

Synthesis, characterization and catalytic activity of novel monomeric and polymeric vanadyl Schiff base complexes

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Abstract

This article describes the synthesis and characterization of two novel, as well as four previously reported, Schiff base complexes of oxovanadium(IV) and the study of their catalytic reactivity in the aerobic oxidation of olefins. The novel (5-Br-3-NO₂salen) and (5-Br-3-NO₂meso-stein) ligands were, respectively, synthesized from condensation of 5-bromo-3-nitro-2-hydroxybenzaldehyde with ethylenediamine or *meso*-1,2-diphenyl-1,2-ethylenediamine. The reaction of these ligands with VO(acac)₂ readily resulted in the synthesis of their oxovanadium(IV) complexes [VO(5-Br-3-NO₂salen)] and [VO(5-Br-3-NO₂meso-stein)], respectively. The novel ligands and complexes were deliberately designed to increase the V⁵⁺/V⁴⁺ reduction potentials and to obtain better catalytic performances. [VO(5-Br-3-NO₂salen)] complex was obtained in orange polymeric form but [VO(5-Br-3-NO₂sal-meso-stein)] complex was obtained in green monomeric form. The monomeric form of the latter complex along with its high (V⁵⁺/V⁴⁺) reduction potential makes it a suitable candidate for the aerobic oxidation of olefins. Systematic substitutions on the ancillary ligand have allowed V⁵⁺/V⁴⁺ reduction potentials to be tuned over a range of approximately 475 mV. Catalytic activity increases with increasing V⁵⁺/V⁴⁺ reduction potential and catalytic selectivity varies by changes in the ligands.

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Keywords: Aerobic selective oxidation; Monomeric form; Polymeric form; Catalytic oxidation of olefins; Oxovanadium(IV) complexes

1. Introduction

Tetradentate Schiff base complexes of oxovanadium(IV) have been extensively studied. These complexes form either a green monomeric structure with square-pyramidal coordination geometry around the metal center or an orange polymeric linear chain structure (V=O···V=O···) [1]. The green monomeric structure is observed for complexes like [VO(salen)] (salen: *N,N'*-salicylideneethylenediamine) but the orange polymeric linear chain structure is observed for those complexes like [VO(5-NO₂salen)] (5-NO₂salen: *N,N'*-di-5-nitrosalicylideneethylenediamine) having electron withdrawing nitro substituents at the 5-position of the salicylaldehyde moiety [2]. IR spectra of vanadyl Schiff base complexes show two kinds of V=O stretching bands around (960–990 cm⁻¹) for the monomeric ones and (850–880 cm⁻¹) for the polymeric forms [3,4]. The catalytic reactivity of vanadyl Schiff base complexes

has been extensively studied [5–9]. In earlier works, we have synthesized some Schiff base complexes of oxovanadium(IV) and we have studied the catalytic reactivity of these complexes as catalyst for the aerobic oxidation of olefins [8,9]. Previous studies [7] have indicated that as the number of electron withdrawing substituents on the ancillary ligand system increases, the reduction potential for V⁵⁺/V⁴⁺ also increases. The increase in this reduction potential results in the better catalytic performance of the complexes. On the other hand, it is also reported [3] that Schiff base complexes of oxovanadium(IV) with electron withdrawing groups tend to form polymeric forms. Having this in our mind we decided to synthesize oxovanadium(IV) complexes of tetradentate Schiff base ligands with more electron withdrawing substituents on the ligand system and with monomeric forms.

In this paper, we report the synthesis and characterization of novel polymeric and monomeric oxovanadium(IV) Schiff base complexes derived from ethylenediamine and *meso*-1,2-diphenyl-1,2-ethylenediamine as the diamine and 5-nitro-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde and 5-bromo-3-nitro-2-hydroxybenzaldehyde as the aldehyde and

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the study of the catalytic reactivity of these complexes with the general formula VOL^x ($x = 1-6$) (Scheme 2).

2. Experimental

2.1. Physical measurements

IR spectra were recorded as KBr pellets using Unicam Matson 1000 FT-IR spectrophotometer. ^1H NMR spectra were obtained on a Bruker FT NMR 500 (500 MHz) spectrophotometer using CDCl_3 and $(\text{CD}_3)_2\text{SO}$ as solvents. The electronic spectra were recorded on a CARY 100 Bio UV-vis spectrophotometer. Elemental analyses (C, H, and N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analysesysteme, GmbH). The oxidation products were identified by GC with a CHROMPACK CP9001 gas chromatograph. Cyclic voltammetry was performed using a 757VA Computrace Metrohm. The working, auxiliary and reference electrodes were glassy carbon, gold wire, and AgCl/Ag , respectively. Electrochemical measurements were performed at room temperature under argon with 0.1 M tetrabutylammoniumtetrafluoroborate as supporting electrolyte and 10^{-3} M concentrations of the complexes.

2.2. Materials

Unless otherwise noted, commercial materials were used as received. Acetonitrile and cyclohexene were purified by standard procedures prior to use. Oxygen gas was passed through a calcium chloride drying tube before admission to the reaction mixture. Reference samples of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (Fluka) were distilled and stored in a refrigerator.

2.3. Synthesis of Schiff base ligands

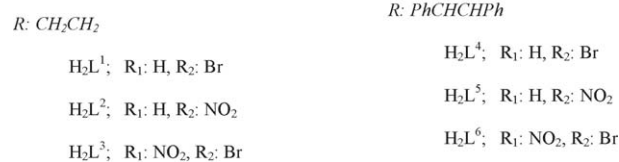
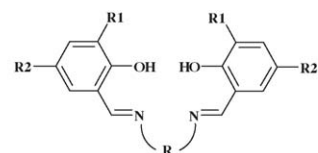
The Schiff base ligands were quantitatively prepared by the reaction of *meso*-1,2-diphenyl-1,2-ethylenediamine [10] or ethylenediamine with 2 equivamounts of X-salicylaldehyde ($X = \text{H}, 5\text{-Br}, 5\text{-NO}_2$) and 5-bromo-3-nitro-salicylaldehyde [11] in ethanol.

2.3.1. Synthesis of H_2L^x ($x = 1, 2, 4, 5$)

H_2L^x ($x = 1, 2, 4, 5$) were prepared according to literature procedures [8,9]. Analytical data were found to be in good agreement with literature data (Scheme 1).

2.3.2. Synthesis of H_2L^3 : (5-bromo-3-nitro-salen)

To a vigorously stirred ethanolic solution (40 mL) of 5-bromo-3-nitro-salicylaldehyde (0.492 g, 2 mmol) was added dropwise a solution of ethylenediamine (1 mmol) in 40 mL of ethanol. After the addition was complete, the mixture was stirred and refluxed for 45 min. The mixture was then cooled and the yellow precipitate of the ligand was collected by filtration, washed with ethanol and dried in a desiccator. Yield: 0.423 g (82%). Anal. calcd. for $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{N}_4\text{O}_6$: C, 37.24; H, 2.32; N, 10.85. Found: C, 36.98; H, 2.45; N, 10.53. IR (KBr, cm^{-1}): 1653



Scheme 1.

$[\nu(\text{C}=\text{N})]$, 3442 $[\nu(\text{O}-\text{H})]$. ^1H NMR (500 MHz, CDCl_3): 13.3 (s, 2H, OH), 8.5 (s, 2H, Ar-CH=N), 6.8–7.8 (m, 4H, Ar), 4.2 (s, 4H, alkane) (Scheme 1).

2.3.3. Synthesis of H_2L^6 : (5-bromo-3-nitro-sal-meso-stien)

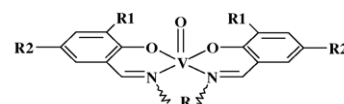
To a vigorously stirred ethanolic solution (40 mL) of 5-bromo-3-nitro-salicylaldehyde (0.492 g, 2 mmol) was added dropwise a solution of *meso*-1,2-diphenyl-1,2-ethylenediamine (0.212 g, 1 mmol) in 40 mL of ethanol. After the addition the mixture was stirred and refluxed for 1 h. The mixture was then cooled and the orange precipitate of the ligand was collected by filtration and washed with ethanol and dried in air. Yield: 0.487 g (73%). Anal. calcd. for $\text{C}_{28}\text{H}_{20}\text{Br}_2\text{N}_4\text{O}_6$: C, 50.33; H, 3.01; N, 8.38. Found: C, 50.61; H, 3.17; N, 8.57. IR (KBr, cm^{-1}): 1638 $[\nu(\text{C}=\text{N})]$, 3437 $[\nu(\text{O}-\text{H})]$. ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$): 14.2 (s, 2H, OH), 8.4 (s, 2H, Ar-CH=N), 6.9–8 (m, 14H, Ar), 4.9 (s, 2H, alkane) (Scheme 1).

2.4. Preparation of the vanadyl Schiff base complexes

All of the complexes were prepared by the reaction of Schiff base ligands with equivamounts of $[\text{VO}(\text{acac})_2]$ in methanol.

2.4.1. Synthesis of the VOL^x ($x = 1, 2, 4, 5$)

All of the VOL^x complexes with ($x = 1, 2, 4, 5$) were prepared according to literature procedures [8,9]. Analytical data were found to be in good agreement with literature data (Scheme 2).



Scheme 2.

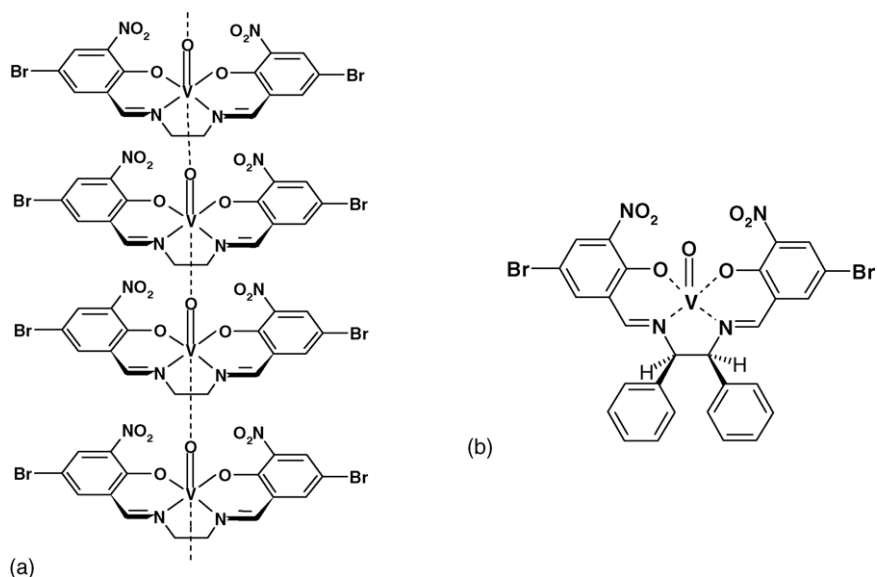


Fig. 1. Polymeric form of VOL³ (a) and monomeric form of VOL⁶ (b).

2.4.2. Synthesis of the [VO(5-Br-3-NO₂salen)]

To a hot methanolic solution (70 mL) of VO(acac)₂ (0.265 g, 1 mmol) was added 5-bromo-3-nitrosalen (0.515 g, 1 mmol) and pyridine (1.5 mL), and the mixture was vigorously stirred for 1.5 h at 75 °C. The resulting orange polymeric precipitate was collected by filtration, washed with ethanol and ether successively and dried in air. Yield: 0.529 g (87%). Anal. calcd. for C₁₆H₁₀Br₂N₄O₇V·1.5H₂O: C, 31.60; H, 2.14; N, 9.21. Found: C, 31.85; H, 2.34; N, 9.05. IR (KBr, cm⁻¹): 876 [ν (V=O)], 1646 [ν (C=N)]. UV–vis spectrum [DMSO (nm), ϵ (1 mol⁻¹ cm⁻¹): 730 (105), 530 (220) (shoulder) (Fig. 1).

2.4.3. Synthesis of the [VO(5-Br-3-NO₂sal-meso-stein)]

To a hot methanolic solution (70 mL) of VO(acac)₂ (0.265 g, 1 mmol) was added 5-bromo-3-nitrosalen (0.668 g, 1 mmol) and pyridine (1.5 mL). The mixture was vigorously stirred for 3 h at 75 °C. The resulting green monomeric precipitate was collected by filtration and washed with ethanol and ether and dried in air. Yield: 0.534 g (72%). Anal. calcd. for C₂₈H₁₈Br₂N₄O₇V·0.5H₂O: C, 45.31; H, 2.56; N, 7.54. Found: C, 45.71; H, 2.66; N, 7.31. IR (KBr, cm⁻¹): 997 [ν (V=O)], 1630 [ν (C=N)]. UV–vis spectrum [DMSO (nm), ϵ (1 mol⁻¹ cm⁻¹): 754 (130), 564 (250) (shoulder) (Fig. 1b).

2.5. Catalytic oxidation of cyclohexene

Oxidation of cyclohexene using various vanadyl complexes VOL^x (x = 1–6) were carried out in a 100 mL Schlenk tube. All glasswares were oven-dried prior to use. In a typical experiment, the catalyst (0.011 mmol) was dissolved in freshly distilled acetonitrile (25 mL) at 40 °C. The system was purged with argon gas. The flask was then charged with 100 mmol of freshly distilled cyclohexene, and O₂ was continuously replenished. The contents were stirred at 78 ± 2 °C for 24 h, then the GC internal standard (1,2-dichlorobenzene) was added and the mixture was subjected to GC analysis.

3. Results and discussion

3.1. Characterization of vanadyl complexes

The desired oxovanadium(IV) complexes were obtained by the reaction of tetradentate ligands with VO(acac)₂ [12]. The yields of the complexes were reasonable. The IR spectrum of the novel complex VOL³ shows VO stretching vibration at around 876 cm⁻¹ which is indicative of polymeric form of the complex [3–5]. On the other hand, the IR spectrum of the novel complex VOL⁶ shows this vibration band at 997 cm⁻¹ which is indicative of its monomeric form. The C=N stretching vibrations of the ligands are centered around 1645 ± 10 cm⁻¹ which shift approximately 10 cm⁻¹ to lower wave numbers upon coordination to VO. Electronic spectra of the complexes show d–d bands around 560 and 760 nm in DMSO which are similar to those in the spectra of VOL^x in polar solvents [13]. Elemental analyses also confirm the synthesis of the complexes.

3.2. Electrochemical studies

Electrochemical studies were carried out in anhydrous acetonitrile and DMF solutions by cyclic voltammetry at room temperature. Fig. 2 shows the cyclic voltammogram of 10⁻³ M solution of VOL⁶ in DMF at 80, 200, 300 mV/s scan rates. The redox processes were reversible and the cathodic peak currents of the complexes were increased and the peaks were shifted to more negative potentials with increasing the scan rates.

3.3. Oxidation of cyclohexene catalyzed by vanadyl complexes VOL^x (x = 1–6)

The vanadyl Schiff base complexes (VOL^x, x = 1–6) were tested as catalysts for aerobic oxidation of cyclohexene. In this report, it is proposed that the catalytic performance of the vanadyl complexes increases with increasing electronegativity

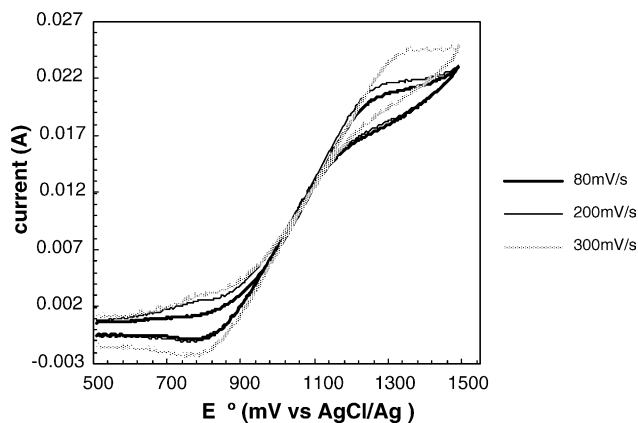


Fig. 2. CV curve of 10^{-3} M VOL^6 in acetonitrile solution containing 0.1 M tetrabutylammoniumtetrafluoroborate as supporting electrolyte; scan rates was 200 mV/s.

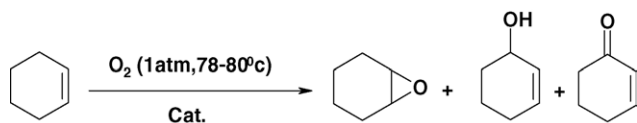


Fig. 3. Oxidation of cyclohexene by O_2 using Schiff base complexes as catalyst.

of the salen ligand systems. Typical catalytic reaction conditions involve acetonitrile solutions at $78 \pm 2^\circ\text{C}$ stirred under continuously replenished dioxygen for 24 h. Under these conditions, cyclohexene oxidation to a mixture of epoxide, allyl alcohol and allyl ketone was observed for complexes (Fig. 3). The reactions were monitored by quantitative GC determination of the oxygenated products. Samples were quenched by the addition of excess triphenylphosphine to destroy the remaining peroxide.

The catalytic activities were measured at $78 \pm 2^\circ\text{C}$ during 24 h. The product distributions in the oxidation of cyclohexene at $78 \pm 2^\circ\text{C}$ and 24 h are shown in Fig. 4. The catalytic performance of the novel complex VOL^6 is more than the other complexes, which is the direct consequence of its higher $\text{V}^{5+}/\text{V}^{4+}$ reduction potential and its monomeric form.

The vanadium-catalyzed aerobic oxidation proceeds with a moderate selectivity for epoxidation (49% for VOL^6 ; Table 1).

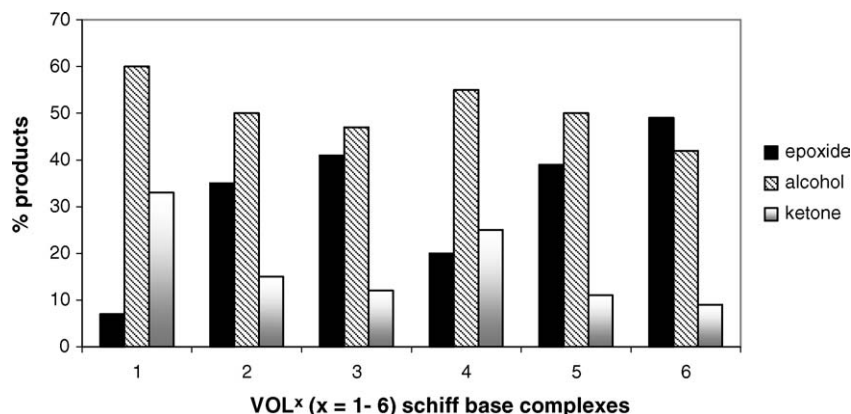


Fig. 4. Product selectivity for the aerobic oxidation of cyclohexene catalyzed by VOL^x ($x = 1-6$).

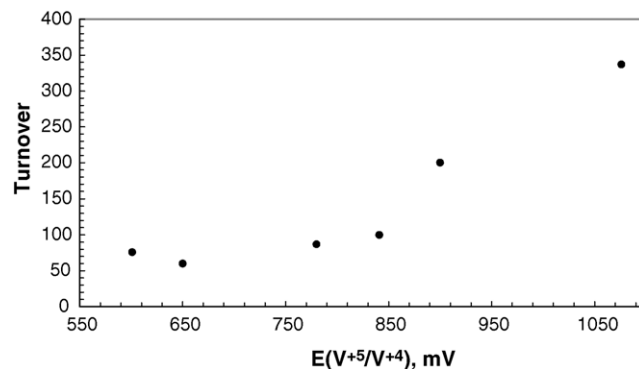
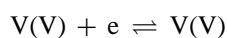


Fig. 5. Correlation of catalyst activity (turnover) vs. $\text{V}^{5+}/\text{V}^{4+}$ reduction potential (mV) for VOL^x ($x = 1-6$).

The salen catalysts are very stable to oxidative degradation under the reaction conditions. Catalytic reactions are not affected by the presence or absence of light. In the absence of the catalysts or in presence of the ligands alone, little or no oxidation occurs. A striking feature of these catalysts is the correlation of catalytic activity with the redox potentials. Catalytic activity increases with increasing $\text{V}^{5+}/\text{V}^{4+}$ reduction potentials (Fig. 5).




In addition to the redox potentials, the fine structural details of the complexes would play an important role. The reactivity and selectivity of the catalysts for the process of the oxidation of olefins with molecular oxygen seem to be a direct consequence of the electron-withdrawing substituents on the ligand skeleton. Substitution of nitro and bromo groups results in high reduction potential of $\text{V}^{5+}/\text{V}^{4+}$ for the complexes. Systematic ancillary ligand substitutions have allowed $\text{V}^{5+}/\text{V}^{4+}$ reduction potentials to be tuned over a range of approximately 475 mV and the reactivity of the catalysts to be modulated by control of the redox potentials and the metal-oxo electrophilicity.

We concluded that the redox process of all vanadyl complexes used in this study follows the reaction:



In this report, we produce an active family of catalysts for the epoxidation of cyclohexene by O_2 under mild conditions using inexpensive and readily available Schiff base ligands.

Table 1
Catalytic oxidation of cyclohexene by O₂ and formal redox potentials for (V⁴⁺/V⁵⁺)^a

Complex	V=O stretching (cm ⁻¹)	E°(V ⁵⁺ /V ⁴⁺) (mV vs. AgCl/Ag)	Color	Conversion (turnover) ^b	Products (%)		
							
VOL ¹	978	601	Green	20 (76)	7	60	33
VOL ²	881	780	Orange	23 (87)	35	50	15
VOL ³	876	900	Orange	53 (200)	41	47	12
VOL ⁴	981	650	Green	16 (60)	20	55	25
VOL ⁵	903	841	Orange	26 (100)	39	50	11
VOL ⁶	976	1076	Green	89 (337)	49	42	9

^a Electrochemical measurements made in anhydrous acetonitrile or DMF containing 0.1 M tetrabutylammoniumtetrafluoroborate. Irreversible reduction was observed for the complexes at potentials less than 1500 mV accompanied by decomposition of the complexes.

^b Turnover = (conversion × C_{initial})/[Q] × t.

The correlation between potentials 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.

Acknowledgments

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