. Struct. 484 (1999) 229-234.

[5] K.B. Gudasi, S.A. Patil, R.S. Vadari, R.B. Shenoy, M.S. Patil, Transition. Met. Chem. 30 (2005) 1014-1019.

[6] M.J. Xie, X.D. Yang, W.P. Liu, S.P. Yan, Z.H. Meng, J. Inorg. Biochem. 104 (2010)851-857.

[7] L.Z. Li, Z.H. Guo, Q.F. Zhang, T.D. Xu, Q. Wang, Inorg. Chem. Commun. 13 (2010) 1166-1169.

[8] M. Sutradhar, T.R. Barman, G. Mukherjee, M.G.B. Drew, S. Ghosh, Polyhedron 34 (2012) 92-101.

[9] R.E. Berry, E.M. Armstrong, R.L. Beddoes, D. Collison, S.N. Ertok, M. Helliwell, C.D. Garner, Angew. Chem. Int. Ed. Engl. 38 (1999) 795-798.

[10] K. Kanamori, Coord. Chem. Rev. 237 (2003) 147-161.

[11] G.W. Gribble, Acc. Chem. Res. 31 (1998) 141-152.

[12] A. Butler, C.J. Carrano, Coord. Chem. Rev. 109 (1991) 61-105.

[13] P. Frank, R.M.K. Carlson, E.J. Carlson, K.O. Hodgson, Coord. Chem. Rev. 237 (2003) 31-39.

[14] R.R. Eady, Coord Chem. Rev. 237 (2003) 23-30.

[15] D. Rehder, G. Santoni, G.M. Licini, C. Schulzke, B. Meier, Coord. Chem. Rev. 237 (2003) 53-63

[16] P.J. Stankicwicz, A.S. Tracy, D.C. Crans, H.A. Sigel, Vanadiumand: its Role in Life, Met Ions Biol Syst. Marcel Dekker,New York (1995).

[17] G.L. Mendz, Arch. Biochem. Biophys. 291 (1991) 201-211

[18] M. Sutradhar, L.M.D.R.S. Martins, M. Fátima C. Guedes da Silva, A.J.L. Pombeiro, Coord. Chem. Rev. 301–302 (2015) 200–239.

[19]. S. Menati, H. Amiri Rudbari, M. Khorshidifard, F. Jalilian, J. Mol. Struct. 1103 (2016) 94-102.

[20] G. Sarmah, S.K. Bharadwaj, A. Dewan, A. Gogoi, U. Bora, Tetrahedron Lett. 55 (2014) 5029-5032.

[21] K. Kanmani Raja, L. Lekha, R. Hariharan, D. Easwaramoorthy, G. Rajagopal, J. Mole. Struct. 1075 (2014) 227-233.

[21] P.M. Reis, J.A.L. Silva, J.J.R. Frausto da Silva, A.J.L. Pombeiro, J. Mol. Cata.l A. 224 (2004) 189-195.

[22] C.X. Yin, R.G. Finke, J. Am. Chem. Soc. 127 (2005) 9003-9013

[23] A.G. Ligtenbarg, J.R. Hage, B.L. Feringa, Coord. Chem. Rev. 237 (2003) 89-101.

[24] L.G. Cuervo, Y.N. Kozlov, G. Süss-Fink, G.B. Shul’pin, J. Mol. Catal A. 218 (2004) 171-177.

[25] a) A.A. Nejo, G.A. Kolawole, A.R. Opoku, C. Muller, J. Wolowska, J. Coord. Chem. 62 (2009) 3411-3424 b) M.A. Fik, A. Gorczyński, M. Kubicki, Z. Hnatejko, A. Wadas, P.J. Kulesza, A. Lewińska, M. Giel-Pietraszuk, E. Wyszko ,V. Patroniak, Polyhedron 97 (2015) 83–93.

[26] a) A.A. Nejo, G.A. Kolawole, A.R. Opoku, J. Wolowska, P. O’Brien, Inorg. Chim. Acta. 362 (2009) 3993-4001 b) D.C. Crans, J. Org. Chem. 80 (2015) 11899–11915.

[27] a) M. Sutradhar, G. Mukherjee, M. Kar, S.S. Saha, M.G.B. Drew, S. Ghosh, Inorg. Chim. Acta. 368 (2011) 13-20 b) M. Xie, D. Chen, F. Zhang, G.R. Willsky, D.C. Crans, W. Ding, J. Inorg. Biochem. 136 (2014) 47–56

[28] a) S.Y. Ebrahimipour, I. Sheikhshoaie, A.C. Kautz, M. Ameri, H. Pasban-Aliabadi, H. Amiri Rudbari, G. Bruno, C. Janiak, Polyhedron, 93 (2015) 99-105 b) A, Sinha, K. Banerjee, A. Banerjee, S. Das, S.K. Choudhuri, J. Organomet. Chem. 772–773 (2014) 34–41 c) Q. Guo, L. Li , J. Dong, H. Liu, T. Xu, J. Li, Spectrochim. Act. A. 106 (2013) 155–162.

[29] a) E. Kioseoglou, S. Petanidis, C. Gabriel, A. Salifoglou, Coord. Chem. Rev. 301–302 (2015) 87-105 b) Y. Cao, C. Yi, H. Liu, H. Li, Q. Li, Z. Yuan, G. Wei, Trans. Met. Chem.(2016) 1-8.

[30] a) A.A. Abou-Hussein, W. Linert, Spectrochim. Act A. 141 (2015) 223–232 b) M.K. Sahani, S.K. Pandey, O.P. Pandey, S.K. Sengupta, J. Mol. Struct. 1074 (2014) 401–407.

[31] a) O.M.I. Adly, A. Taha, S.A. Fahmy, J. Mole. Struct. 1083 (2015) 450-459 b) C. Datta, D. Das, P. Mondal, B. Chakraborty, M. Sengupta, C.R. hattacharjee, Eur. J. Med. Chem. 97 (2015) 214–224.

[32] G. Grivani, A. Ghavami, M. Kuceráková, M. Dušek, A. D. Khalaji, J. Mol. Struct. 1076 (2014) 326–332.

[33] G. Grivani, V. Tahmasebi, A.D. Khalaji, V. Eigner, M. Dušek, J. Coord. Chem. 67 (2014) 3664-3677.

[34] G. Grivani, V. Tahmasebi, A.D. Khalaji, Polyhedron 68 (2014) 144-150.

[35] G. Grivani, V. Tahmasebi, A.D. Khalaji, K. Fejfarovác, M. Dušek, polyhedron 51 (2013) 54-60.

[36] M.C. Burla, M. Camalli, B. Carrozzini, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 36 (2003) 1103.

[37] V. Petricek, M. Dusek, L. Palatinus, Jana2006. Structure determination software programs. Institute of Physics, Praha,Czech Republic (2008).

[38] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[39] R. Ando, S. Mori, M. Hayashi, T. Yagyu, M. Maeda, Inorg. Chim. Acta. 357 (2004) 1177-1184.

[40] C.J. Chang, J.A. Labinger, H.B. Gray, Inorg. Chem. 36 (1997) 5927- 5930.

[41] G. Grivani, A.D. Khalaji, V. Tahmasebi, K. Gotoh , H. Ishida, Polyhedron 31 (2012) 265-271

[42] G. Grivani, G. Bruno, H.A. Rudbari, A.D. Khalaji, P. Pourteimouri, Inorg. Chem. Commun. 18 (2012) 15-20.

[43] K. Fujiwara, T. Ishida, Polyhedron 30 (2011) 3073-3078.

[44] J. Rahchamani, M. Behzad, A. Bezaatpour, V. Jahed, G. Dutkiewicz, M. Kubicki, M. Salehi, Polyhedron 30 (2011) 2611-2618.

[45] M.P. Weberski, C.C McLauchlan, C.G Hamaker, Polyhedron 25 (2006) 119-123.

[46] S. Rayati, M. Koliaei, F. Ashouri, S. Mohebbi, A. Wojtczak, Appl. Catal A. 346 (2008) 65-71.

[47] M.R. Maurya, H. Saklani, S. Agarwal, Catal. Commun. 5 (2004) 563-568.

- Two new vanadium (IV) Schiff base complexes, $VO(L^1)_2$,$VO(L^2)_2$, were synthesized
- They were characterized by X-ray, CHN analysis and FT-IR and UV-Vis spectroscopy
- X-ray crystallography showed the distorted square pyramidal geometries
- The catalytic activity of them investigated in epoxidation of alkenes
- The naphtalate moiety shows lower activity than the other substituted moieties