Inorganic Chemistry Communications 18 (2012) 15–20

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Synthesis, characterization and crystal structure determination of a new oxovanadium(IV) Schiff base complex: The catalytic activity in the epoxidation of cyclooctene

Gholamhossein Grivani [a,*], Giuseppe Bruno [b], Hadi Amiri Rudbari [b],
Aliakbar Dehno Khalaji [c], Pegah Pourteimouri [a]

[a] School of Chemistry, Damghan University, Damghan, 36715-364, Iran
[b] Dipartimento di Chimica Inorganica, Vill. S. Agata, Salita Sperone 31, Università di Messina, 98166 Messina, Italy
[c] Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran

ARTICLE INFO

Article history:
Received 18 October 2011
Accepted 29 December 2011
Available online 12 January 2012

Keywords:
Vanadyl Schiff base complex
Crystal structure
Square pyramidal
Catalytic activity
Epoxidation

ABSTRACT

A new oxovanadium(IV) Schiff base complex, $V^{IV}OL_2$ (**1**), was prepared by the reaction of a bidentate Schiff base ligand **L** and $VO(acac)_2$ (**L** = *N*-salicylidin-2-chloroethylimine). The Schiff base ligand, **L**, and its oxovanadium(IV) complex, **1**, were characterized by the elemental analysis (CHN) and FT-IR spectroscopy. In addition, ^{1}H-NMR was employed for characterization of the ligand. The crystal structure of **1** was determined by the single crystal X-ray analysis. The Schiff base ligand **L** acts as a chelating ligand and coordinates via one nitrogen and one oxygen atom to the vanadium center. The complex **1** crystallizes in the monoclinic system, with space group $P2_1/n$, having one symmetry-independent V^{4+} ion coordinating in an approximately square pyramidal N_2O_3 geometry by two imine nitrogen, two phenolato oxygen atoms from two Schiff base ligands in a square plane and one oxygen atom in an apical position. The catalytic activity of the complex **1** was tested in the epoxidation of cyclooctene. The results showed that the complex **1** was highly active and selective catalyst in optimized conditions in the epoxidation of cyclooctene.

Schiff base compounds, the aldehyde- or ketone analogs in which the carbonyl group is replaced by an imine or azomethine group, are considered privileged ligands, because of their simple preparation in an one-pot condensation of aldehydes (or ketones) and primary amines in an alcohol solvent. The metal complexes of them have been extensively investigated for more than a century and employed in different aspects including biological studies [1–6], magneto chemistry [7], non-linear optics [8], photo physical studies [9], catalysis [10], materials chemistry [11], chemical analysis [12], absorption and transport of oxygen [13]. In the past two decades the coordination chemistry of vanadium and specifically the Schiff base complexes of oxovanadium(IV) and dioxovanadium(V) with N, O and S-donor chelating ligands has received considerable attention due to its vital roles in a variety of biochemical processes such as haloperoxidation [14], phosphorylation[15], insulin mimicking [16–18], nitrogen fixation[19], tumor growth inhibition and prophylaxis against carcinogenesis [20].

The epoxidation of alkenes is one of the most widely studied reactions in organic chemistry since epoxides are key starting materials for a wide variety of products. The catalytic epoxidation of olefins by transition metal complexes is an area of intense research activity [21,22]. Recently a large number of publications, described the synthesis, structural study and catalytic activity of oxovanadium Schiff base complexes in oxidation of various organic substrates [23–25]. Essentially in all these complexes the metal center is surrounded by N O coordination environment. We started to the synthesis and characterization of a series of new bidentate (NO) Schiff base ligands by the condensation of alkylammonium halides with various s salicylaldehyde derivatives and their metal complexes to investigate the catalytic and biological activities of them. In this research we report the synthesis, characterization and crystal structure determination of a new oxovanadium(IV) Schiff base complex containing chloroethyl chain and its catalytic activity in epoxidation of cyclooctene.

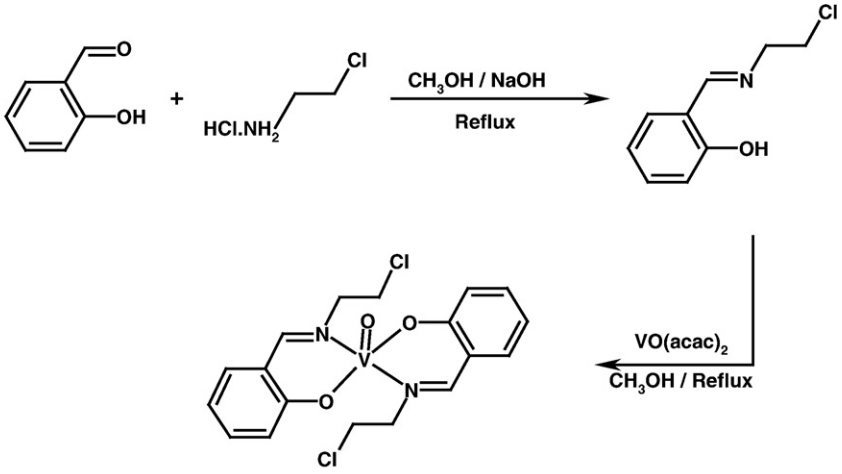
By reaction of salicylaldehyde and 2-chloroethyl ammonium hydrochloride in refluxing methanol the Schiff base ligand **L** (Scheme 1) was prepared [26]. The ligand **L** salts were previously described in ref [27]. The new VOL_2 Schiff base complex, **1**, was also prepared by the simple reaction of $VO(acac)_2$ and **L** (Scheme 1) in refluxing methanol [28]. The Schiff base ligand **L** and its vanadyl complex were characterized by the elemental analysis (CHN) and FT-IR spectroscopy. The results of CHN analysis confirmed the chemical composition of **L** and **1**.

The FT-IR spectrum of **L** shows a sharp band in the 1640 cm^{-1}, attributed to the stretching vibration frequency of imine (–C═N–). In

---

[*] Corresponding author. Tel./fax: +98 2325235431.
E-mail address: grivani@du.ac.ir (G. Grivani).

1387-7003/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2011.12.044



Scheme 1. Preparation procedures of Schiff base ligand, **L**, and its Oxovanadium(IV) complex, **1**.

the FT-IR spectrum of **1**, this band shifts to the lower wave number, 1620 cm^{-1}, indicating the coordination of azomethine to the vanadium(IV) center. Another characteristic of the FT-IR spectrum of **1** is the exhibition of a sharp band in the 984 cm^{-1}, corresponding to the V═O stretching vibration. The appearance of a band in this region indicates the existence of monomeric five coordinated V═O units instead of the polymeric ···V═O···V═O··· units [29–31]. This is approved by the single crystal structure determination of the VO**L**$_2$ (Fig. 1).

The molecular structure of **1** with the atom-numbering scheme is presented in Fig. 1. The crystallographic data revealed that the vanadium (IV) ion was surrounded by two oxygen and two nitrogen atoms from two Schiff base ligands and one oxygen atom from an oxo ligand in the five-coordinated geometry. The two ligands coordinate to the vanadium center in *trans* geometry with respect to each other. The geometry around the vanadium(IV) ion is a distorted square-pyramid, as indicated by the unequal metal-ligand bond distances and angles: i.e. V–O1 = 1.8968(15), V–O2 = 1.9131(14), V–N1 = 2.1079(16), V–N2 = 2.1085(16) and V–O3 = 1.5925(15) Å and O(3)–V–O(1) = 112.24(8), O(3)–V–O(2) = 111.12(8), O(1)–V–O(2) = 136.63(8), O(3)–V–N(1) = 99.64(7), O(1)–V–N(1) = 87.00(7), O(2)–V–N(1) = 86.73(7), O(3)–V–N(2) = 100.31(7), O(1)–V–N(2) = 84.84(7), O(2)–V–N(2) = 86.77(6) and N(1)–V–N(2) = 160.04(7)°. All distances and angles in **1** agree well with the same distances in other vanadium (IV) complexes [32–35]. Molecular packing of the **1** can be viewed molecules held together by non-classical C–H···O intermolecular hydrogen bonds (Fig. 2, Table 1).

The catalytic activity of the new vanadyl Schiff base complex VO**L**$_2$ (**1**) was tested in the epoxidation of cyclooctene [36]. Different parameters such as the effect of solvent, oxidant, catalyst amount and the alkene/oxidant ratio were studied in the epoxidation of cyclooctene. Fig. 3 and Table 2 show the results of the catalytic activity of **1** in the epoxidation of cyclooctene in different solvents in the presence of tert-butylhydroperoxide (TBHP). As it is seen, the catalytic activity of **1** in CHCl$_3$ and CCl$_4$, with low coordination ability, is higher than in MeOH, THF, CH$_3$CN and H$_2$O/CH$_3$CN with high coordination ability. The different reaction media were used to obtain the suitable oxidant in the epoxidation of cyclooctene (Table 3). The high yield was obtained in the presence of TBHP in CHCl$_3$. Then the alkene/oxidant

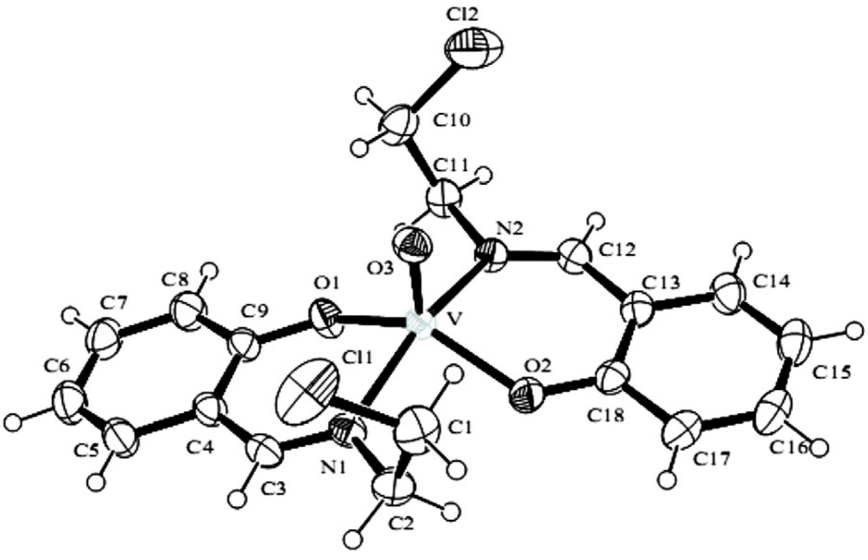


Fig. 1. Molecule of **1**, showing the atom numbering schemes. Displacement ellipsoids are drawn at the 50% probability level.

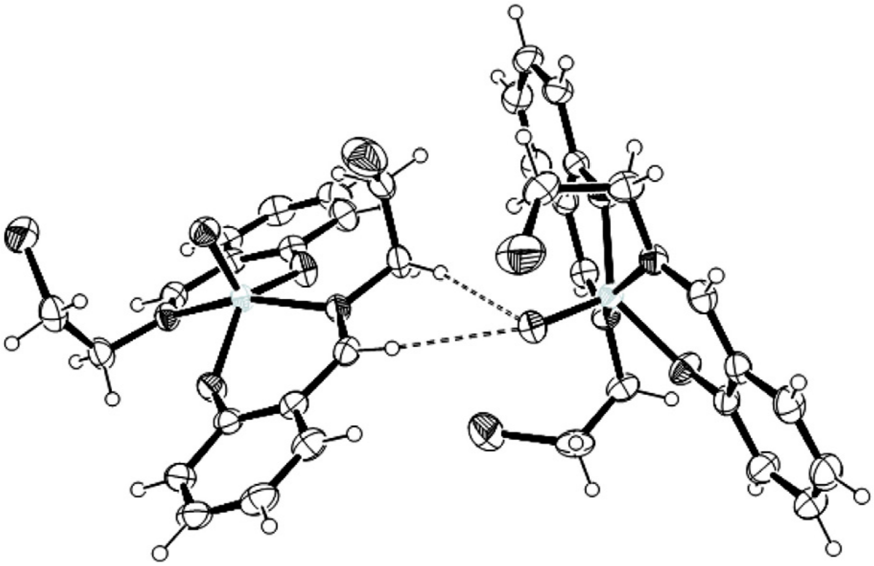


Fig. 2. Crystal packing of **1**, showing inter-molecular hydrogen bonds (dashed lines).

ratio was also investigated (Fig. 4 and Table 4). Among the 1:4, 1:3 and 1:2 ratios, the 1:3 ratio showed the maximum epoxidation yield. We also checked the effect of changing the amount of Schiff base complex **1** on the epoxidation of cyclooctene(Table 5). Three amounts of **1** (0.009, 0.013 and 0.019 mmol) were used in the epoxidation of cyclooctene in $CHCl_3$ in the presence of TBHP but the maximum epoxidation yield was made by 0.013 mmol of **1** (Fig. 5). In conclusion the catalytic activity and selectivity of the vanadyl Schiff base complex **1** in optimized conditions with TON of 32 (mol of cycloocten converted by mol of catalyst) is high (84% conversion and 100% cyclooctene epoxide yield).

Recently the catalytic activities of some five coordinated oxovanadium(IV) Schiff base complexes (VOL) with teradentate N_2O_2 or tridentate NO_2 ligands in cyclooctene epoxidation reaction were investigated [37–39]. The investigation results of Rahchamani et al. in the catalytic activities of some oxovanadium(IV) Schiff base complexes in cyclooctene epoxidation reaction with TBHP and H_2O_2 in CH_3CN showed the higher conversion of cyclooctene by the TBHP than H_2O_2 with the 58% conversion as the highest conversion [37]. Monfared et al. observed the trend: $CH_3CN > MeOH > EtOH > THF > (CH_3)_2CO > CHCl_3 > MeCOEt > CCl_4 > DMF$ in investigation of the catalytic activities of three oxovanadium hydrazone Schiff base complexes in epoxidation of the cyclooctene with H_2O_2 in these solvents [38]. Rayati et al. [39] have also investigated the catalytic activities of two oxovanadium(IV) Schiff base complexes in cyclooctene epoxidation reaction with TBHP by using Chloroform, acetonitrile and dichloromethane as solvent and obtained the highest conversion (94–95%) in the chloroform. In summary based on the results of these researches the high epoxidation yield by related oxovanadium Schiff base complexes in the presence of TBHP is obtained in the solvents CCl_4 and $CHCl_3$ that our results consist with them.

Recently we have investigated the catalytic activity of the oxovanadium(IV) Schiff base complex similar to **1** in that the ethyl chloride chain was substituted with ethyl bromide and observed the similar trend in the solvent effect of cyclooctene epoxidation reaction [40]: $CCl_4 > CHCl_3 > CH_3CN > CH_3CN/H_2O > THF > MeOH$. But in this research the activity of Schiff base complex **1** in $CHCl_3$ is higher than in CCl_4. Thus it seems that the substitution of the ethyl bromide chain with ethyl chloride inverses (or decreases) the catalytic activity of the Schiff base complex **1** in CCl_4 respect to the $CHCl_3$.

The mechanistic aspects of the epoxidation reaction of oxovanadium complexes were reviewed recently by Conte et al. [41]. The proposed mechanism of epoxidation reaction by oxovanadium (IV) Schiff base complex **1** in the presence of TBHP was showed in Scheme 2. It is established that in epoxidation reaction catalyzed by oxovanadium complexes in the presence of TBHP the active species are the **II** [41]. The titration curve of Schiff base complex **1** ($VO\mathbf{L}_2$) with TBHP was monitored by electronic absorption spectroscopy. These spectral

Table 1
Experimental hydrogen bond geometries (Å, °) of **1**.

D-H···A	D-H	H···A	D···A	D-H···A
C11═H11a···O3	0.970	2.441	3.395	167.491
C12═H12···O3	0.931	2.564	3.446	158.373

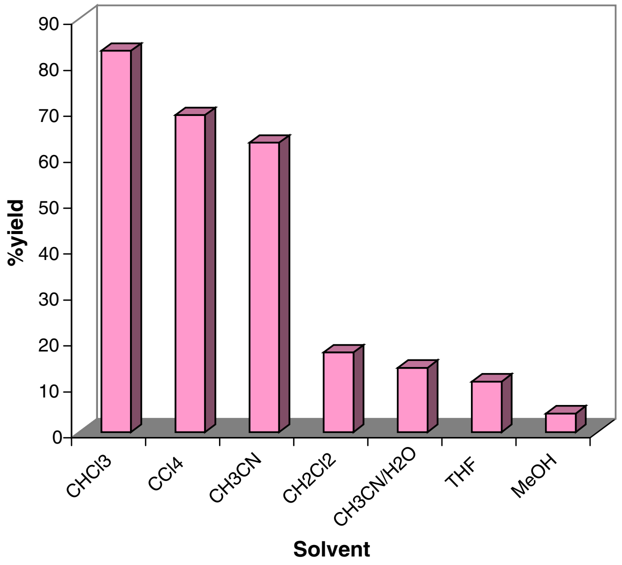


Fig. 3. The catalytic epoxidation of cyclooctene in different solvents in the presence of TBHP by the vanadyl Schiff base complex **1** in the reflux conditions. Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (1.5 mmol) oxidant and (0.013 mmol) complex **1**.

Table 2
The solvent effect on the catalytic epoxidation of cyclooctene in the presence of TBHP by the vanadyl Schiff base complex **1** in the reflux conditions[a].

Solvent	Time (min)	% Conversion
$CHCl_3$	240	84
CCl_4	240	69
CH_3CN	240	63
CH_2Cl_2	240	17.5
CH_3CN/H_2O(3:2)	240	14
THF	240	11
MeOH	240	4

Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (1.5 mmol) oxidant and (0.013 mmol) complex **1**.

[a] Reaction conditions.

Table 3
Epoxidation of cyclooctene in the presence of different oxidants by the vanadyl Schiff base complex **1** in different conditions by **1**.[a]

Solvent	Oxidant	Time (min)	% conversion[b]
CH_3CN/H_2O (3:2)	H_2O_2	240	19
CCl_4	H_2O_2	240	No reaction
MeOH	H_2O_2	240	7
$CHCl_3$	H_2O_2	240	1
THF	H_2O_2	240	No reaction
CH_3CN	H_2O_2	240	No reaction
CH_3CN/H_2O (3:2)	$NaIO_4$	240	6
$CHCl_3$	TBHP	240	84

[a] Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, oxidant, (1.5 mmol), and (0.013 mmol) complex **1.**

[b] Based on GLC.

changes are presented in Fig. 6. The titration of a solution of the oxovanaduim(IV) Schiff base complex **1** (VOL_2) in chloroform (ca. 10^{-4} M solution) by addition of 5 μl of TBHP resulted in slow decreasing of intensity of the band at 352 nm and gradual appearance of two new bands in 328 and 305 nm and increasing of the intensities of these new bands by continuation of titration. At the end of titration the band at 352 nm was disappeared. At the same time, the bands appearing at 591 and 529 nm due to the d–d transitions of $[V^{IV}OL_2]$ slowly disappeared upon addition of TBHP. In similar to the results observed in the literature [42–44], these spectral changes and the presence of an isosbestic point at 337 nm suggest the oxidation of V^{IV} and the interaction of the vanadium(V) complex formed with TBHP, to give oxoperoxovanadium(V) species. In addition the FT-IR spectrum of the complex at the end of the epoxidation reaction of cyclooctene in chloroform in the presence of TBHP resulted in disappearing of the band at 984 cm^{-1} due to $V^{IV}{=}O$ stretching vibration frequencies and appearing of a new band at 1018 cm^{-1} that attributed to $V^{V}{=}O$ stretching vibration frequencies due to the formation of $V^{V}{=}O$ in species such as **II**.

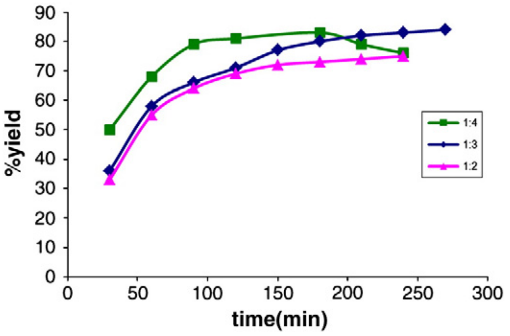


Fig. 4. The effect of alkene/oxidant ratio in the epoxidation of cyclooctene in $CHCl_3$ as solvent by the vanadyl Schiff base complex **1** in the reflux conditions. Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (2 mmol, 1.5 mmol and 1 mmol for 1:4, 1:3 and 1:2 ratios, respectively) oxidant and (0.013 mmol) complex **1**.

Table 4
The effect of alkene/oxidant ratio in the epoxidation of cyclooctene in $CHCl_3$ as solvent by the vanadyl Schiff base complex **1** in the presence of the TBHP in the reflux conditions[a].

Run	Solvent	Time (min)	% conversion		
			1:2[b]	1:3[b]	1:4[b]
1	$CHCl_3$	30	33	36	50
2	$CHCl_3$	60	55	58	68
3	$CHCl_3$	90	64	66	79
4	$CHCl_3$	120	69	71	81
5	$CHCl_3$	150	72	77	–
6	$CHCl_3$	180	73	80	83
7	$CHCl_3$	210	74	82	79
8	$CHCl_3$	240	75	83	76
9	$CHCl_3$	270	75	84	76

Reation conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (2 mmol, 1.5 mmol and 1 mmol for 1:4, 1:3 and 1:2 ratios, respectively) oxidant and (0.013 mmol) complex **1.**
Alkene/oxidant ratio.

[a] Reaction conditions.

[b] Alkene/oxidant ratio.

Table 5
The effect of the amount of the vanadyl Schiff base complex **1** in the epoxidation of cyclooctene in $CHCl_3$ as solvent in the presence of the TBHP in reflux conditions[a].

Run	Solvent	Time (min)	% conversion		
			0.009[b]	0.013[b]	0.019[b]
1	$CHCl_3$	30	26	36	46
2	$CHCl_3$	60	47	58	68
3	$CHCl_3$	90	60	66	71
4	$CHCl_3$	120	67	71	76
5	$CHCl_3$	150	73	77	79
6	$CHCl_3$	180	76	80	80
7	$CHCl_3$	210	79	82	79
8	$CHCl_3$	240	–	83	–
9	$CHCl_3$	270	–	84	–

Reaction conditions: (5 ml) solvent, (0.5 mmol)cyclooctene, (1.5 mmol) oxidant and (0.019, 0.013 and 0.009 mmol) complex **1.**
mmol of catalyst.

[a] Reaction conditions.

[b] mmol of catalyst.

The observed trend in Fig. 3 for solvent effect also agrees with this mechanism. As the coordination ability of the solvent is increased, the solvent binding instead of TBHP binding to vanadium center is also increased and the formation of species **III** is prevented and retarded the progress of epoxidation reaction.

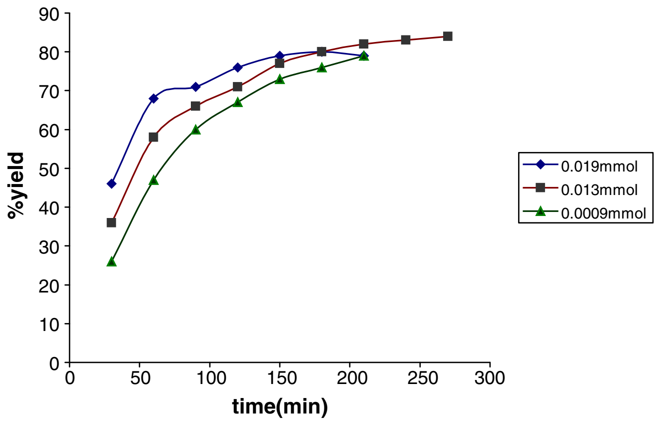


Fig. 5. The effect of the amounts of the vanadyl Schiff base complex **1** in the epoxidation of cyclooctene in $CHCl_3$ as solvent in reflux conditions. Reaction conditions: (5 ml) solvent, (0.5 mmol) cyclooctene, (1.5 mmol) oxidant and (0.019, 0.013 and 0.009 mmol) complex **1**.

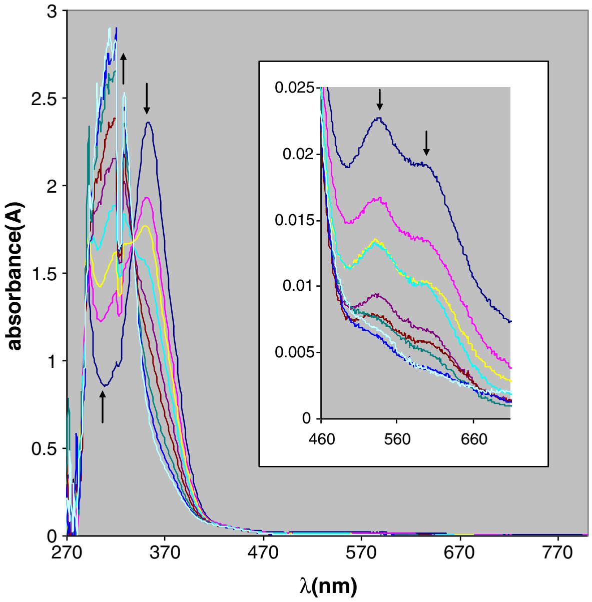


Fig. 6. UV–vis spectral changes observed during titration of the $V^{IV}OL_2$ Schiff base complex with TBHP. The spectra were recorded after successive additions of 5 μl of TBHP to 10 ml a ca. 10^{-4} M solution of $V^{IV}OL_2$ in chloroform.

In conclusion we synthesized the new oxovanadium(IV) Schiff base complex VO**L**$_2$ (**1**) containing chloroethyl chain. The single crystal X-ray analysis showed that the V(IV) placed in a distorted five coordinated square pyramidal N_2O_3 geometry. The catalytic activity of complex **1** was tested in the epoxidation of cyclooctene. The results showed that the vanadyl Schiff base complex **1** was very active and selective in the epoxidation of cyclooctene in the optimized conditions.

Acknowledgments

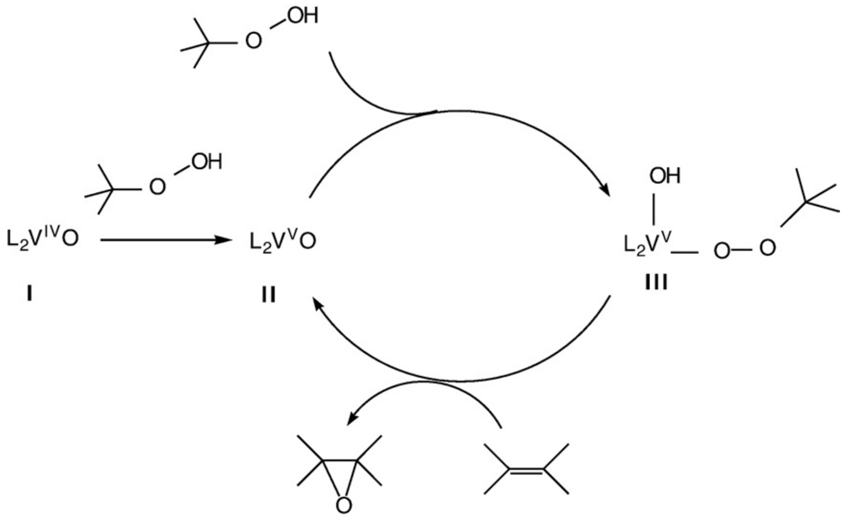
We acknowledge the Damghan University (DU) for partial support of this work.

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 846793. 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.

References

[1] M. Rajasekar, S. Sreedaran, R. Prabu, V. Narayanan, R. Jegadeesh, N. Raaman, A.K. Rahiman, Synthesis, characterization, and antimicrobial activities of nickel(II) and copper(II) Schiff-base complexes, J. Coord. Chem. 63 (2010) 136–146.
[2] S.M. Abdallah, G.G. Mohamed, M.A. Zayed, M.S. Abou El-Ela, Spectroscopic study of molecular structures of novel Schiff base derived from o-phthaldehyde and 2-aminophenol and its coordination compounds together with their biological activity, Spectrochim. Acta. A 73 (2009) 833–840.
[3] C.J. Dhanaraj, M.S. Nair, Synthesis, characterization, and antimicrobial studies of some Schiff-base metal(II) complexes, J. Coord. Chem. 62 (2009) 4018–4028.
[4] M.S. Karthikeyan, D.J. Parsad, B. Poojary, K.S. Bhat, B.S. Holla, N.S. Kumari, Synthesis and biological activity of Schiff and Mannich bases bearing 2,4-dichloro-5-fluorophenyl moiety, Bioorg. Med. Chem. 14 (2006) 7482–7489.
[5] P. Panneerselvam, R.R. Nair, G. Vijayalakshmi, E.H. Subramanian, S.K. Sridhar, Synthesis of Schiff bases of 4-(4-aminophenyl)-morpholine as potential antimicrobial agents, Eur. J. Med. Chem. 40 (2005) 225–229.
[6] C. Wang, X. Wu, S. Tu, B. Jiang, Syntheses and crystal structures of two Schiff base copper(II) complexes with urease inhibitory activity, Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 39 (2009) 78–82.
[7] K.S. Murray, The magnetochemistry of homo-and hetero-tetranuclear first-row *d*-block complexes, Adv. Inorg. Chem. 43 (1995) 261–358.
[8] A. Houlton, N. Jasim, R.M.G. Roberts, J. Silver, D. Cunningham, P. McArdle, T. Higgin, Molecular materials containing donor and acceptor groups: synthesis, structure and spectroscopic properties of ferrocenyl Schiff bases, J. Chem. Soc. Dalton Trans. (1992) 2235–2241.
[9] J.W. Lu, Y.H. Huang, S.I. Lo, H.H. Wei, New μ-oxo-bridged tetranuclear Cu(II) complex with Schiff-base ligand: synthesis, crystal structure and magnetic properties, Inorg. Chem. Commun. 10 (2007) 1210–1213.
[10] S. Di Bella, Fragala, I, Two-dimensional characteristics of the second-order nonlinear optical response in dipolar donor–acceptor coordination complexes, New J. Chem. 26 (2002) 285–290.
[11] P.G. Cozzi, L.S. Dolci, A. Garelli, M. Montalti, L. Prodi, N. Zaccheroni, Photo physical properties of Schiff-base metal complexes, New J. Chem. 27 (2003) 692–697.
[12] N.C. Gianneschi, S.T. Nguyen, C.A. Mirkin, Signal amplification and detection via a supramolecular allosteric catalyst, J. Am. Chem. Soc. 127 (2005) 1644–1645.
[13] G.A. Morris, H. Zhou, C.L. Stern, S.T. Nguyen, A general high-yield route to bis(salicylaldimine) zinc(II) complexes: application to the synthesis of pyridine-modified salen-type zinc(II) complexes, Inorg. Chem. 40 (2001) 3222–3227.
[14] A. Butler, J.V. Walker, Marine haloperoxidases, Chem. Rev. 93 (1993) 1937–1944.
[15] C.R. Cornman, E.P. Zovinka, M.H. Meixner, Vanadium(IV) complexes of an active-site peptide of a protein tyrosine phosphatase, Inorg. Chem. 34 (1995) 5099–5100.
[16] P. Noblı 'a,, M. Vieites, B.S. Parajo 'n-Costa, E.J. Baran, H. Cerecetto, P. Draper, M. Gonza 'lez, O.E. Piro, E.E. Castellano, A. Azqueta, A.L. Cera 'in, A. Monge-Vega, D. Gambino, Vanadium(V) complexes with salicylaldehyde semicarbazone derivatives bearing in vitro anti-tumor activity toward kidney tumor cells (TK-10): crystal structure of [V^VO_2(5-bromosalicylaldehyde semicarbazone)], J. Inorg. Biochem. 99 (2005) 443–451.
[17] Y. Shechter, I. Goldwaser, M. Mironchik, M. Fridkin, D. Gefel, Historic perspective and recent developments on the insulin-like actions of vanadium; toward developing vanadium-based drugs for diabetes, Coord. Chem. Rev. 237 (2003) 3–11.



Scheme 2. The proposed mechanism for the epoxidation of alkenes by the oxovanadium complex VO**L**$_2$(**1**) in the presence of TBHP.

[18] A.M.B. Bastos, J.G. da Silva, P.I.S. Maia, V.M. Deflon, A.A. Batista, A.V.M. Ferreira, L.M. Botion, E. Niquet, H. Beraldo, Oxovanadium(IV) and (V) complexes of acetylpyridine-derived semicarbazones exhibit insulin-like activity, Polyhedron 27 (2008) 1787–1794.

[19] R.R. Eady, Current status of structure function relationships of vanadium nitrogenase, Coord. Chem. Rev. 237 (2003) 23–30.

[20] K.H. Thompson, J.H. McNeill, C. Orvig, Vanadium compounds as insulin mimics, Chem. Rev. 99 (1999) 2561–2572.

[21] S.L. Benjamin, K. Burgess, Metal-catalyzed epoxidations of alkenes with hydrogen peroxide, Chem. Rev. 103 (2003) 2457–2474.

[22] K.A. JØrgensen, Transition-metal-catalyzed epoxidations, Chem. Rev. 89 (1989) 431–458.

[23] M.R. Maurya, S. Sikarwar, M. Kumar, Oxovanadium(IV) complex of β-alanine derived ligand immobilised on polystyrene for the oxidation of various organic substrates, Catal. Commun. 8 (2007) 2017–2024.

[24] C. Bolm, Vanadium-catalyzed asymmetric oxidations, Coord. Chem. Rev. 237 (2003) 245–256.

[25] M.R. Maurya, A. Kumar, M. Ebel, D. Rehder, Syntheses and crystal structures of two Schiff base copper(II) complexes with urease inhibitory activity, Inorg. Chem. 45 (2006) 5924–5937.

[26] To a 250 ml round bottom flask containing 150 ml absolute ethanol were added 10 mmol of salicyaldehyde, 10 mmol of 2-chloroethyl ammonium hydrochloride and 10 mmol of NaOH and the content was refluxed with stirring for 5 h. After cooling to room temperature the content was added to 100 ml of water in 0 °C in a baker and kept it in an ice bath for 2 h. The yellow crystals were filtered off and washed with slightly cold water and dried in an oven. Yield, 84%. m. p. 52 °C. *Anal.* Calc. for $C_9H_{10}ClNO$: C, 58.85; H, 5.45; N, 7.63%. Found: C, 58.51; H, 5.37; N, 7.48%. FT-IR (KBr pellet, cm^{-1}): *v* (C═N) 1640 cm^{-1}. ^1H-NMR($CDCl_3$; δ, ppm):13.00 (s, ^1H: −O−**H**), 8.39 (s, ^1H: −**H**C═N−), 7.34 (t, ^1H: Ph−**H**), 7.30(d, ^1H:Ph−**H**), 6.99 (d, ^1H:Ph−**H**), 6. 90 (t, ^1H: Ph−**H**), 3.92 (t, ^2H: −C**H₂**Cl), 3.81 (t, ^2H: −N−C**H₂**−).

[27] P. Pfeiffer, H. Krebs, Zur stereochemie innerkomplexer kupfersalze, J. Prakt. Chem. 155 (1940) 77–114.

[28] In a 100 ml round bottom flask, 5 mmol of **L** were dissolved in 40 ml of MeOH and to this solution were added 2.5 mmol of $VO(acac)_2$ (in 10 ml of MeOH) and the content was refluxed with stirring for 4 h. After evaporating of the solvent to 1/5 value, the solution was kept in refrigerator for one week. Then the greenish crystals were filtered off and washed with n-hexane and dried in an oven. Yield: 62%. m.p. 175 °C. *Anal.* Calc. for $C18H18Cl_2N_2O_3V$: CHN: Anal.Calc. for $C_{18}H_{18}N_2O_3ClV$: C, 50.00; H, 4.16; N, 6.48. Found: C, 49.48; H, 4.02; N, 6.27%. FT-IR (KBr pellet, cm^{-1}): *v* (C═N) 1620, *v* (V═O) 984.

[29] R. Ando, S. Mori, M. Hayashi, T. Yagyu, M. Maeda, Structural characterization of pentadentate salen-type Schiff-base complexes of oxovanadium(IV) and their use in sulfide oxidation, Inorg. Chim. Acta 357 (2004) 1177–1184.

[30] R. Ando, H. Ono, T. Yagyu, M. Maeda, Characterization of oxovanadium (IV)–Schiff-base complexes and those bound on resin, and their use in sulfide oxidation, Inorg. Chim. Acta 357 (2004) 2237–2244.

[31] C.J. Chang, J.A. Labinger, H.B. Gray, Aerobic epoxidation of olefins catalyzed by electronegative vanadyl salen complexes, Inorg. Chem. 36 (1997) 5927–5930.

[32] V.T. Kasumov, F. Koksal, M. Aslanoglu, Y. Yerli, Synthesis, spectroscopic characterization and reactivity studies of oxovanadium(IV) complexes with bulky N, N_-polymethylenebis(3,5-tBu2salicylaldimine) ligands, Spectrochim. Acta A 77 (2010) 630–637.

[33] S. Mohebbi, M. Abdi, Unsymmetrical mononuclear and insoluble polynuclear oxo-vanadium(IV) Schiff-base complexes, J. Coord. Chem. 61 (2008) 3410–3419.

[34] S.M.E. Khalil, M.M. Mashaly, A.A.A. Emara, Copper(II), nickel(II), oxovanadium(IV) and dioxouranium(VI) complexes of novel asymmetric tetradentate Schiff base ligands derived from 6-methyl-3-formyl-4-hydroxy-2-(^1H)-quinolone. Part V, Synth. React. Inorg. Met-Org Chem. 25 (1995) 1373–1389.

[35] H. Temel, Ü. Çakır, H.İ. Uğraş, Synthesis and characterization of a novel oxovanadium(IV) complex and conductometric studies with N, N′-bis(Salicylidene)-1,2-bis-(p-aminophenoxy)ethane, Synth. React. Inorg. Met-Org Chem. 34 (2004) 819–831.

[36] General procedures for epoxidation of cyclooctene: In a 25 ml round bottom flask were added cyclooctene (0.5 mmol), oxidant (1.5 mmol), solvent (5 ml) and complex **1** (0.013 mmol) and the content was refluxed. The reaction was monitored by GLC and the yields were recorded as GLC yield based on the starting cyclooctene.

[37] J. Rahchamani, M. Behzad, A. Bezaatpour, V. Jahed, G. Dutkiewicz, M. Kubicki, M. Salehi, Oxidovanadium complexes with tetradentate Schiff bases: synthesis, structural, electrochemical and catalytic studies, Polyhedron 30 (2011) 2611–2618.

[38] H.H. Monfared, R. Bikas, P. Mayer, Homogeneous green catalysts for olefin oxidation by mono oxovanadium(V) complexes of hydrazone Schiff base ligands, Inorg. Chim. Acta 363 (2010) 2574–2583.

[39] S. Rayati, M. Koliaei, F. Ashouri, S. Mohebbi, A. Wojtczak, A. Kozakiewicz, Oxovanadium(IV) Schiff base complexes derived from 2,2′-dimethylpropandiamine: a homogeneous catalyst for cyclooctene and styrene oxidation, Appl. Catal. A: Gen. 346 (2008) 65–71.

[40] G. Grivani, A.D. Khalaji, V. Tahmasebi, K. Gotoh, H. Ishida, Synthesis, characterization and crystal structures of new bidentate Schiff base ligand and its vanadium(IV) complex: the catalytic activity of vanadyl complex in epoxidation of alkenes, Polyhedron 31 (2012) 265–271.

[41] V. Conte, A. Coletti, B. Floris, G. Licini, C. Zonta, Mechanistic aspects of vanadium catalysed oxidations with peroxides, Coord. Chem. Rev. 255 (2011) 2165–2177.

[42] M.R. Maurya, A. Arya, P. Ada˜o, J.C. Pessoa, Immobilisation of oxovanadium(IV), dioxomolybdenum(VI) and copper(II) complexes on polymers for the oxidation of styrene, cyclohexene and ethylbenzene, Appl. Catal. A: Gen. 351 (2008) 239–252.

[43] M.R. Maury, A. Kumar, Oxovanadium(IV) based coordination polymers and their catalytic Oxovanadium(IV) based coordination polymers and their catalytic, J. Mol. Catal. A: Chem. 250 (2006) 190–198.

[44] M.R. Maurya, A.K. Chandrakar, S. Chand, Oxovanadium(IV) and copper(II) complexes of 1,2-diaminocyclohexanebased ligand encapsulated in zeolite-Y for the catalytic oxidation Oxovanadium(IV) and copper(II) complexes of 1,2-diaminocyclohexane, J. Mol. Catal. A: Chem. 270 (2007) 225–235.