

# Synthesis, characterization and study of vanadyl tetradentate Schiff base complexes as catalyst in aerobic selective oxidation of olefins

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## Abstract

Novel vanadyl Schiff base complexes with the general formula  $VOL^x$  ( $x = 7-18$ ) were synthesized and characterized by physicochemical methods. Only an orange polymeric form was obtained for  $VOL^{13}$ , both brown polymeric and green monomeric forms were obtained for  $VOL^x$ ,  $x = 16, 17$ . These observations suggest that in these complexes oxovanadium(IV) exhibit a coordination number of five. Systematic substitution on the ancillary ligand have allowed V(V)/V(IV) reduction potentials to be tuned over a range of approximately 130 mV. The complexes are catalysts for the aerobic oxidation of cyclohexene. Catalytic activity increases with increasing V(V)/V(IV) reduction potential and the catalytic selectivity varied by changes in the ligands. The catalytic system described here is an efficient and inexpensive method for oxidation of olefins, with advantages of high activity, selectivity, re-usability and short reaction times. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Aerobic selective oxidation; Selective epoxidation; Catalytic oxidation of olefins; Vanadyl tetradentate Schiff base; Vanadyl Schiff base complexes; Oxovanadium(IV) complexes

## 1. Introduction

Selective epoxidation of olefins catalyzed by  $d^0$  metal complexes Mo(IV), V(V) and Ti(IV) have become the most important industrial process due to the recent utilization of the *tert*-butyl alcohol co-product for the manufacture of propylene oxide as an octane booster in gasoline (Halcon process) [1]. Also this process is of importance in the production of fuels, commodity chemicals, and fine chemicals [2]. The use of dioxygen as an oxidant for such processes is particularly attractive from both economic and environmental stand point [3]. However, triplet ground

state of  $O_2$  disfavors reactions with singlet organic compounds. Finding a path for the selective oxidation of organic feedstock using dioxygen could lead to improvements in the management of our natural resources [4]. Perhalogenated metal porphyrins are active catalysts for the oxidation of hydrocarbons by  $O_2$  under mild conditions (25–60 °C, 4–8 atm) [5–7]. The difficulty of synthesis is one problem limiting the use of perhalogenated metal porphyrins as catalysts in hydrocarbon oxidation [4]. Therefore, we have embarked upon a program aimed at developing catalysts that mimic perhalogenated metal porphyrins which are more easily prepared. We chose Schiff base complexes for the investigation, as its ligand framework is similar to that of a porphyrin [8,9]. In addition, the remarkable electronic and striking tunability of Schiff

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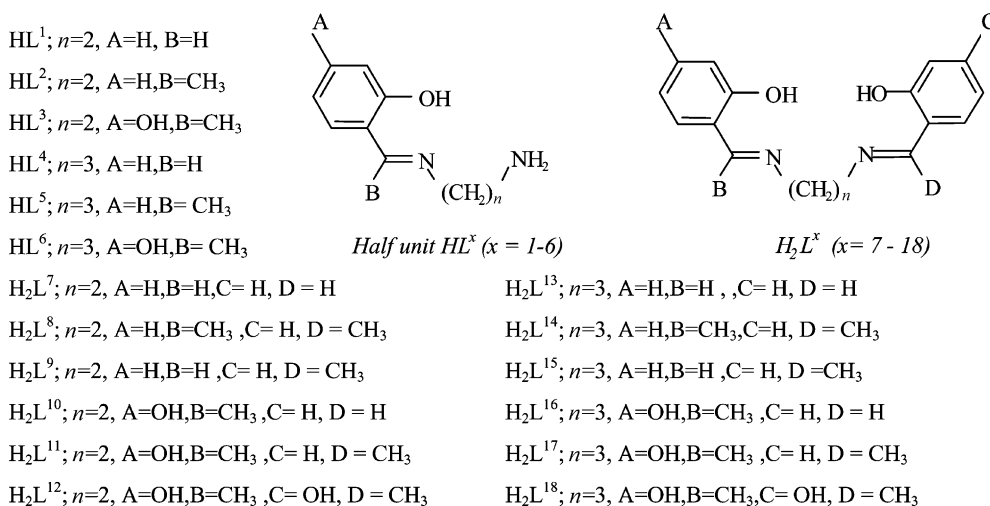


Fig. 1. General structure of precursors (half units) and tetradentate ligands.

bases make them possible to carry out systematic reactivity studies based on ancillary ligand modification [10,11]. In earlier works, we have synthesized some Schiff base complexes [12–14]. Here we report that a novel vanadyl Schiff base complexes are moderately selective catalysts for aerobic olefin epoxidation. Unsymmetrical Schiff base ligands were readily prepared from commercially available starting materials by the Schiff base condensation of 2,4-dihydroxyacetophenon; 2-hydroxyacetophenon or 2-hydroxysalicylaldehyde and 1,2-diaminoethane or 1,3-diaminopropane in a simple molar ratio with the general formula HL<sup>x</sup> (x = 1–6) as precursors (half units) and H<sub>2</sub>L<sup>x</sup> (x = 7–18) as tetradentate ligands (Fig. 1).

## 2. Experimental

### 2.1. Physical measurements

Infrared spectra were recorded as KBr pellets using Unicam Matson 1000 FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra by a Bruker FT-NMR AC-80 (80 MHz) and 500 (500 MHz) spectrophotometers using TMS as internal standard and CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>SO as solvent. Elemental analyses (C, H, N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analysesysteme KBr pellets, GmbH, west Germany). Melting points were determined by

BUCHI Melting point B-540. The products were identified by GC with a CHROMPACK CP 9001 gas chromatograph, and comparison with retention times of authentic samples and GC–MS systems consist of a GC HP 6890 series and a MS HP 5973 MSD. Cyclic Voltammetry was performed using a Bioanalytical systems. The working, auxiliary, and reference electrodes were glassy carbon, platinum wire, and AgCl/Ag, respectively. Electrochemical measurements were performed at room temperature (25 °C) under argon with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte by EG&G potentiostat/galvanostat at 273 A.

### 2.2. Materials

Oxygen gas was passed through a calcium chloride drying tube before admission to the reaction system. Cyclohexene was distilled under argon and stored in a refrigerator. 1,2-Diaminoethane, 1,3-diaminopropane, 2'-hydroxyacetophenone, 2',4'-dihydroxyacetophenone, 2-hydroxy benzaldehyde and vanadyl acetylacetonate were used as received from commercial suppliers, and were purified by literature methods. Schiff base ligands were prepared by the condensation of the appropriate diamine and an aldehyde or ketones. Typical syntheses of the ligands and their complexes are given in Section 2.3. Table 1 lists the analytical

Table 1

<sup>1</sup>H NMR chemical shift ( $\delta$  in ppm) of compounds  $H_nL^x$  ( $n = 1, 2; x = 1-18$ )

Compound <sup>a</sup>	O–H	NH <sub>2</sub>	CH=N	CH <sub>3</sub> (azomethine)	H (aromatic)	Methylene
HL <sup>1</sup>	12.5	3.2 (br)	7.9	–	6.5–8.0	2.5, 3.9
HL <sup>3</sup>	16.2, 16.9	3.6 (br)	–	1.9	6.1–7.8	2.3, 3.4
HL <sup>5</sup>	16.3	3.8 (br)	–	2.1	6.5–7.6	2.3, 3.5
HL <sup>6</sup>	16.7	4.1 (br)	–	2.3	6.1–6.3, 7.4	2.7, 3.5
H <sub>2</sub> L <sup>7</sup>	13.1	–	8.3	–	6.6–7.5	3.9
H <sub>2</sub> L <sup>8</sup>	16.0	–	–	2.5	6.7–7.9	4
H <sub>2</sub> L <sup>9</sup>	15.8	–	8.2	2.4	6.6–7.8	3.9
H <sub>2</sub> L <sup>10</sup>	15.3, 16.5	–	8.1	2.5	6.2–7.5	3.8
H <sub>2</sub> L <sup>11</sup>	16.4, 16.7	–	–	2.1, 2.4	6.0–7.4	3.1–3.4
H <sub>2</sub> L <sup>12</sup>	16.6	–	–	2.5	6.1–7.9	3.7
H <sub>2</sub> L <sup>13</sup>	13.4	–	8.3	–	6.6–7.6	2.1, 3.7
H <sub>2</sub> L <sup>14</sup>	16.2	–	–	2.4	6.7–7.7	3.8, 2.3
H <sub>2</sub> L <sup>15</sup>	14.6, 15.5	–	8.2	2.3	6.7–7.7	3.7, 2.5
H <sub>2</sub> L <sup>16</sup>	15.5, 16.7	–	8.2	2.3	6.2–7.5	3.8, 2.5
H <sub>2</sub> L <sup>17</sup>	16.1, 16.8	–	–	2.1, 2.3	6.2–7.8	3.7, 2.5
H <sub>2</sub> L <sup>18</sup>	16.9, 16.3	–	–	2.2	6.1–7.4	3.7, 2.8

<sup>a</sup> br: broad; s: singlet; m: multiple; d: doublet; t: triplet.

data of complexes. Reference samples of cyclohexene oxides, 2-cyclohexen-1-ol and 2-cyclohexen-1-one (Aldrich) were distilled and stored in the refrigerator. The solvents (CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, EtOH) were distilled and dried before use. DMF, DMSO were used without purification. Solvents for electrochemical experiments were re-distilled and passed through a column of activated alumina.

### 2.3. Synthesis of ligands

The unsymmetrical Schiff bases were obtained by condensation of the half units and the appropriate aldehyde or ketones. Also half units were synthesized by mono condensation of the appropriate diamines, aldehyde or ketones. Overall scheme for the preparations are shown in Fig. 2. H<sub>2</sub>L<sup>x</sup> ( $x = 7,$

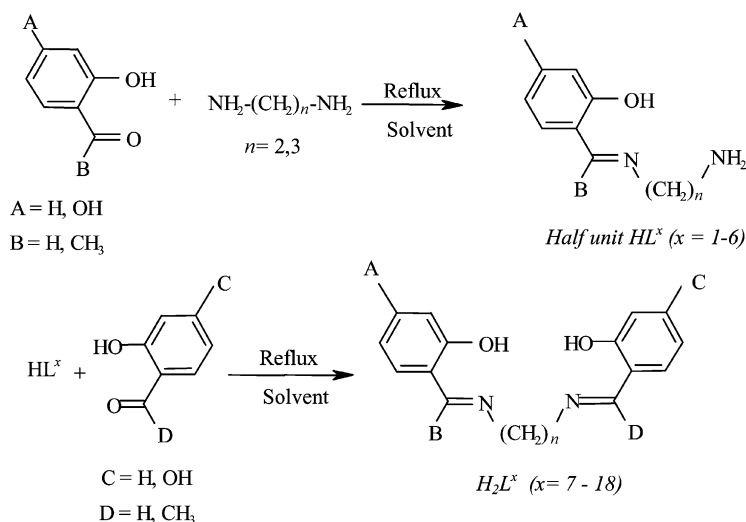


Fig. 2. Overall synthesis path for the preparation half units and tetradentate Schiff bases.

Table 2  
Physical properties and some spectral data of Schiff bases<sup>a</sup>

Compound formula	Formula weight (yield %)	Color	Melting point (°C)	Selective IR bands (cm <sup>-1</sup> )			Founded (calculated)		
				O–H	C=N	C–O	%C	%H	%N
H <sub>2</sub> L <sup>7</sup> C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	268.32 (93)	Y	128.6–129.8	3400	1638	1284	71.38 (71.62)	6.28 (6.01)	10.18 (10.44)
H <sub>2</sub> L <sup>8</sup> C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	296.37 (54)	Y	160 <sup>b</sup>	3300	1615	1246	72.74 (72.95)	6.88 (6.80)	9.33 (9.45)
H <sub>2</sub> L <sup>9</sup> C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	282.34 (42)	Y	170 <sup>b</sup>	3380	1638	1286	72.26 (72.32)	6.09 (6.43)	9.68 (9.92)
H <sub>2</sub> L <sup>10</sup> C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	298.34 (38)	DY	195 <sup>b</sup>	3450	1615	1246	68.33 (68.44)	6.30 (6.08)	9.35 (9.34)
H <sub>2</sub> L <sup>11</sup> C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	312.37 (45)	Y–G	240 <sup>b</sup> , >400	3430 (3620)	1584	1246	69.01 (69.21)	6.68 (6.45)	8.74 (8.97)
H <sub>2</sub> L <sup>12</sup> C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>	328.37 (35)	LG	260 <sup>b</sup> , >400	3600 (3450)	1592	1246	65.75 (65.84)	6.37 (6.14)	8.69 (8.53)
H <sub>2</sub> L <sup>13</sup> C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	282.34 (87)	Y–D	51.9–53.1	3300	1638	1284	72.11 (72.32)	6.13 (6.43)	10.05 (9.92)
H <sub>2</sub> L <sup>14</sup> C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	310.40 (69)	Y	127.2–129.0	3400	1615	1307	73.34 (73.52)	7.18 (7.14)	8.89 (9.02)
H <sub>2</sub> L <sup>15</sup> C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	294.35 (39)	Y	115.6–117.1	3400	1638	1284	73.25 (73.45)	6.22 (6.16)	9.22 (9.52)
H <sub>2</sub> L <sup>16</sup> C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	312.37 (41)	Y	171.8–173.0	3410	1638	1284	68.92 (69.21)	6.70 (6.45)	8.77 (8.97)
H <sub>2</sub> L <sup>17</sup> C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub>	326.40 (25)	Y–O	230 <sup>b</sup> , >400	3430	1615	1307	69.72 (69.92)	6.88 (6.79)	8.65 (8.58)
H <sub>2</sub> L <sup>18</sup> C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>	342.40 (30)	YG	245 <sup>b</sup> , >400	3453	1607	1246	66.48 (66.65)	6.53 (6.48)	8.02 (8.18)

<sup>a</sup> Infrared spectra measurement as KBr pellets. Here, w: width, s: sharp; Y: yellow; G: green; O: orange; B: brown; D: dark; L: light.

<sup>b</sup> Decomposed.

Table 3  
Elemental analysis, vibrations parameters and some physical properties<sup>a</sup>

Compound formula	Formula weight (yield %)	Color, melting point (°C)	Selective IR bands (cm <sup>-1</sup> )		Important abs. bands (nm) ( $\epsilon$ , M/cm)		Founded (calculated)		
			V=O	C=N	$\lambda_{\max}$	Shoulder	%C	%H	%N
VOL <sup>7</sup> VC <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	333.24 (93)	G (299.5–301.2)	992	1607	577.2 (275)	474 (956)	57.48 (57.67)	4.35 (4.23)	8.23 (8.41)
VOL <sup>8</sup> .C <sub>2</sub> H <sub>5</sub> OH VC <sub>20</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub>	407.36 (75)	G (280 <sup>b</sup> , >400)	976	1584	571.1 (283)	479 (1100)	58.71 (58.97)	5.68 (5.94)	6.70 (6.88)
VOL <sup>9</sup> VC <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	347.27 (61)	G (>400)	954	1607	572.5 (330)	463 (970)	58.64 (58.80)	4.55 (4.64)	8.23 (8.07)
VOL <sup>10</sup> VC <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	363.26 (55)	G (>400)	967	1615	568.3 (298)	435 (1050)	56.38 (56.21)	4.65 (4.44)	7.52 (7.71)
VOL <sup>11</sup> VC <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	377.29 (50)	G (>400)	969	1584	559.6 (261)	442 (980)	57.12 (57.30)	4.89 (4.81)	7.52 (7.45)
VOL <sup>12</sup> .C <sub>2</sub> H <sub>5</sub> OH VC <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	439.36 (75)	G (>400)	989	1600	530.5 (170)	415 (1125)	54.80 (54.67)	5.78 (5.51)	6.26 (6.38)
VOL <sup>13</sup> VC <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	347.27 (85)	O (130 <sup>b</sup> , >400)	861	1630	522.3 (179)	438 (890)	58.49 (58.80)	4.82 (4.64)	7.95 (8.07)
VOL <sup>14</sup> VC <sub>19</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	375.32 (65)	DG (285 <sup>b</sup> , >400)	961	1615	547.5 (205)	431.3 (984)	60.67 (60.80)	5.55 (5.37)	7.19 (7.46)
VOL <sup>15</sup> VC <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	359.28 (67)	G (290.1–291.8)	955	1615	570.8 (290)	455 (940)	59.89 (60.18)	4.68 (4.49)	7.97 (7.80)
VOL <sup>16</sup> VC <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	377.30 (53)	B–G (260.3–261.7)	878	1615	561.4 (318)	447 (912)	57.07 (57.30)	4.86 (4.81)	7.49 (7.45)
VOL <sup>17</sup> .C <sub>2</sub> H <sub>5</sub> OH VC <sub>19</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>	437.30 (64)	B (270 <sup>b</sup> , >400)	859	1607	575.5 (190)	410 (1150)	57.41 (57.68)	6.08 (5.99)	6.21 (6.40)
VOL <sup>18</sup> .C <sub>2</sub> H <sub>5</sub> OH VC <sub>19</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub>	453.30 (70)	Y–G (210 <sup>b</sup> , >400)	938	1607	549.8 (335)	460 (1020)	55.82 (55.64)	6.08 (5.78)	5.94 (6.18)

<sup>a</sup> Infrared spectra measurement as KBr pellets. Here, w: width, s: sharp; Y: yellow; G: green; O: orange; B: brown; D: dark.

<sup>b</sup> Decomposed.

13) and their complexes were prepared by literature methods [23].

### 2.3.1. Synthesis of half units: $HL^x$ ( $x = 1-6$ )

To the vigorously stirred and cool dilute solution of the diamine (20 mmol) in anhydrous ethanol (100 ml), was added dropwise a cooled solution of salicylaldehyde or 2'-hydroxyacetophenone or 2',4'-dihydroxyacetophenone (15 mmol) in anhydrous ethanol (80 ml). After the addition was complete, the mixture was stirred for some minutes (15–30 min) and then refluxed for 15–45 min. The resulting solution was evaporated in vacuum to remove the solvent and the excess diamine.

### 2.3.2. Synthesis of $H_2L^x$ ( $x = 7-18$ )

To the stirred solution of the precursor (half units  $HL^x$  ( $x = 1-6$ )) (10 mmol) in anhydrous ethanol (60 ml) was added a solution of salicylaldehyde or 2'-hydroxyacetophenone or 2',4'-dihydroxyacetophenone (10 mmol) in anhydrous ethanol (20–30 ml). In some cases ( $H_2L^x$ ,  $x = 10, 16, 17$ ), a few drops of piperidine were added to the mixture reaction and refluxed (30–120 min). The mixture was concentrated in vacuum by evaporation of the solvent until a colored solid precipitated. The product was filtered and washed with the appropriate solvent ( $H_2L^x$ ,  $x = 7, 8, 10, 13, 14$  ethanol;  $x = 9, 15, 16$  acetonitrile;  $x = 11, 12$  chloroform;  $x = 17, 18$  MeOH) and re-crystallized to give colored crystals. Yields ranged from 25 to 95% based the diamine used (in stoichiometric molar ratio). Physical properties and some spectral data are given in Tables 1 and 2.

### 2.4. Preparation of vanadyl complexes:

#### $VOL^x$ ( $x = 7-18$ )

The vanadyl complexes were prepared under ambient condition. To a hot solution of  $H_2L^x$  ( $x = 7-18$ ) (1.7 mmol) in a mixed solvent (for  $H_2L^x$ ,  $x = 7, 8, 10$ ;  $CH_3Cl$  10 ml/EtOH 15 ml/MeOH 10 ml and  $x = 9, 11, 12$ ; DMSO 80 ml and  $x = 12-18$ ; EtOH 10 ml/MeOH 40 ml/DMSO 20 ml) a hot solution of VO(acac) (1.7 mmol) in methanol (10 ml) was added. The mixture was heated and a few drops of triethylenamine were added. The reaction mixture was refluxed for 30–60 min. The colored solution concentrated and cooled to yield colored powders or

crystals. In some cases the products were oily. A little cooled ether was added until a solid product precipitated. Re-crystallization from EtOH; EtOH/ $CHCl_3$ ; DMSO/EtOH; DMSO/MeOH and MeOH/ $CHCl_3$  mixtures in 1:1 ratio for  $VOL^x$ ;  $x = 7, 8, 12, 13, 9, 10, 14, 15, 11, 17, 18$ , respectively, gave analytically pure products (53–93% yield). Analytical data and some physical properties for complexes are listed in the Table 3.

### 2.5. Catalytic oxidations

Catalytic oxidation was performed in stirred flasks. All glassware was oven-dried prior to use. In a typical experiment, 10  $\mu$ mol of the vanadyl complexes were dissolved in freshly distilled acetonitrile (15 ml) or DMF (10 ml) at 40 °C. The system was evacuated and purged with argon gas. After saturation of the solution with dioxygen, 100 mmol freshly distilled cyclohexene was injected. The reactions were carried out at 78–81 °C for 24 h under 1 atm of  $O_2$  (continually replenished). The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC) and GC–MS coupling.

## 3. Result and discussion

### 3.1. Characterization of ligands

The symmetric and non-symmetric ligands were prepared by the reaction of half units  $HL^x$  ( $x = 1-6$ ) with the desired aldehyde or ketones. The yellow or orange crystalline products were isolated in excellent yields (>80%). It is noteworthy that some of physical properties and spectral data of the non-symmetrical Schiff bases lie between the symmetrical ones. The ligands were characterized by  $^1H$  NMR, IR spectroscopy and elemental analysis (Tables 1 and 2).

$^1H$  NMR spectra of the tetradentate Schiff base ligands of  $N_2O_2$  donor sets possess two phenolic groups and azomethine groups.  $^1H$  NMR of Schiff base ligands shows the aromatic protons as multiplet in the range 6.1–7.8 ppm and O–H protons of the phenolic groups in the range 12.5–16.9 ppm. The azomethine protons appear at 7.9–8.2 ppm. IR spectral data of

the compounds and their relative assignments are shown in Table 1. Several IR absorption bands in the 1450–1650  $\text{cm}^{-1}$  region can be attributed to the C=O, C=N and C=C stretching vibrations [12–14].

The infrared spectra of the half units show two bands at range 3380–3250  $\text{cm}^{-1}$ . These two bands are assigned to the primary amine stretchings. An intense sharp band at 1615  $\text{cm}^{-1}$  in the spectrum of  $\text{HL}^x$ ;  $x = 1, 4$ ; and a broad band at 1584–1638  $\text{cm}^{-1}$  in the  $\text{H}_2\text{L}^x$  are assigned to the azomethine vibrations. The lack of a band due to free OH stretching vibration in the spectra of  $\text{H}_2\text{L}^x$ , is consistent with the finding of Kovacic [15].

### 3.2. Characterization of oxovanadium(IV) complexes

A new series of some oxovanadium(IV) complexes with tetradentate Schiff base ligands was prepared and characterized (Table 3 and Fig. 3).

Treatment of the Schiff base ligands with  $\text{VO}(\text{acac})_2$  under aerobic conditions gave the desired oxovanadium(IV) complexes [17]. Overall yields were reasonable (53–93%). The vanadyl compounds which were identified by IR, UV–VIS spectroscopy and elemental analysis (Table 3), are remarkably stable to air, water and heat. It was also possible to prepare those mentioned complexes by in situ reactions (template method). In our previous work, we used this unique method to synthesis the some unsymmetrical Schiff bases complexes [12–14,16]. All complexes present very strong and broad bands corresponding to  $\nu(\text{C}=\text{N})$  centered around 1584–1630  $\text{cm}^{-1}$ . The bands are probably broadened because of they overlap with the aromatic ring-carbon stretchings. IR spectra of these complexes show  $\nu(\text{V}=\text{O})$  in the region 859–878  $\text{cm}^{-1}$  for  $\text{VOL}^x$ ,  $x = 13, 16, 17$ , and at 938–992  $\text{cm}^{-1}$  for other ones. Tetradentate Schiff base oxovanadium(IV) complexes generally show  $\nu(\text{V}=\text{O})$  around 860  $\text{cm}^{-1}$  for a polymeric form and around 970  $\text{cm}^{-1}$  for a

monomeric form [18,19]. Thus, orange  $\text{VOL}^{13}$  and  $\text{VOL}^{16}$ ,  $\text{VOL}^{17}$  are assigned to the polymeric structure. Green  $\text{VOL}^x$ ;  $x = 7$ –12, 15, 15, 18; are assigned to monomeric five coordinate structures. The IR spectra of  $\text{VOL}^x$ ;  $x = 8, 12, 17, 18$ ; show two  $\nu(\text{O}-\text{H})$  bands in the region 3543–3601  $\text{cm}^{-1}$ . The two bands are assigned to the O–H stretching frequency of water and ethanol molecule [20].

Electronic spectra of the complexes in this study show d–d bands around 13,000 and 18,300  $\text{cm}^{-1}$  and CT bands around 25,000 and 38,000  $\text{cm}^{-1}$  in DMSO solution, which are similar to those in the spectra of  $\text{VOL}^x$  in polar solvents [21]. In the visible absorption spectra, the first band ( $\text{dxy} \rightarrow \text{dxz}, \text{dyz}$ ) normally appears broad, between approximately 650 and 900 nm, and in some cases it is hardly distinct from the tail of bands at lower wavelengths (for complexes  $\text{VOL}^x$ ;  $x = 9, 10, 13$ –15, 17). A band at  $545 \pm 30$  nm is apparently common to all complexes. However, while for some a distinct maximum appears (for  $\text{VOL}^x$ ;  $x = 7, 13$  in DMSO); this band often appears as a shoulder on higher intensity bands (for  $\text{VOL}^x$ ,  $x = 8$ –11, 14–16, 18 in DMSO). In a very few cases not even such a shoulder is apparent (for  $\text{VOL}^x$ ,  $x = 12, 17$  in DMSO). This shoulder probably corresponds to the second band ( $\text{dxy} \rightarrow \text{dx}^2\text{y}^2$ ) [22]. The electronic spectra of  $\text{VOL}^x$  ( $x = 8, 11, 13, 14$ ) show d–d bands around 16,000–18,000  $\text{cm}^{-1}$  in acetonitrile. However, the d–d band around 17,000  $\text{cm}^{-1}$  is hidden by a charge transfer band around 22,000  $\text{cm}^{-1}$  for other complexes.

Evaporation of acetonitrile or ethanolic solution of  $\text{VOL}^x$ ;  $x = 13, 16, 17, 18$ , gave amorphous green products. On standing in air, these gradually turned back to orange and brown, respectively. The IR data of these amorphous products show  $\nu(\text{V}=\text{O})$  at 938–992  $\text{cm}^{-1}$ , indicating monomeric structures. Further investigation of these products was not carried out. The molar conductance values in DMF at the concentration of  $10^{-3}$  M are too low to account for any dissociation of the complexes. Also the molar conductance of the complexes was measured in DMSO, indicating non-electrolytic nature.

### 3.3. Electrochemical studies

The electrochemical behavior of the catalysts investigated using voltammetry. Electrochemical studies

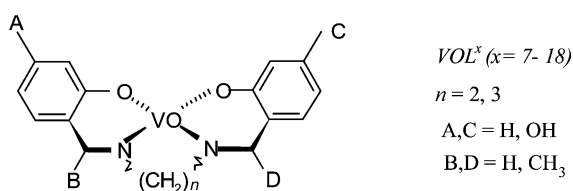


Fig. 3. General structure of oxovanadium(IV) complexes.

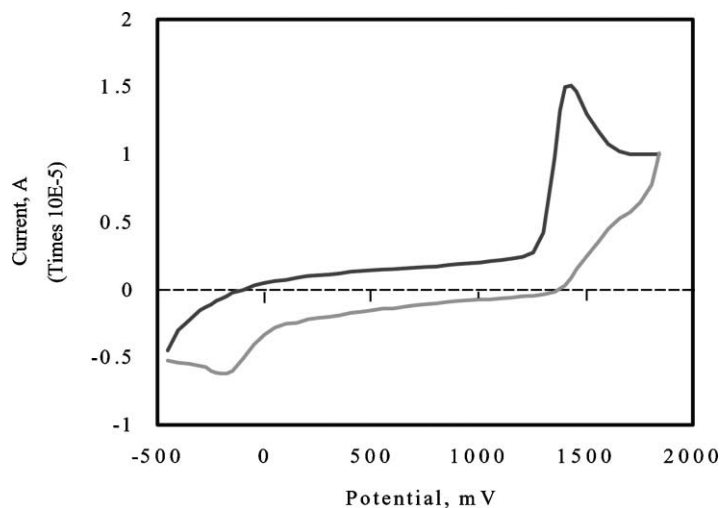


Fig. 4. Cyclic voltammograms of 1 mmol  $\text{H}_2\text{L}^9$  in DMF solution containing 0.1 M TBAH as a supporting electrolyte. Scan rate was 100 mV/s.

were carried out in either acetonitrile or dimethylformamide solution by cyclic voltammetry at room temperature. In order to study the electron transfer processes of the complexes, we investigated the electrochemical redox processes of the ligands. Typical cyclic voltammogram of  $\text{H}_2\text{L}^9$  in DMF solution is shown in Fig. 4. As can be seen in this figure, the redox processes were highly irreversible. Fig. 5 shows the cyclic voltammograms of 1 mM of  $\text{VOL}^9$  complex in acetonitrile solution at various scan rates. As can

be seen in Fig. 5, the redox processes were reversible, also the cathodic peak current of the complexes was increased and the peak potentials shifted to more negative direction with the increase of the scan rate.

Compounds examined in both solutions (DMF, acetonitrile) showed small shifts of those redox potentials between solvents ( $<0.03$  V). The vanadyl complexes,  $\text{VOL}^x$ ;  $x = 7, 8, 9, 12, 13, 14, 18$  exhibit reversible and  $\text{VOL}^x$ ;  $x = 10, 11, 15, 16, 17$  exhibited clean and quasi-reversible electrochemistry.

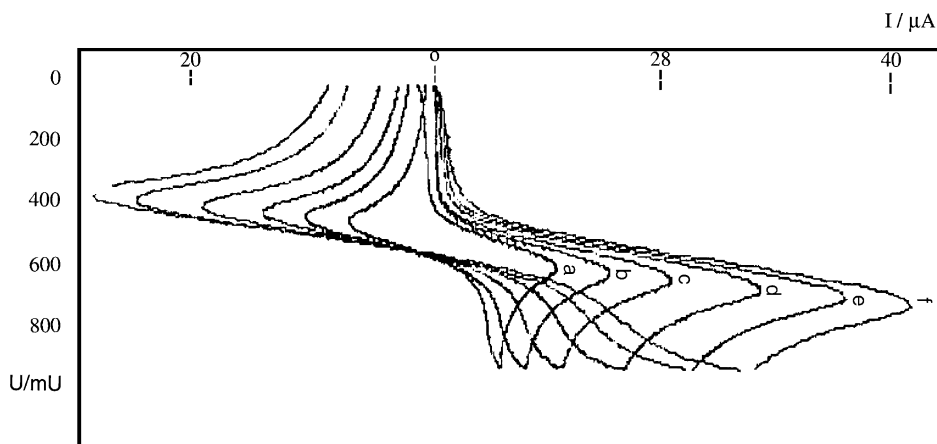


Fig. 5. Cyclic voltammograms of 1 mmol  $\text{VOL}^9$  in acetonitrile solution containing 0.1 M TBAH as a supporting electrolyte. Scan rates were (in mV/s) (a) 50, (b) 100, (c) 200, (d) 400, (e) 700, (f) 1000, respectively.



Table 4

Catalytic oxidation of cyclohexene by O<sub>2</sub> and formal potentials for redox couples vanadium(V/IV)<sup>a</sup>

Complex	$E^0$ (V(V)/V(IV)) (mV) versus AgCl/Ag ( $\Delta E_p$ (mV))	Conversion (%)	Products, relative ratio		
VOL <sup>7</sup>	543 (58)	81	15	29	56
VOL <sup>8</sup>	490 (75)	63	51	30	19
VOL <sup>9</sup>	515 (65)	69	48	25	27
VOL <sup>10</sup>	480 (100)	23	9	80	11
VOL <sup>11</sup>	490 (95)	28	47	35	18
VOL <sup>12</sup>	506 (78)	25	3	75	22
VOL <sup>13</sup>	517 (71)	63	56	32	12
VOL <sup>14</sup>	465 (60)	52	48	37	15
VOL <sup>15</sup>	485 (98)	25	18	24	58
VOL <sup>16</sup>	578 (102)	18	12	71	17
VOL <sup>17</sup>	550 (114)	23	53	18	29
VOL <sup>18</sup>	421 (68)	17	3	70	27

<sup>a</sup> Electrochemical measurement made in anhydrous acetonitrile or DMF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH). Irreversible reduction was observed for the complexes at potential less than -1400 mV accompanied by decomposition of the complexes.

Overall, the V(V)/V(IV) reduction potential shifts by approximately 130 mV from the parent VOL<sup>7</sup> to VOL<sup>18</sup> (Table 4). Irreversible ligand oxidation of the complexes occurs only at high potentials (>1.4 V). Therefore, we can conclude that these complexes are oxidatively robust. The number of electrons transferred in the electrode reaction for a reversible couple can be determined from the separation between the peak potential [24].

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.0591}{n}$$

where  $E_{pa}$ ,  $E_{pc}$ , and  $n$  are anodic potential, cathodic potential and the number of electrons transferred, respectively. Thus, one electron process exhibits a  $\Delta E_p$  approximately 0.059 V. At slower scan rate, The peak separation for the cathodic and anodic cyclic voltammetric peak potentials is very close to 60–70 m, indicating that the number of electrons transferred should be 1.0. The peak separation for the unsymmetrical complexes is larger than symmetrical ones. These result show that the electrochemical redox processes of vanadyl complexes with unsymmetrical Schiff base ligands are quasi-reversible charge transfer. Also the oxidation potential for the complexes with the substituted ligands or longer chelate ring ( $n = 3$ ) show less positive value than that of the complexes with unsubstituted ligands or shorter chelate ring ( $n = 2$ ). Therefore, we conclude that the oxidation potentials

of the VOL<sup>x</sup> are affected by the size of the chelate ring of ligands. However, upon oxidation, the green compounds turned to an intense violet. Re-reduction yielded VOL<sup>x</sup> unchanged. The process could be repeated many times without any evidence of a chemical degradation. Cyclic voltammetry on VOL<sup>x</sup> ( $x = 7-12, 14, 15$ ) reveals a reduction potential value in the range expected for a five-coordinated mono oxo-vanadium species on the basis of other members in this series. The fact that the reduction is completely reversible indicates that the five-coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale [25,26].

### 3.4. Catalytic reactivity of complexes

The vanadyl salen complexes (VOL<sup>x</sup>;  $x = 7-18$ ) were tested as catalysts for aerobic oxidation of hydrocarbons. Our work suggests that the unusual catalytic properties observed with simple salen ligand systems. In all the experiments cyclohexene was utilized as substrate. Typical catalytic reaction conditions involve acetonitrile and DMF solutions at elevated temperatures (78–81 °C). Stirred under 1 atm of O<sub>2</sub> (continuously replenished), with periodic product sampling. Under these conditions, cyclohexene oxidation to mixture of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one was observed for major complexes. The reaction

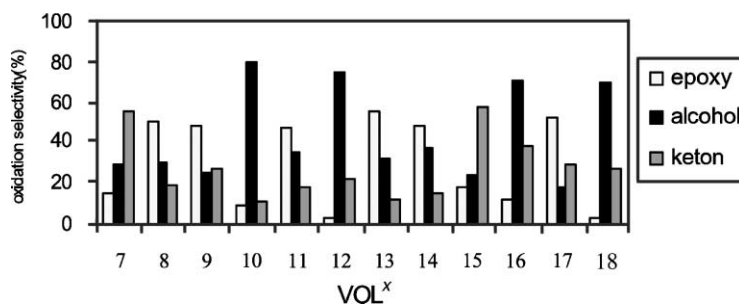


Fig. 6. Product selectivity for the aerobic oxidation of cyclohexene catalyzed by VOL<sup>x</sup>,  $x = 7-18$ .

was monitored by quantitative GC determination of the oxygenated products formed, sample quenched by addition of excess triphenyl phosphine to destroy remaining peroxide, and these products were identified by GC–MS coupling. Internal standard 1,2-dichlorobenzene was used for cyclohexene. The product distributions in cyclohexene oxidation are shown in Fig. 6. The vanadium-catalyzed aerobic oxidation of cyclohexene proceeds with a moderate selectivity for epoxidation (>50% for VOL<sup>x</sup>;  $x = 8, 16, 17$ , Fig. 6).

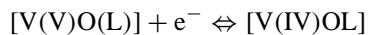
Several control experiments were performed. Catalysis is not affected by the presence or absence of light. The salen catalysts are very stable to oxidative degradation under reaction conditions. In the absence of catalyst or in presence of ligand alone, little or no oxidation occurs.

A striking feature of these catalysts is the correlation of catalytic activity with redox potential. In addition to redox potential, the fine structural details of the complexes would play an important role. Ligand distortions caused by substitution may strongly influence the reorganization energy of the ground state towards that of the transition state in redox reaction and thus, lower the overall activation energy, relative to the less distribution salen system. As for some of the complexes which have very different activity and selectivity in spite of their similar V(IV)/V(V) potentials.

#### 4. Conclusion

We have succeeded in designing an active family and robust catalysts for cyclohexene oxidation by dioxygen under mild conditions using inexpensive

and readily available salen ligands. Systematic ancillary ligand substitutions have allowed V(V)/V(IV) reduction potentials to be tuned over a range of approximately 130 mV and the reactivity of the catalysts to be modulated by control of redox potential and metal-oxo electrophilicity. Further, if the complexes were completely unsymmetrical, it should be possible to increase both the selectivity and catalytic activity. We concluded that the oxidation potentials of the VOL<sup>x</sup> are affected by chelate ring size of the ligands. Upon oxidation, the green compounds turned to an intense violet or blue colored. Re-reduction yielded VOL<sup>x</sup> unchanged. The process could be repeated many times without any evident chemical degradation. Cyclic voltammetry on VOL<sup>x</sup> ( $x = 7-12, 14, 15$ ) reveals a reduction potential value in the range expected for a five-coordinated mono oxovanadium species on the basis of other members in this series. The fact that the reduction is completely reversible indicates that the five-coordinate geometry is stable in both oxidation states, at least on the cyclic voltammetry time scale. From these results, we concluded that the redox process of all vanadyl Schiff base complexes used in this study are following the reaction.



The catalytic system described here is an efficient and inexpensive method for the oxidation of olefins, with the advantages of high activity, selectivity, re-usability and short reaction times. The correlation between potential and activity seems to be subject to subtle structural effects that were not readily apparent in these systems. This may in fact offer additional possibilities for manipulating reactivity, so that both

electronic and steric factors can be controlled independently and simultaneously. Such a situation provides an unusually intriguing opportunity for connecting the result of basic research to development of the practical catalysts.

Further work directed towards the development of an efficient homogeneous catalyst for asymmetric oxidation of olefins to their corresponding epoxy compounds is under progress.

### Acknowledgements

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