Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.21013

83 (2017) 306–313
July

Transition metal bis iminium complexes: Synthesis, characterization, and electrochemistry. Homogeneous epoxidation of cyclohexene with H_2O_2 using the oxovanadium complex as catalyst

Moufida Merzougui*, Kamel Ouari

Laboratoire d'Electrochimie, d'Ingénierie Moléculaire et de Catalyse Rédox (LEIMCR), Faculty of Technology, Sétif-1 University, Sétif DZ-19000, Algeria, email: moufida_merzougui@univ-setif.dz (M. Merzougui), kamel_ouari@univ-setif.dz (K. Ouari)

Received 27 December 2016; Accepted 4 June 2017

ABSTRACT

A series of mononuclear iron, manganese and oxovanadium complexes containing a tetradentate Schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and 1,2-diaminoethane are prepared. The resulting products were characterized by elemental analysis, infrared, electronic absorption and molar conductance measurement. The complexes have been found to possess 1:1 metals to ligand stoichiometry and the molar conductance data revealed that the metal complexes were non-electrolytes. Molecular structure of the oxovanadium Schiff base complex, VOL, was determined by single-crystal X-ray diffraction. Cyclic voltammetry studies of complexes, investigated in DMF on a glassy carbon (GC) electrode under nitrogen atmosphere, revealed that all of the complexes showed a single electron quasi-reversible redox waves through diffusion controlled processes. The diffusion coefficients are determined using GC rotating disk electrode. The Levich plot, $I_{lim} = f(\omega^{1/2})$, was used to calculate the diffusion-convection controlled currents. The catalytic activity of the VOL complex in the epoxidation of cyclohexene, in the presence of hydrogen peroxide H_2O_2 as oxidant, was investigated using different reaction parameters such as temperature, alkene/oxidant ratio and the catalyst amount. The results showed that a conversion of 80.4% was obtained with the epoxide selectivity of 29% using a ratio of 1:4 of the cyclohexene:H_2O_2 (substrate:oxidant).

Keywords: Complexes; Schiff base; Crystal Structure; Cyclic Voltammetry; Diffusion; Epoxidation

1. Introduction

In the last decades, transition metal of tetradentate Schiff base ligands NNOO have been increasingly investigated for their biological, medicinal and catalytic activities [1–3]. The epoxidation of olefins is of great interest due to the importance of the resulting epoxides, which are essential precursors in the synthesis of various important plasticizers, perfumes and epoxy resins [4].

Recently, there is a strong need for the development of new catalytic processes based on efficient catalysts which employ safer oxidants, such as H_2O_2, O_2 and air, and produce little waste. The employment of hydrogen peroxide is an attractive option both on environmental and economic grounds. It is cheap, readily available and gives water as the only byproduct.

Various iron and manganese complexes are well known as catalysts for the epoxidation of olefins [5–8]. Among them, oxovanadium complexes of Schiff base ligands have received considerable attention [9–11]. Grivani et al. [12–14] reported new oxovanadium complexes with bidentate Schiff base ligands, derived from salicylaldéhyde [12,13] and 2-Hydroxy-1-naphthaldehyde [14]. These complexes act as active and selective homogeneous catalysts in the epoxidation of alkenes. It seems from these studies that the naphtalate moiety decreases the activity of the vanadium center respect to the substituted salicylate.

---

*Corresponding author.

Presented at the First International Symposium on Materials, Electrochemistry and Environment (CIMEE 2016), 22–24 September 2016, Tripoli, Lebanon

Monfared et al., published new oxovanadium complexes with tridentate Schiff base ligands [15]. These complexes exhibit high catalytic activity in the oxidation of cyclohexene with conversion up to 90%. These systems are moderately selective catalysts for olefin epoxidation, afford a mixture of cyclohexene oxide (29%), 2-cyclohexene-1-ol (55%) and 2-cyclohexene-1-one (8%).

Herein, we report the synthesis of a series of transition metal Schiff base complexes derived from the condensation of the 1,2-diaminoethane, 2-hydroxy-1-naphthaldehyde and metal salts, $MnCl_2$, $FeCl_2$ and $VO(acac)_2$, with a template method. The synthesized compounds were characterized by elemental analysis, FTIR and UV-Vis spectroscopy. The crystal structure of the tetradentate oxovanadium Schiff base complex was previously reported [16]. The electrochemical properties of the complexes were studied by cyclic voltammetry at a glassy carbon (GC) electrode in DMF solvent. The diffusion coefficients of the metal Schiff base complexes have been determined using the Levich plot on a GC rotating disk electrode. The catalytic activity of the oxovanadium complex was investigated in the epoxidation of cyclohexene with H_2O_2 (30%) as oxidant.

2. Experimental

2.1. Materials and measurements

All chemical reagents and solvents were purchased from Merck or Aldrich and used without further purification. Elemental analysis were performed on an Elementar-Vario EL III CHNS analyzer. Infrared spectra were obtained on a Shimadzu FTIR spectrophotometer, using potassium bromide (KBr) pellets (4000–400 cm^{-1}). Electronic spectra, in the range 200–900 nm, were recorded in DMF using a Shimadzu UV-1800 spectrophotometer.

Molar conductance of metal complexes was determined in DMF (10^{-3} M) at room temperature using MeterLab CDM- 210 conductivity meter. Melting points of the ligand and the corresponding metal complexes were measured on a Kofler Bank 7779 apparatus. Molecular structure of oxovanadium complex was resolved on a Bruker APEX II DUO Kappa-CCD diffractometer.

Electrochemical experiments were performed on a PGZ-301 potentiostat, cyclic voltammograms (CV) and rotating disk Electrode (RDE) measurements were recorded at room temperature in DMF containing 0.1 M $LiClO_4$ as supporting electrolyte, using a glassy carbon (GC) as working electrode (Ø = 3 mm), platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Before each electrochemical investigation, the electrolyte was purged with nitrogen during 15 min. A Shimadzu GC-2014 chromatograph, equipped with a FID detector, was used to analyze the oxidation products.

2.2. Preparation of H_2L ligand

The Schiff base ligand, H_2L, was prepared by refluxing 2-hydroxy-1-naphthaldehyde (344 mg, 2 mmol) with 1,2-diaminoethane (66.8 µL, 1 mmol) in methanol (5 mL). The reaction was stirred and refluxed for 3 h under nitrogen atmosphere. Reaction complete, based on TLC analysis, the resulting compound was filtered and washed with methanol and diethylether [16,17].

2.3. Preparation of metal complexes

All the complexes were prepared in methanol by direct condensation reaction of 1,2-diaminoethane, 2-hydroxy-1-naphthaldehyde and the appropriate metallic salt, manganese chloride $MnCl_2$, iron chloride $FeCl_2$, and/or bis (acetylacetonato) oxovanadium $VO(acac)_2$ in 1:2:1 molar ratio, respectively. The reactions were stirred and refluxed for 3 h under nitrogen atmosphere, Fig. 1. The precipitates formed are undergone the same treatment as that of the ligand H_2L [16,17].

The iron and manganese complexes, FeClL and MnClL, reactions were initiated in air atmosphere for one hour

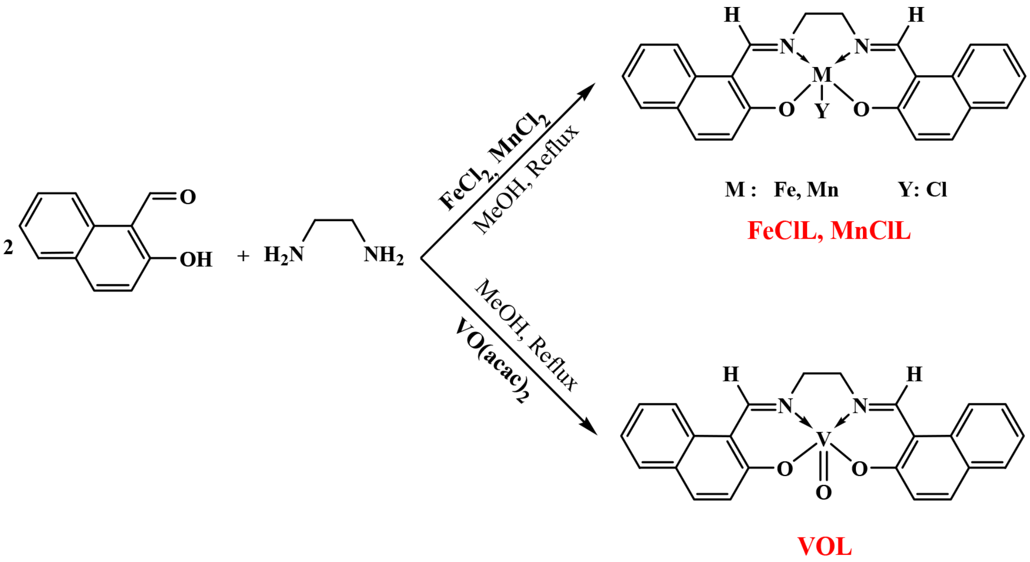

Fig. 1. Synthesis of the transition metal complexes ML.

in order to oxidize the divalent metal M (II) to trivalent M (III). The reaction is continued for 2 h under nitrogen atmosphere.

2.4. General procedure of the epoxidation reaction catalyzed with VOL

The homogenous catalytic oxidations were carried out in a 25 mL round bottom flask equipped with a magnetic stirrer and immersed in a thermostated oil bath. To a solution of 3.3 µmol of oxovanadium complex VOL, dissolved in 7 mL of DMF/CH_3CN solution (3:7, v/v), was added 1 mmol of cyclohexene. 3 mmol of hydrogen peroxide (30% aqueous) were then added by small portions and the resulting mixture was refluxed for 6 h at 70°C.

The progress of the reactions was monitored by GC and the oxidation products were identified by comparing their retention times with those of authentic samples.

3. Results and discussion

3.1. Synthesis and characterization

The Schiff base ligand H_2L was synthesized following the literature method [16,17]. The elemental analysis, IR, UV–vis, ^1H and ^{13}C NMR data of this compound are reported previously [18,19]. All the synthesized complexes are solid and their melting points exceed to 260°C.

The very low values of molar conductance of the complexes, 10^{-3} M in DMF, indicating that they are electrically neutral [20]. The main physical and chemical characteristics of the ligand and the corresponding complexes are summarized in Table 1.

The structures of the complexes were confirmed by elemental analysis, FTIR and UV-vis spectroscopy. Elemental analysis of the complexes fit well with a 1:1 metal to ligand, and they are in good agreement with the calculated values.

In the electronic spectrum of the free ligand, the absorption bands at 307 and 362 nm are assigned to $\pi \rightarrow \pi^*$ transitions of the naphthalene rings [21]. While the absorption bands at 400 and 420 nm are respectively attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the azomethine chromophores [21]. Upon complexation with manganese and oxovanadium metals, the $\pi \rightarrow \pi^*$ transitions of the naphthalene rings are undergone to a bathochromic shift, of about 20 nm, Fig. 2, [9]. The azomethine bands are shifted to longer wavelength in the case of manganese complex, while they are disappeared in the case of oxovanadium and iron complexes. This indicates a coordination of the metals through the nitrogen atoms of the azomethine groups. The electronic spectra of oxovanadium and iron complexes showed broad shoulders in the ranges 350–420 and 500–650 nm. These bands are due to MLCT and a d-d transition [3,22].

Table 1
Physical and chemical characteristics of the ligand and the corresponding complexes

Compound	Color	ρ(%)	T_f (°C)	Λ (cm²/ Ω mol)
H_2L	Yellow	92.4	215	2.72
VOL	Green	77.6	>260	8.78
FeClL	Black	76.2	>260	10.30
MnClL	Black	82	>260	35.27

The IR spectra exhibit several prominent bands in the 4000–400 cm⁻¹ region. The spectra of iron, manganese and oxovanadium complexes displayed strong C═N stretch at 1606, 1603 and 1618 cm⁻¹, respectively. These bands are assigned to the azomethine, C═N, stretching vibrations [19] and they are shifted to lower wavenumbers by 30 cm⁻¹ from the corresponding free ligand, indicating coordination of the nitrogen to the metal center, leading to lower electron density on the azomethine [23]. This coordination is confirmed by the presence of several medium intensity bands between 420 and 480 cm⁻¹ in the spectra of complexes suggesting the existence of metal—N stretching vibrations [18].

The bands observed around 1340 cm⁻¹ correspond to the stretching vibration of C–O in the naphtholate moieties of the complexes [18,19]. These wavenumbers are lower than that observed in the corresponding ligand spectrum. This suggests an increase of the C–O bond electron density and strengthening of the force constant due to the coordination of the naphtholate oxygen to the metal center, as reported in the literature [24]. FT-IR spectra of the Schiff base ligand and the metal complexes are shown in Fig. 3.

The sharp band observed at 987 cm⁻¹ in the FT-IR spectrum of VOL complex is attributed to V═O vibration, indicating the monomeric form of this complex in the solid state, as confirmed by the single crystal X-ray diffraction [3].

Elemental analysis, UV-vis and FT-IR results of the Schiff base ligand and the metal complexes are presented in Table 2.

3.2. Crystal structure of VOL complex

Suitable single crystals of the oxovanadium complex, VOL, were grown by slow layer diffusion of DMSO into a MeOH solution at room temperature. The crystal structure

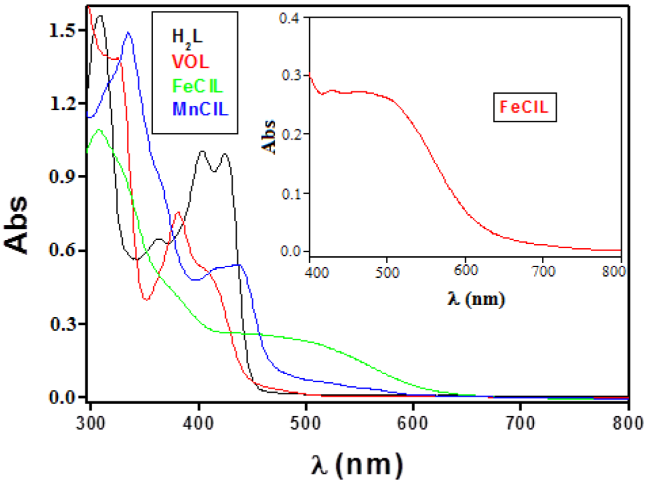

Fig. 2. Electronic spectra of the ligand and metal complexes in DMF. The inset shows an expanded spectrum of the complex FeClL between 400 and 800 nm.

of this complex is reported previously by our group [16], an ORTEP view of the VOL complex with the atoms numbering scheme is given in Fig. 4.

The X-ray structural study reveals that this complex crystallizes in the monoclinic system with $P2_1/c$ space group. The vanadium center is coordinated to the tetradentate Schiff base ligand with the two nitrogen and the two naphtholate oxygen atoms and an oxygen atom in the axial position to complete the N_2O_3 coordination sphere. The geometry around the vanadium center is described as a slightly distorted square pyramidal.

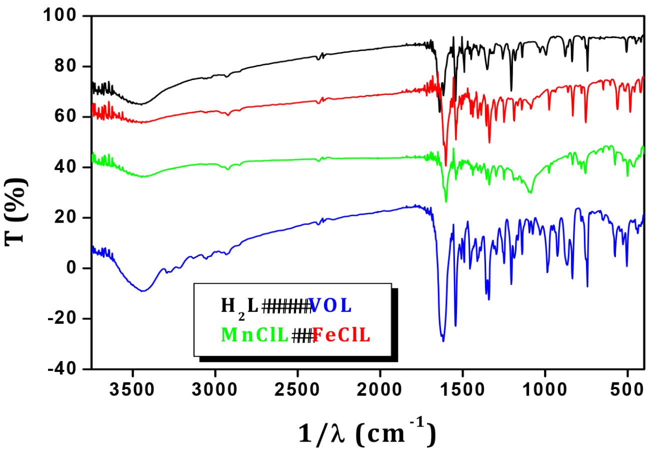

Fig. 3. FT-IR spectra of the ligand and the metal complexes.

The crystal is stabilized by a network of intermolecular hydrogen bonds, C–H … O and C–H… π interactions, between the naphthalene rings of the neighboring molecules.

3.3. Electrochemistry

The redox properties of the transition metal complexes were investigated by cyclic voltammetry under nitrogen atmosphere. The cyclic voltammetric data of the complexes are presented in Table 3. The cyclic voltammograms of 1 mmol of VOL and MnClL complexes, in DMF at various scan rates, are shown in Fig. 5 and 6, respectively.

At a scan rate of 100 mV/s, all complexes displayed a quasi-reversible one-electron redox process with half wave potentials, $E_{1/2}$, at –281, –326 and +374 mV/SCE for MnClL, FeClL and VOL, respectively. Thus, these redox processes are assigned to the Mn(III)/Mn(II) [22], Fe(III)/Fe(II) [25], and VO(V)/VO(IV) couple waves [26].

A linear relationship between the cathodic peak currents and the square root of the scan rates $[i_{pc} = f(v^{1/2})]$ is observed, Inset of Fig. 6, this fact implies that this electrochemical process is mainly diffusion-controlled [27].

In order to determine the diffusion coefficient, a hydrodynamic voltammetry experiment is carried out using a glassy carbon rotating disk electrode (RDE) at various rotation rates, Fig. 7.

Under the studied conditions, a linear correlation between the limiting current and the square root of the

Table 2
Spectroscopic and analytical data for the Schiff base ligand and the transition metal complexes

Compound	Elemental analysis Calc. (Found)			UV-vis	FT-IR		
	% C	% H	%N	λ_{max} (nm)	ν C=N	ν O–H	ν C–O
H_2L	/	/	/	307, 362, 401, 425	1638	3450	1350
VOL	66.52% (66.83)	4.19 (4.35)	6.46 (6.32)	323, 380, 610	1618	3444	1340
FeClL	62.98 (63.04)	3.96 (3.90)	6.12 (6.18)	307, 380, 510	1606	3446	1338
MnClL	63.1 (63.17)	3.97 (4.02)	6.13 (6.01)	335, 416, 437, 567	1603	3440	1338

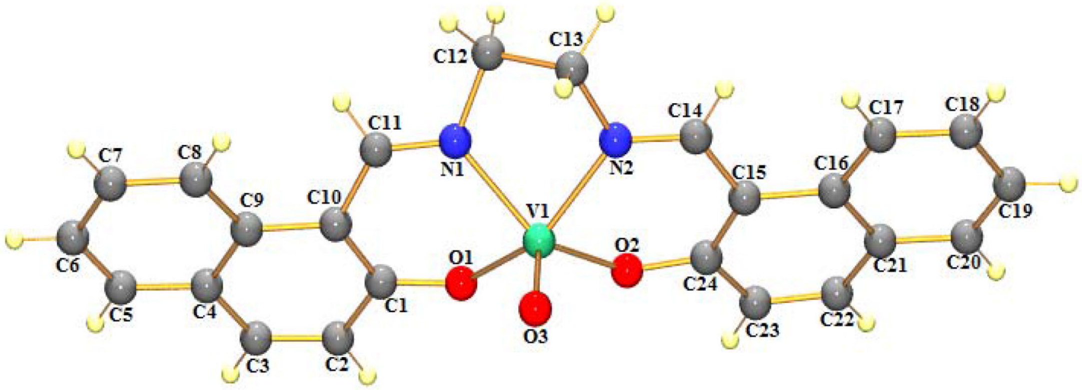

Fig. 4. ORTEP POV-RAY view of VOL complex with 50% ellipsoid probability.

Table 3
Cyclic voltammetric data of the complexes at 100 mV/s under N_2

Compound	Epa	Epc	ΔE	$E_{1/2}$	Ipa	Ipc	Ipa/Ipc
FeClL	–290	–362	72	–326	6.01	6.24	0.96
MnClL	235	315	90	–281	16.17	20.9	0.79
VOL	415	333	82	374	14.66	14.3	1.02

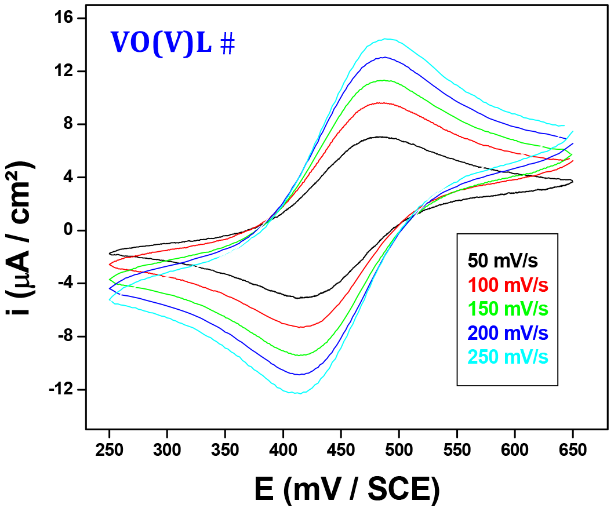

Fig. 5. Cyclic voltammograms of VOL complex in 0.1 M $LiClO_4$/DMF solution at various scan rates.

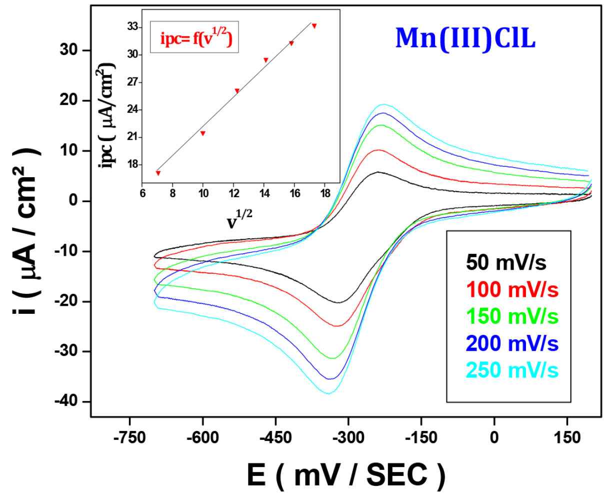

Fig. 6. Cyclic voltammograms of Mn(III)ClL complex in 0.1 M $LiClO_4$/DMF solution at various scan rates. The inset shows the cathodic currents vs $v^{1/2}$.

rotating rate is observed, leading to the determination of the value of the proportionality constant in the Levich equation for a one electron reduction. From the slopes of the i_{lim} vs. $\omega^{1/2}$ plots, using Levich equation, diffusion coefficients of the three complexes were calculated. They are 2.7 × 10^{-6} cm²/s, 2.15 × 10^{-6} and 8.16 × 10^{-6} cm²/s for VOL, FeClL and MnClL respectively.

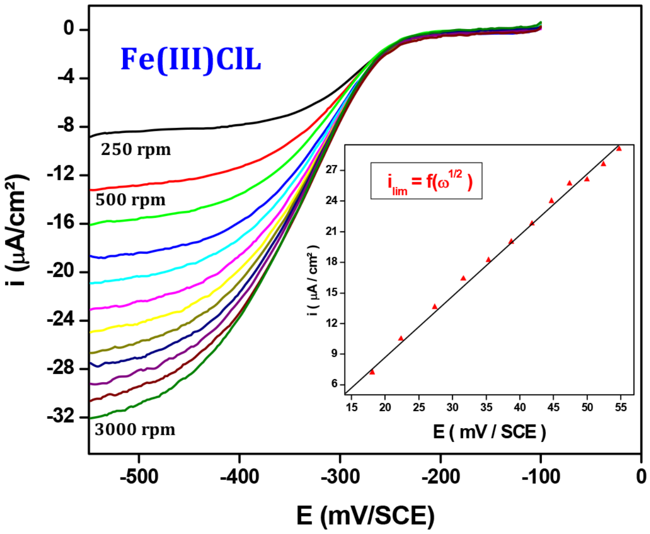

Fig. 7. Voltammograms of Fe(III)ClL complex at RDE in 0.1 M $LiClO_4$/DMF solution. Rotation rates: from 250 to 3000 rpm. The inset shows the Levich plot.

3.4. Catalytic activity

The homogeneous catalytic activity of the oxovanadium Schiff base complex, VOL, was investigated in the epoxidation reaction of cyclohexene with 30% aqueous H_2O_2. However, some parameters, such as temperature, alkene/oxidant ratio and the amount of the catalyst turn out to be important and, therefore, were optimized.

In order to get the best reaction temperature, the epoxidation reaction was carried out with 1 mmol of cyclohexene, 3 mmol of H_2O_2 in DMF/CH_3CN solution (3:7, v/v) with 3 µmol of the catalyst VOL at various temperatures for 6 h.

At 60°C, the oxidation of cyclohexene is very low. By increasing the reaction temperature from 60°C, the cyclohexene conversion increased to 47% after 6 h at 80°C. As soon as, the reaction temperatures are above 80°C, the conversion is lowered to 25%. The selectivity of cyclohexene oxide is also slowly decreased from 24.5 at 80°C to 23.13% at 90°C. This is probably due to the fact that at high temperatures, decomposition of the oxidant H_2O_2 takes place [28,29]. The main oxidation products are cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, Fig 8, with a slightly higher selectivity towards 2-cyclohexene-1-ol [15,30]. Thus, the 80°C is found to be the optimized reaction temperature, Fig. 9.

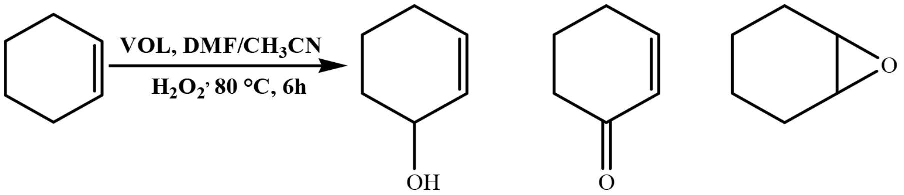

Fig. 8. Oxidation of cyclohexene by H_2O_2 using VOL complex as catalyst.

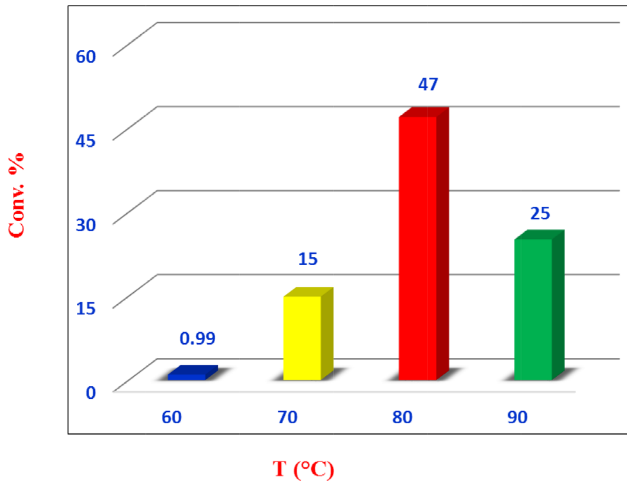

Fig. 9. Effect of the temperature on the oxidation of cyclohexene. Reaction conditions: Cyclohexene (1 mmol), VOL (3 mmol), DMF/CH_3CN (7/3: v/v mL), H_2O_2 (3 mmol), Reaction time: 6 h.

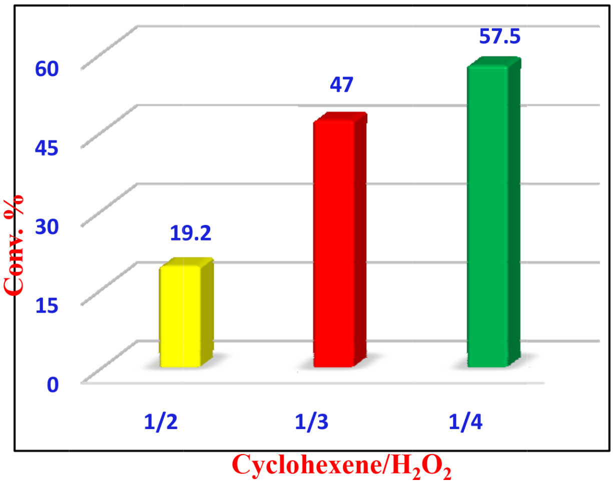

Fig. 10. Effect of the ratio cyclohexene/H_2O_2 on the oxidation reaction. Reaction conditions: Cyclohexene (1 mmol), VOL (3 mmol), DMF/CH_3CN (7/3: v/v mL), T = 80°C, Reaction time: 6 h.

As can be seen in Fig. 10, the increasing of the cyclohexene/H_2O_2 ratio from 1:2 to 1:4 enhanced the conversion from 19.2 to 57.5%. The maximum conversion of cyclohexene is obtained with a molar ratio of 1:4. This may be due to the fast formation of active intermediates with higher amount of oxidant [31]. Therefore, a 1:4 ratio being considered adequate, providing the highest conversion of cyclohexene with the selectivities of 32.51, 36.15, and 31.33% for cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, respectively.

The increasing of the catalyst amount from 0.9 to 1.1 mg improves the conversion of cyclohexene from 27.07 to 80.4%, up to 1.1 mg of the catalyst, a drastic decrease of the conversion is observed. This may be due to the degradation of the oxidant based on the increased of active centers in the catalyst [32]. The amount of the catalyst is then optimized to 1.1 mg (2.5 μmol), with a moderate selectivity of 29% to cyclohexene oxide.

The epoxidation of cyclohexene with H_2O_2 is catalyzed by other similar oxovanadium Schiff base complexes and the same epoxide selectivities were approximately obtained as it is reported previously by Monfared and co-workers [15,30]. The distribution of the oxidation reaction products is shown in Table 4.According to our results, VOL catalyst was very selective for the production of 2-cyclohexene-1-ol from cyclohexene. Thus, the VOL Schiff base complex is found to be a very active and selective catalyst to produce this alcohol, 2-cyclohexene-1-ol.

The oxidation mechanism of olefins by hydrogen peroxide catalyzed by the oxovanadium catalyst, VOL, is similar to those reported in the literature [15,33]. The cyclohexene substrate is predisposed to both allylic and double bond oxidation. The reaction was initiated by one electron oxidation of oxovanadium VO(IV) to VO(V) by hydrogen peroxide, Fig 11B, where active catalytic intermediate species [V^VOOL] are formed, Fig. 11C. These intermediates transfer an oxygen atom of hydrogen peroxide to the cyclohexene in a concerted reaction, leading to the formation of the epoxide Fig. 11D.

Monfared et al. [15] showed that the allylic oxidation of cyclohexene occurs via the vanadium(IV)-peroxo biradical which abstracts a hydrogen atom from the substrate to produce an active intermediate. Reduction of the substrate radical by V(IV)-intermediate, gives 2-cyclohexene-1-ol and V(V)- intermediate. The 2-cyclohexene-1-one is formed by the oxidation of the alcohol.

4. Conclusion

A series of transition metal Schiff base complexes of iron, manganese and oxovanadium were synthesized and characterized by spectroscopic methods. The molecular structure of oxovanadium complex was determined by single crystal X-ray analysis. The X-ray crystal structure reveals that the vanadium is five-coordinate and the geometry around it is a slightly distorted square pyramidal.

The electrochemical behavior of the metal center in the complexes exhibits quasi-reversible one electron redox processes, with current ratio i_{pa}/i_{pc} close to unity and the peak-

Table 4
Effect of the amount of the catalyst VOL on the oxidation of cyclohexene*.

m	*n* (µmol)	Ratio	Conversion %	Selectivity %		
(mg)		Cyclohexene/ VOL		Cyclohexene oxide	2-Cyclohexene-1-ol	2-Cyclohexene-1-one
0.9	2	500	27.07	11.80	69.2	18.99
1.1	2.5	400	80.4	29	38.4	32.6
1.33	3	300	57.52	32.51	36.15	31.33
2.2	5	200	53	33.12	35.98	30.85
4.4	10	100	41	35.82	37.47	26.72

*Reaction conditions: cyclohexene (1 mmol), H_2O_2 (4 mmol), DMF/CH_3CN (7/3: v/v mL), T = 80°C, Reaction time: 6 h.

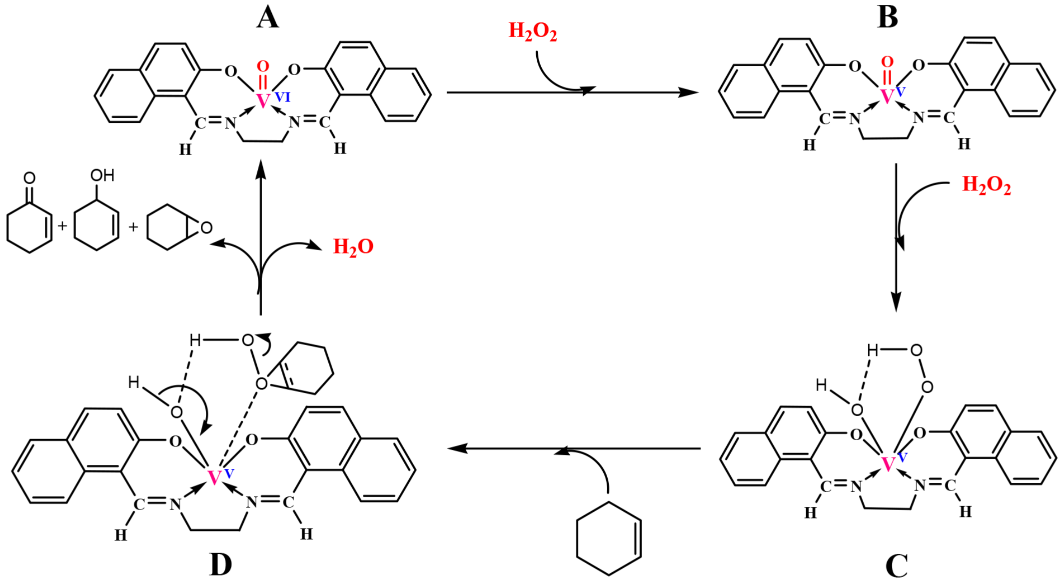

Fig. 11. Proposed oxidation mechanism of cyclohexene by hydrogen peroxide catalyzed by VOL complex.

to-peak separation values, ΔE_p, are in the range 70–90 mV. The linear relationship observed between the anodic peak currents, i_{pa}, and the square root of the scan rates, $v^{1/2}$, indicates a diffusion-controlled nature at the electrode process. The diffusion coefficients are calculated from the Levich plots, $I_{lim} = f(\omega^{1/2})$.

The catalytic activity of the VOL complex was investigated in the epoxidation of cyclohexene by using the environmentally benign and clean oxidant H_2O_2. The reaction conditions were optimized and the results showed that the catalyst VOL gives excellent conversion, of 80.4%, and moderate selectivity to cyclohexene oxide, about 29%.

Acknowledgements

The authors gratefully acknowledge financial support from the Algerian Ministry of Higher Education and Scientific Research. They also acknowledge the help of Dr Jean Weiss from the CLAC laboratory for the access to the Microanalysis and radio-crystallography Services at the Chemistry Institute of the University of Strasbourg - France.

References

[1] H.A. Rudbari, M.R. Iravani, V. Moazam, B. Askar, M. Khorshidifard, N. Habibi, G. Bruno, Synthesis, characterization, X-ray crystal structures and antibacterial activities of Schiff base ligands derived from allylamine and their vanadium(IV), cobalt(III), nickel(II), copper(II), zinc(II) and palladium(II) complexes, J. Mol. Struct., 1125 (2016) 113–120.

[2] M.Xie, L. Li, X. Yang, W. Liu, S. Yan, Y. Niu, Z. Meng, A new insulin-enhancing agent: [N,N′-bis(4-hydroxysalicylidene)-o-phenylenediamine]oxovanadium(IV) and its permeability and cytotoxicity, Eur. J. Med. Chem., 45 (2010) 2327–2335.

[3] M. Bagherzadeh, M. Amini, A new vanadium Schiff base complex as catalyst for oxidation of alcohols, J. Coord. Chem., 63 (2010) 3849–3858.

[4] M. Turkyilmaz, M. Kacan, Y. Baran, Structure, spectroscopic, thermal properties and catalytic activity of iron(III)-Schiff base complexes, Inorg. Chim. Acta, 395 (2013) 255–259.

[5] J. Adhikary, A. Guha, T. Chattopadhyay, D. Das, Heterogenization of three homogeneous catalysts: A comparative study as epoxidation catalyst, Inorg. Chim. Acta, 406 (2013) 1–9.

[6] P. Kar, A. Ghosh, Synthesis, structure and alkene epoxidation activity of an alternating phenoxido and formato bridged manganese(III)–salen complex, Inorg. Chim. Acta, 395 (2013) 67–71.

[7] S. Rayati, E. Bohloulbandi, Multi-wall carbon nanotube-supported manganese(III) porphyrin: An efficient and reusable catalyst for the oxidation of alkenes with H_2O_2 under ultrasonic irradiation, C. R. Chimie, 17 (2014) 62–68.

[8] H.H. Monfared, S. Alavi, P. Mayer, A novel homodinuclear manganese(III) complex with N, N′-bis(salicylidene)diethylenetriamine: synthesis, structure and catalytic activity, Inorg. Chim. Acta, 419 (2014) 89–95.

[9] M. Ghorbanloo, S. Jafari, R. Bikas, M.S. Krawczyk, T. Lis, Dioxidovanadium(V) complexes containing thiazol-hydrazone NNN-donor ligands and their catalytic activity in the oxidation of olefins, Inorg. Chim. Acta, 455 (2017) 15–24.

[10] V. Tahmasebi, G. Grivani, G. Bruno, Synthesis, characterization, crystal structure determination and catalytic activity in epoxidation reaction of two new oxidovanadium(IV) Schiff base complexes, J. Mol. Struct., 1123 (2016) 367–374.

[11] J. Pisk, J.C, Daran, R. Poli, D. Agustin, Pyridoxal based ONS and ONO vanadium(V) complexes: Structural analysis and catalytic application in organic solvent free epoxidation, J. Mol. Catal. A: Chem., 403 (2015) 52–63.

[12] G. Grivani, G. Bruno, H.A. Rudbari, A.D. Khalaji, P. Pourteimouri, Synthesis, characterization and crystal structure determination of a new oxovanadium(IV) Schiff base complex: The catalytic activity in the epoxidation of cyclooctene, Inorg. Chem. Commun., 18 (2012) 15–20.

[13] 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.

[14] V. Tahmasebi, G. Grivani, G. Bruno, Synthesis, characterization, crystal structure determination and catalytic activity in epoxidation reaction of two new oxidovanadium(IV) Schiff base complexes, J. Mol. Struct., 1123 (2016) 367–374.

[15] 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.

[16] M. Merzougui, K. Ouari, J. Weiss, Ultrasound assisted synthesis, characterization and electrochemical study of a tetradentate oxovanadium diazomethine complex, J. Mol. Struct., 1120 (2016) 239–244.

[17] K. Ouari, S. Bendia, J. Weiss, C. Bailly, Spectroscopic, crystal structural and electrochemical studies of zinc(II)-Schiff base complex obtained from 2,3-diaminobenzene and 2-hydroxy naphthaldehyde, Spectrochim. Acta, Part A, 135 (2015) 624–631.

[18] C.R. Bhattacharjee, P. Goswami, P. Mondal, Synthesis, reactivity, thermal, electrochemical and magnetic studies on iron(III) complexes of tetradentate Schiff base ligands, Inorg. Chim. Acta, 387 (2012) 86–92.

[19] Y. Choia, W. Kim, K. Chung, M. Chung, H. Nam, Catalytic effect of transition metal_II -N,N′-bis_naphthaldehyde diimines on reduction of thionyl chloride, Microchem. J., 65 (2000) 3–15.

[20] B.T. Thaker, R.S. Barvalia, Microwave assisted synthesis and characterization of unsymmetrical tetradentate Schiff base complexes of VO(IV) and MoO(V), Spectrochim. Acta, Part A, 84 (2011) 51–61.

[21] A.M. Ajlouni, Z.A. Taha, W. Momani, A.K. Hijazi, M. Ebqa'ai, Synthesis, characterization, biological activities, and luminescent properties of lanthanide complexes with N,N′-bis(2-hydroxy-1-naphthylidene)-1,6-hexadiimine, Inorg. Chim. Acta, 388 (2012) 120–126.

[22] P. Chakraborty, S. Majumder, A. Jana, S. Mohanta, Syntheses, structures, catecholase activity, spectroscopy and electrochemistry of a series of manganese(III) complexes: Role of auxiliary anionic ligand on catecholase activity**,** Inorg. Chim. Acta, 410 (2014) 65–75.

[23] S. Yadav, M. Ahmad, K.S. Siddiqi, Metal-ion directed synthesis of N_2O_2 type chelate complexes of Ni(II), Cu(II) and Zn(II): Spectral, thermal and single crystal studies, Spectrochim. Acta, Part A, 98 (2012) 240–246.

[24] K. Ouari, A. Ourari, J. Weiss, Synthesis and Characterization of a Novel Unsymmetrical Tetradentate Schiff Base Complex of Zinc(II) Derived from N,N′-bis (5-Bromosalicylidene) 2,3-Diaminopyridine (H_2L): Crystal Structure of [Zn(II)L]Pyridine, J. Chem. Crystallogr., 40 (2010) 831–836.

[25] S. Majumder, S. Dutta, L.M. Carrella, E. Rentschler, S. Mohanta, Syntheses, structures, electrochemical measurements and magnetic properties of two iron(III) complexes derived from N,N′-o-phenylenebis (3-ethoxysalicylaldimine), J. Mol. Struct., 1006 (2011) 216–222.

[26] P. Galloni, A. Coletti, B. Floris, V. Conte, Electrochemical properties of VO salen complexes, Inorg. Chim. Acta, 420 (2014) 144–148.

[27] M. Kasuno, M. Hayano, M. Fujiwara, T. Matsushita, Effects of chloride ions on electrochemical reactions of manganese(III) complexes, Polyhedron, 28 (2009) 425–430.

[28] W. Fan, Y. Leng, J. Liu, P. Jiang, J. Zhao, Mo Schiff base-tungstate ionic hybrid with enhanced heterogeneous catalytic activity for epoxidation reactions, Appl. Catal., A, 506 (2015) 173–179.

[29] C.K. Modi, B.G. Gade, J.A. Chudasama, D.K. Parmar, H.D. Nakum, A.L. Patel, Synthesis, spectral investigation and catalytic aspects of entrapped VO(IV) and Cu(II) complexes into the supercages of zeolite-Y, Spectrochim. Acta, Part A, 140 (2015) 174–184.

[30] H.H. Monfared, S. Kheirabadi, N.A Lalami, P. Mayer, Dioxo- and oxovanadium(V) complexes of biomimetic hydrazone ONO and NNS donor ligands: Synthesis, crystal structure and catalytic reactivity, Polyhedron, 30 (2011) 1375–1384.

[31] S. Rayati, A. Ghaemi, N. Sadeghzadeh, Electronic effects of substituents on the oxidation potentials of vanadyl complexes with tetradentate Schiff base ligands derived from 1,2-propylenediamine, Catal. Commun., 11 (2010) 792–796.

[32] H.S. Abbo, S.J.J. Titinchi, Transition metal coordination polymers: Synthesis and catalytic study for hydroxylation of phenol and benzene, Appl. Catal. A, 435–436 (2012) 148–155.

[33] B. Tamami, S. Ghasemi, Modified crosslinked polyacrylamide anchored Schiff base–cobalt complex: A novel nano-sized heterogeneous catalyst for selective oxidation of olefins and alkyl halides with hydrogen peroxide in aqueous media, Appl. Catal., A, 393 (2011) 242–250.