Synthesis, crystal structures, and catalytic oxidation properties of oxidovanadium(V) complexes with Schiff base ligands

Kui-Hua Yang

Received: 16 January 2014/Accepted: 19 March 2014/Published online: 2 April 2014 © Springer International Publishing Switzerland 2014

Abstract Two new Schiff base ligands 2-chloro-N'-(5-fluoro-2-hydroxybenzylidene)benzohydrazide (H₂L^a) and 4-fluoro-2-{[2-(2-hydroxyethylamino)ethylimino]methyl} phenol (HL^b) were synthesized and characterized. Their respective oxidovanadium complexes, [VOL^a(OMe) (MeOH)]·MeOH (1) and [VO(μ -O)L^b]₂ (2), were synthesized and characterized by spectroscopy and single-crystal X-ray diffraction. The coordination sphere of each V atom is octahedral. Both complexes showed selective heterogeneous catalytic properties with 74–98 % conversion, for the oxidation of cyclohexene, cyclopentene, and benzyl alcohol using H₂O₂ as primary oxidant.

Introduction

In recent years, the development of efficient new catalysts for various organic reactions has received considerable attention [1–6]. Among the transition metals, vanadium has proved to be particularly useful for catalytic applications. Oxidovanadium(IV) complexes with various types of ligands have been shown to possess effective catalytic ability [7–11]. Several reports have indicated that oxidovanadium complexes with Schiff base ligands can catalyze the epoxidation of alkenes [12–17]. These epoxidation products are important industrial materials. Hydrogen peroxide is particularly attractive as an oxidant, as it is cheap, reasonably stable, readily available, and gives only water as a by-product. Herein, we report the synthesis,

K.-H. Yang (⊠)

e-mail: kuihua_yang@163.com

characterization, and catalytic properties of two new oxidovanadium(V) complexes, [VOL^a(OMe)(MeOH)]·MeOH (1) and [VO(μ -O)L^b]₂ (2), with Schiff base ligands 2-chloro-*N'*-(5-fluoro-2-hydroxybenzylidene)benzohydrazide (H₂L^a) and 4-fluoro-2-{[2-(2-hydroxyethylamino)eth-ylimino]methyl}phenol (HL^b).

Experimental

Reagents and measurements

All chemicals of AR grade were obtained from Sigma-Aldrich and used as received. ¹H NMR spectra were recorded on a 500 MHz Bruker NMR spectrometer using DMSO- d^6 solvent. IR spectra were obtained as KBr plates using a Bruker FT IR spectrophotometer. Elemental analyses (C, H, N) were obtained with a PerkinElmer CHN analyzer 2400. GC analyses were carried out with a GC-17A Shimadzu instrument.

Synthesis of H₂L^a

5-Fluorosalicylaldehyde (10 mmol, 1.40 g) and 2-chlorobenzohydrazide (10 mmol, 1.70 g) were dissolved in methanol (30 mL), and the mixture was stirred under reflux for 30 min. Most of the solvent was then removed by distillation to give a colorless precipitate. This was collected by filtration and recrystallized from methanol, washed successively with cold methanol and diethyl ether, and then air-dried. Yield: 83 %. Anal. Calc. for C₁₄H₁₀. ClFN₂O₂: C, 57.4; H, 3.4; N, 9.6. Found: C, 57.6; H, 3.6; N, 9.5 %. Selected IR data (v cm⁻¹, KBr): 3,371 (v_{O-H}), 3,218 (v_{N-H}); 1,632 (v_{C=N}). ¹H NMR (ppm): 12.13 (1H, br,

School of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang 621000, People's Republic of China

OH), 10.54 (1H, br, NH); 8.75 (1H, s, CH = N); 7.4–7.7 (5H, m, HAr), 7.21 (1H, d, HAr), 7.00 (1H, d, HAr).

Synthesis of HL^b

5-Fluorosalicylaldehyde (10 mmol, 1.40 g) and β-hydroxyethylenediamine (10 mmol, 1.04 g) were dissolved in methanol (30 mL), and the mixture was stirred under reflux for 30 min. Most of the solvent was then removed by distillation to give a colorless precipitate, which was collected by filtration, washed successively with cold methanol and diethyl ether, and then air-dried. Yield: 57 %. Anal. Calc. for C₁₁H₁₅FN₂O₂: C, 58.4; H, 6.7; N, 12.4. Found: C, 58.3; H, 6.6; N, 12.3 %. Selected IR data (v cm⁻¹, KBr): 3,360 (v_{O-H}), 3,232 (v_{N-H}); 1,618 (v_{C=N}). ¹H NMR (ppm): 11.87 (1H, br, OH), 10.72 (1H, br, NH); 8.53 (1H, s, CH = N); 7.60 (1H, s, HAr), 7.20 (1H, d, HAr), 6.98 (1H, d, HAr), 3.69 (2H, t, NCH₂), 3.50 (2H, t, CH₂OH), 2.89 (2H, t, NCH₂CH₂NH), 2.73 (2H, t, NHCH₂).

Synthesis of complex 1

 H_2L^a (0.2 mmol, 58.6 mg) and VO(acac)₂ (0.2 mmol, 53.0 mg) were mixed and added to methanol (20 mL), and the mixture was boiled under reflux until the color of the solution turned to deep brown. Block-shaped single crystals of the complex were obtained by slow evaporation of the solution in air. The crystals were isolated by filtration, washed successively with cold methanol and diethyl ether, and then air-dried. Yield: 69 %. Anal. Calc. for C₁₇H₁₉. ClFN₂O₆V: C, 45.1; H, 4.2; N, 6.2. Found: C, 45.3; H, 4.3; N, 6.1 %. Selected IR data (v cm⁻¹, KBr): 3,422 (v_{O-H}); 3,211 (v_{N-H}); 1,621 (v_{C=N}); 980 (v_{V=O}).

Synthesis of complex 2

HL^b (0.2 mmol, 45.2 mg) and VO(acac)₂ (0.2 mmol, 53.0 mg) were added to ethanol (20 mL), and the mixture was boiled under reflux until the color of the solution turned to yellow–green. Yellow single crystals of the complex were obtained after slow evaporation of the solution in air. These were isolated by filtration, washed successively with cold methanol and diethyl ether, and then air-dried. Yield: 45 %. Anal. Calc. for $C_{22}H_{28}F_2N_4O_8V_2$: C, 42.9; H, 4.6; N, 9.1. Found: C, 43.1; H, 4.7; N, 8.9 %. Selected IR data (v cm⁻¹, KBr): 3,430 (v_{O–H}); 3,246 (v_{N–H}); 1,605 (v_{C=N}); 972 (v_{V=O}).

X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determination of unit cell parameters and data collection was performed with Mo-K α radiation ($\lambda = 0.71073$ Å). The collected data were reduced with SAINT [18], and multi-scan absorption corrections were made using SAD-ABS [19]. Unit cell dimensions were obtained with leastsquares refinements, and both structures were solved by direct methods. Both complexes were refined against F^2 by full-matrix least-squares methods using SHELXTL [20]. V atoms in the complexes were located from electron density maps. The non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on



Scheme 1 Synthesis of the Schiff bases and their complexes

 F^2 . The methanol hydrogen atom of **1** and the amino hydrogen atom of **2** were located from difference Fourier maps and refined isotropically, with O–H and N–H distances restrained to 0.85(1) and 0.90(1) Å, respectively.



Fig. 1 Perspective view of the complex molecule of 1 with atom labeling scheme. Displacement ellipsoids are drawn at 30 % probability level; hydrogen atoms are depicted as spheres of arbitrary radii

Table 1 Crystal data, data collection, and structure refinement

The remaining hydrogen atoms were added theoretically as riding on the concerned atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-980582 for **1** and 980583 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.com.ac.uk].

Catalytic oxidation experiments

The liquid phase catalytic oxidations were carried out in a 25-mL round-bottom flask equipped with a magnetic stirrer and immersed in a thermostated oil bath at 60 °C. H_2O_2 (3 mmol) was added to the flask containing the catalyst (2.0 µmol V), NaHCO₃ (1 mmol), and a representative alkene, namely cyclohexene (1 mmol) in the required

Table 2 Coordinate bond lengths (Å) and bond angles (°)

			1			
Complex	1	2	Bond lengths			
Molecular formula	C ₁₇ H ₁₉ ClFN ₂ O ₆ V	C ₂₂ H ₂₈ F ₂ N ₄ O ₈ V ₂	V1–01	1.852(3)	V1-O2	1.976(3)
Formula weight	452.7	616.4	V1-O3	1.580(4)	V104	1.761(3)
Crystal system	Monoclinic	Monoclinic	V1-N1	2.126(4)	V105	2.293(4)
Space group	Cc	$P2_1/c$	C7-N1	1.291(6)	N1-N2	1.390(5)
a (Å)	17.813(3)	10.3484(5)	N2-C8	1.290(6)	C8–O2	1.296(6)
b (Å)	12.017(3)	11.0233(5)	Bond angles			
c (Å)	10.135(2)	10.6659(5)	O3-V1-O4	102.16(19)	O3-V1-O1	100.2(2)
β (°)	98.211(2)	92.000(2)	O4-V1-O1	102.76(17)	O3-V1-O2	96.53(19)
V (Å ³)	2,147.1(6)	1216.0(1)	O4-V1-O2	93.81(16)	O1-V1-O2	153.33(16)
Ζ	4	2	O3-V1-N1	95.51(18)	O4-V1-N1	159.82(16)
$D_{\rm c} ~({\rm g}~{\rm cm}^{-3})$	1.401	1.683	O1-V1-N1	83.38(16)	O2-V1-N1	74.39(15)
F(000)	928	632	O3-V1-O5	176.15(18)	O4-V1-O5	81.36(17)
$\mu \ (\mathrm{mm}^{-1})$	0.628	0.841	O1-V1-O5	80.43(16)	O2-V1-O5	81.60(16)
θ range (°)	3.00-25.50	2.66-25.50	N1-V1-O5	80.75(15)		
hkl range	$-21 \le h \le 21$	$-12 \le h \le 12$	2			
	$-14 \le k \le 13$	$-13 \le k \le 12$	Bond lengths			
	$-12 \leq l \leq 12$	$-12 \le l \le 12$	V1-O1	1.902(1)	V1-O3	1.684(1)
Reflections			V1-O4	1.612(1)	V1-03A	2.299(1)
Collected	9,702	11,490	V1-N1	2.149(2)	V1-N2	2.198(2)
Unique	3,919	2,265	Bond angles			
Observed $[I > 2\sigma(I)]$	3,137	1,990	O4-V1-O3	107.61(7)	O4-V1-O1	100.69(7)
R _{int}	0.0399	0.0292	O3-V1-O1	99.29(6)	O4-V1-N1	95.87(6)
Parameters	260	176	O3-V1-N1	155.32(6)	O1-V1-N1	83.29(6)
Restraints	3	1	O4-V1-N2	89.58(7)	O3-V1-N2	94.76(6)
Final <i>R</i> index $[I > 2\sigma(I)]$	0.0576, 0.1452	0.0281, 0.0722	O1-V1-N2	159.12(6)	N1-V1-N2	77.56(6)
R index (all data)	0.0754, 0.1614	0.0347, 0.0766	O4-V1-O3A	170.35(6)	O3-V1-O3A	78.72(6)
Goodness-of-fit on F^2	1.044	1.081	O1-V1-O3A	85.13(5)	N1-V1-O3A	77.05(5)
Maximum/minimum $\Delta \rho$	0.909, -0.383	0.274, -0.216	N2-V1-O3A	82.55(5)		
(e A ⁻)			Symmetry code for A: $1-x$, $2-y$, $-z$			

Table 3 Hydrogen bonding information					
<i>D</i> −H…A	$d (D-H) d (H\cdots A) d (D-H)$		$d (D \cdots A)$	$\angle (D-H\cdots A)$	
1					
$O5-H5\cdots O6^{i}$	0.85(1)	1.80(2)	2.634(6)	169(7)	
O6-H6…N2	0.82	2.23	2.819(6)	129	
2					
$N2-H2\cdots O4^{ii}$	0.90(1)	2.48(3)	3.072(2)	124(2)	
$N2-H2\cdotsO1^{iii}$	0.90(1)	2.46(2)	3.142(2)	134(3)	
O2–H2A…O3	0.82	1.95	2.737(2)	161	

Symmetry codes: (1) -1 + x, -1 + y, -1 + z, (2) 1 - x, 1/2 + y, 1/2 - z; (3) 1 - x, 2 - y, -z

solvent (3 mL). The course of the reaction was monitored using a gas chromatograph equipped with a capillary column and a flame ionization detector. The oxidation products were identified by comparing their retention times with those of authentic samples or alternatively by ¹H NMR and GC-mass analyses. Yields based on the added substrate were determined by a calibration curve. Control reactions were carried out in the absence of catalyst, under the same conditions as the catalytic runs.

Results and discussion

Synthesis and spectra

The condensation reactions of 5-fluorosalicylaldehyde with 2-chlorobenzohydrazide and β -hydroxyethylenediamine



Fig. 3 Perspective view of the dinuclear structure of 2 with atom labeling scheme. Displacement ellipsoids are drawn at 30 % probability level; hydrogen atoms are depicted as spheres of arbitrary radii. Intramolecular hydrogen bonds are shown as *dashed lines*

resulted in the Schiff base ligands H_2L^a and HL^b , respectively (Scheme 1). The complexes were readily prepared by the reaction of the Schiff base ligands and VO(acac)₂ in methanol (Scheme 1). All the compounds are soluble in polar solvents such as methanol, ethanol, and acetonitrile.

The IR spectra of the free Schiff bases contain bands at $1,632 \text{ cm}^{-1}$ for H_2L^a and $1,618 \text{ cm}^{-1}$ for HL^b , which are due to the presence of C = N groups. In the IR spectra of the vanadium complexes, these bands were observed at lower wave numbers, $1,621 \text{ cm}^{-1}$ for 1 and $1,605 \text{ cm}^{-1}$ for 2. This suggests coordination through the nitrogen atom of the C = N groups. Furthermore, broad and medium bands observed at $3,300-3,500 \text{ cm}^{-1}$ are indicative of the presence of O–H containing solvent molecules. Weak and



Fig. 2 Crystal packing of complex 1. The dashed lines denote hydrogen bonds



Fig. 4 Crystal packing of complex 2 as seen along axis-b direction. The dashed lines denote hydrogen bonds

Tuble I catalytic results for eyerometer	Table 4	Catalytic	results	for	cyclohexen
---	---------	-----------	---------	-----	------------

Catalyst	Oxidant	Temperature (°C)	Time (h)	Conversion (%) ^a
1	H_2O_2	25	3	0
1	H_2O_2	60	1	75
2	H_2O_2	25	3	0
2	H_2O_2	60	1	62

The complex (2.0 μmol V), cyclohexene (1 mmol), CH_3CN (3 mL), NaHCO_3 (1 mmol), H_2O_2 (3 mmol)

^a Based on cyclohexene

sharp bands located at 3,200–3,250 cm⁻¹ are indicative of the presence of amino groups. The typical bands at 980 cm⁻¹ for **1** and 972 cm⁻¹ for **2** are assigned to the V = O coordinate bonds.

Crystal structure descriptions

The molecular structure of complex **1** is shown in Fig. 1. Crystal data for the structure are listed in Table 1, and selected bond lengths are given in Table 2. The crystal



Fig. 5 Solvent effect on the epoxidation of cyclohexene. The complexes as catalyst (2.0 μ mol V), cyclohexene (1 mmol), solvent (3 mL), NaHCO₃ (1 mmol), H₂O₂ (3 mmol); 60 °C

compound contains a mononuclear vanadium complex molecule and a methanol molecule of crystallization. The Schiff base ligand coordinates to the V atom through the phenolate oxygen, imino nitrogen, and enolate oxygen. The other three coordinate sites are occupied by one neutral methanol, one deprotonated methanol, and an oxo

Table 5 Catalytic oxidation results of various substrates

oxygen ligand. The three donor atoms of the Schiff base and the deprotonated methanol ligand constitute the equatorial plane of the octahedral coordination sphere, such that the V atom deviates from the plane by 0.296(1)Å. The axial bond V1-O5 is much longer than the other bonds in the complex, distorting the octahedron. This distortion can also be observed from the bond angles, which range from $74.4(2)^{\circ}$ to $102.8(2)^{\circ}$ for the *cis* angles and from $153.3(2)^{\circ}$ to $176.2(2)^{\circ}$ for the *trans* angles. The dihedral angle between the two aromatic rings of the Schiff base ligand is 85.2(3)°. The bond length pattern within the bridging C-C=N-C moiety reflects the delocalization of the electron density throughout this fragment: The formally single bonds are shorter, and formally double bonds are longer than the typical values (Table 2) [20].

In the crystal structure of complex 1, the vanadium complex molecules are linked by methanol molecules through intermolecular O–H···O and O–H···N hydrogen bonds (Table 3), to form 1D chains running along the *c*-axis direction (Fig. 2).

The molecular structure of complex 2 is shown in Fig. 3. Crystal data for the structure are listed in Table 1, and

Substrate	Products	Complex	Yield (%) ^a	Conversion (%)
		1	81	95
		2	66	87
	0			
		1	85	98
		2	70	91
	o			
		1	53	74
		2	45	78
	OH			
		1	90	96
		2	81	92
CH ₂ OH	СНО			

The complex (2.0 µmol V), substrate (1 mmol), CH₃CN (3 mL), NaHCO₃ (1 mmol), H₂O₂ (3 mmol). Temperature: 60 °C

^a Based on the starting substrates

selected bond lengths are given in Table 2. The compound possesses a crystallographic inversion center of symmetry. The V…V distance is 3.104(1) Å. The Schiff base ligand coordinates to the V atom through the phenolate oxygen, imino nitrogen, and amino nitrogen. The other three coordinate sites are occupied by one oxo oxygen and two bridging oxo oxygen ligands. The three donor atoms of the Schiff base and one bridging oxo oxygen (O3) constitute the equatorial plane of the octahedral coordination sphere, such that the V atom deviates from the plane by 0.301(1)Å. As with complex 1, the axial bond V1-O3A is much longer than the other bonds, resulting in distorted octahedral coordination. The bond angles around vanadium range from $77.05(5)^{\circ}$ to $107.61(7)^{\circ}$ for the *cis* angles and from $155.32(6)^{\circ}$ to $170.35(6)^{\circ}$ for the *trans* angles. The hydroxyl groups of the Schiff base ligands and the bridging oxo oxygen are involved in intramolecular hydrogen bonds.

In the crystal structure of complex **2**, the vanadium complex molecules are linked through intermolecular N– $H\cdots O$ hydrogen bonds (Table 3), to form 1D chains running along the direction of the *c*-axis (Fig. 4).

Catalytic studies

Both complexes were investigated as catalysts for the oxidation of various hydrocarbons, with the results shown in Table 4. In the first set of experiments, oxidation of cyclohexene was studied with H_2O_2 in the presence of the complexes. All reactions were carried out with 1 mmol of cyclohexene in acetonitrile at 60 °C. Cyclohexene oxide was the sole product. The results of control experiments revealed that the presence of both catalyst and oxidant were essential for the oxidation; thus, oxidation of cyclohexene in the absence of H_2O_2 was not observed, and in the absence of catalyst the oxidation proceeded only up to 5 % after 48 h. While the reaction at 25 °C was negligible, increasing the reaction temperature to 60 °C resulted in a considerable increase in cyclohexene conversion, up to 75 % for 1 and 62 % for 2 after 1 h.

The effect of solvent was also studied. Methanol, acetonitrile, and dichloromethane were used as solvents for the epoxidation of cyclohexene (Fig. 5). The highest conversion was observed in acetonitrile, while the lowest conversion was observed in dichloromethane. Hence, acetonitrile is a suitable solvent for this reaction.

The catalytic activities of the complexes were further examined for the oxidation of various hydrocarbons at 60 °C for 5 h in acetonitrile solvent (Table 5). In general, complex 1 proved to be a better catalyst than complex 2. Cyclohexene and cyclopentene were both converted to the corresponding epoxides with quantitative selectivity. Cyclohexane was converted to cyclohexanol with yields of

53 % for **1** and 45 % for **2**, and with cyclohexanone as the by-product (1.5 %). Oxidation of benzyl alcohol by the complexes produced benzaldehyde with high yields and quantitative selectivities.

Conclusion

In summary, two new Schiff base ligands and their oxidovanadium(V) complexes have been synthesized and characterized. The complexes are effective catalysts for the oxidation of cyclohexene, cyclopentene, and benzyl alcohol by H_2O_2 as oxidant. Complex 1 with a hydrazone-type Schiff base ligand was a more effective catalyst than the non-hydrazone Schiff base complex 2.

Acknowledgments We would like to acknowledge the financial supports from Mianyang Normal University.

References

- 1. Olivo G, Lanzalunga O, Mandolini L, Di Stefano S (2013) J Org Chem 78:11508
- 2. Brussaard Y, Olbrich F, Schaumann E (2013) Inorg Chem 52:13160
- Vaghi L, Benincori T, Cirilli R, Alberico E, Mussini PR, Pierini M, Pilati T, Rizzo S, Sannicolo F (2013) Eur J Org Chem 36:8174
- Suarez AIO, Lyaskovskyy V, Reek JNH, van der Vlugt JI, de Bruin B (2013) Angew Chem Int Ed 52:12510
- Rajkovic S, Asanin DP, Zivkovic MD, Djuran MI (2013) Polyhedron 65:42
- Adamski A, Kubicki M, Pawluc P, Grabarkiewicz T, Patroniak V (2013) Catal Commun 42:79
- Maurya MR, Haldar C, Khan AA, Azam A, Salahuddin A, Kumar A, Pessoa JC (2012) Eur J Inorg Chem 15:2560
- Orive J, Larrea ES, de Luis RF, Iglesias M, Mesa JL, Rojo T, Arriortua MI (2013) Dalton Trans 42:4500
- Sandoval-Diaz LE, Martinez-Gil JM, Trujillo CA (2012) J Catal 294:89
- Maurya MR, Haldar C, Kumar A, Kuznetsov ML, Avecilla F, Pessoa JC (2013) Dalton Trans 42:11941
- Amini M, Arab A, Soleyman R, Ellern A, Woo LK (2013) J Coord Chem 66:3770
- 12. Liu Z, Anson FC (2001) Inorg Chem 40:1329
- 13. Romanowski G, Kira J (2013) Polyhedron 53:172
- Ando R, Ono H, Yagyu T, Maeda M (2004) Inorg Chim Acta 357:817
- 15. Romanowski G, Wera M (2010) Polyhedron 29:2747
- 16. Suresh P, Srimurugan S, Babu B, Pati HN (2007) Tetrahedron Asymmetry 18:2820
- 17. Rayati S, Sadeghzadeh N, Khavasi HR (2007) Inorg Chem Commun 10:1545
- Bruker (2007) SMART (Version 5.625) and SAINT (Version 6.01). Bruker AXS Inc., Madison, Wisconsin, USA
- Sheldrick GM (1996) SADABS. Program for empirical absorption correction of area detector. University of Göttingen, Germany
- Sheldrick GM (1997) SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA