Synthesis, Crystal Structure, and Catalytic Epoxidation of a New Oxovanadium(V) Complex with Benzohydrazone and Benzohydroxamate Mixed-Ligands¹

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Abstract—Synthesis, characterization, and catalytic properties for styrene epoxidation of a new oxovanadium(V) complex [VOLL'] · CH₃OH (I) derived from N'-(3-bromo-5-chloro-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H₂L) and benzohydroxamic acid (HL') are reported. Complex I was characterized by elemental analyses, IR, UV-Vis spectra and molar conductivity. Single crystal X-ray structure of complex I has been determined (CIF file CCDC no. 1034615). The V atom in the structure is in an octahedral coordination. In the crystal structure, molecules are linked through intermolecular O–H···O, O–H···Br and N– H···O hydrogen bonds, to form 2D layers. Catalytic property for epoxidation of styrene by the complex using PhIO and NaOCl as oxidant has been studied.

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INTRODUCTION

Hydrazones are very popular ligands because they efficiently act as chelates generating a rich variety of coordination compounds, ranging from mononuclear to polynuclear species. In recent years, a great number of complexes with hydrazones have been reported, showing interesting structures and excellent properties, such as catalytic [1-3], magnetic [4-6], and biological [7-9], etc. Vanadium complexes with hydrazones are often described as good epoxidation catalysts [10-13]. The method is mild and is an environment friendly process. As a further study of the catalytic epoxidation of vanadium complexes, in this study, the synthesis, characterization, crystal structure and catalytic epoxidation property of a new oxovanadium(V) complex, $[VOLL'] \cdot CH_3OH$ (I), derived from the benzohydrazone ligand N'-(3-bromo-5-chloro-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H₂L) and benzohydroxamic acid (HL'), are reported.



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EXPERIMENTAL

Material and measurements. All chemicals and solvents used for the synthesis are of analytical grade. 3-Bromo-5-chlorosalicylaldehyde, 2-hydroxybenzohydrazide, benzohydroxamic acid, VO(Fcac)₂, styrene and styrene oxide were purchased from Aldrich and used without further purification. Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodobenzene diacetate. Infrared spectra were recorded as KBr pellets on a JASCO FT-IR 4100 spectrophotometer. Elemental analyses (C, H, N) were carried out using a Perkin Elmer 2400 II elemental analyser. Electronic spectra were recorded on a Perkin Elmer Lambda 40 (UV/Vis) spectrometer in acetonitrile. GC analysis was performed with Agilent 6890N Network GC systems. Molar conductivity of complex I in acetonitrile was measured with a DDS-11A molar conductivity meter.

Synthesis of H_2L . The yellow crystalline product of the benzohydrazone ligand H_2L was prepared by reaction of equimolar quantities of 3-bromo-5-chlorosalicylalde-hyde (1.0 mmol, 0.235 g) with 2-hydroxybenzohydrazide (1.0 mmol, 0.152 g) in methanol and subsequent evaporation of the solvent. The yield was 91%.

IR data (KBr; v, cm⁻¹): 1647 s v(C=O), 1614 s v(C=N). UV (λ , nm ($\epsilon \times 10^3$, L mol⁻¹ cm⁻¹)): 240 (2.89), 295 (4.05), 308 (3.31), 340 (2.71).

For C14H10N2O3ClBr

anal. calcd., %:	C, 45.5;	Н, 2.7;	N, 7.6.
Found, %:	C, 45.3;	H, 2.8;	N, 7.7.

Synthesis of complex I. The appropriate quantity of solid benzohydrazone ligand H_2L (0.5 mmol, 0.184 g) was dissolved in dry methanol (20 mL). A solution of VO(Acac)₂ (0.5 mmol, 0.133 g) in dry methanol (15 mL) was added to this solution followed by the addition of benzohydroxamic acid (0.5 mmol, 0.068 g) in dry methanol (15 mL). The mixture was refluxed for 1 h. The resulting brown solution was then filtered off and the filtrate was left undisturbed. After a week fine deep brown block shaped X-ray diffraction quality single crystals separated out. They were filtered off, washed with methanol and dried in vacuum over anhydrous CaCl₂. The yield was 53%.

IR data (KBr; v, cm⁻¹): 3454 br. m, v(O–H), 1608 s v(C=N), 969 m, v(V=O). UV (λ , nm ($\epsilon \times 10^3$, L mol⁻¹ cm⁻¹)): 225 (7.56), 270 (6.54), 347 (3.61), 445 (2.21).

For $C_{22}H_{18}N_3O_7ClBrV$				
anal. calcd., %:	C, 43.8;	Н, 3.0;	N, 7.0.	
Found, %:	C, 44.0;	Н, 2.9;	N, 6.9.	

X-ray structure determination. Intensity data of complex I were collected at 298(2) K on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). A suitable crystal was affixed to the end of a glass fiber using silicone grease and transferred to the goniostat. The unit cell parameters were obtained from SAINT; absorption corrections were performed with SADABS [14]. Structure of complex I was solved by the direct method and refined by a full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [15]. All the non-hydrogen atoms are refined anisotropically. The hydrogen atoms on the carbon atoms were included in fixed calculated positions, whereas the hydrogen atom of the amino group was located in a difference Fourier map and refined as riding on its N atom. Crystal data for the complex are summarized in Table 1. Selected bond lengths and angles of the complex are given in Table 2.

Supplementary material for structure I has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1034615; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

General method for styrene epoxidation. The epoxidation reactions were carried out at room temperature in acetonitrile under nitrogen atmosphere with constant stirring. The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of the manganese(III) complex (catalyst) and 2.00 mmol iodosylbenzene or sodium hypochlorite (oxidant) in 5.00 mL acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2 with NaH₂PO₄ and NaOH. The composition of reaction medium was determined by GC with styrene and sty-

Table 1.	Crystallographic	data and	experimental	details for
complex	I			

Parameter	Value	
Formula weight	602.7	
Crystal size, mm	$0.27 \times 0.27 \times 0.20$	
Crystal system	Triclinic	
Space group	$P\overline{1}$	
a, Å	7.4392(7)	
b, Å	13.3602(12)	
<i>c</i> , Å	13.4119(12)	
α, deg	113.425(2)	
β, deg	93.809(3)	
γ, deg	103.064(2)	
$V, Å^3$	1173.1(2)	
Ζ	2	
$\rho_{calcd}, mg cm^{-3}$	1.706	
$\mu(MoK_{\alpha}), mm^{-1}$	2.289	
<i>F</i> (000)	604	
Number of measured reflections	10418	
Number of observations $(I > 2\sigma(I))$	4107	
Unique reflections	2485	
Parameters refinement	322	
Number of restraints	7	
$R_1, wR_2 (I > 2\sigma(I))^*$	0.0479, 0.0811	
R_1, wR_2 (all data)*	0.1083, 0.0986	
Goodness of fit of F^2	1.019	
Largest difference peak and hole, $e \text{ Å}^{-3}$	0.383, -0.306	

* $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|, wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}.$

rene epoxide quantified by the internal standard method (chlorobenzene). Styrene oxide was used as standard sample in GC analysis. All other products detected by GC were mentioned as others. For complex I the reaction time for maximum epoxide yield was determined by withdrawing periodically 0.10 mL aliquots from the reaction mixture and this time was used to monitor the efficiency of the catalyst on performing at least two independent experiments. Blank experiments with each oxidant and using the same experimental conditions except catalyst were also performed.

RESULTS AND DISCUSSION

The tridentate benzohydrazone H_2L was easily prepared from the reaction between 3-bromo-5-chloro-

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Bond	<i>d</i> , Å	Bond	d, Å
V(1)–O(1)	1.909(3)	V(1)–O(2)	1.961(3)
V(1)–O(4)	2.204(3)	V(1)-O(5)	1.858(2)
V(1)–O(6)	1.572(3)	V(1)–N(1)	2.084(3)
Angle	ω, deg	Angle	ω, deg
O(6)V(1)O(5)	93.47(13)	O(6)V(1)O(1)	99.19(14)
O(5)V(1)O(1)	103.82(12)	O(6)V(1)O(2)	100.03(14)
O(5)V(1)O(2)	93.94(11)	O(1)V(1)O(2)	152.88(12)
O(6)V(1)N(1)	97.65(13)	O(5)V(1)N(1)	165.30(12)
O(1)V(1)N(1)	83.91(12)	O(2)V(1)N(1)	74.72(12)
O(6)V(1)O(4)	168.50(12)	O(5)V(1)O(4)	75.07(11)
O(2)V(1)O(4)	81.99(11)	O(1)V(1)O(4)	82.99(11)
N(1)V(1)O(4)	93.80(11)		

Table 2. Selected bond lengths (Å) and angles (deg) for complex I

salicylaldehyde and 2-hydroxybenzohydrazide in methanol with 1:1 stoichiometric ratio. Reaction of $VO(Acac)_2$ with H_2L and benzohydroxamic acid in a molar ratio of 1:1:1 in methanol, followed by slow evaporation, affords the single crystals of I. During the synthesis performed under aerobic conditions, the reaction system exhibited an obvious color change from light to deep brown. This suggest the occurrence of oxidation process $(V(IV) \rightarrow V(V))$ induced by the oxygen in air. Crystals of the complex are stable in air. The molar conductivity of the complex in acetonitrile is $15 \,\Omega^{-1} \,\mathrm{cm}^2 \,\mathrm{mol}^{-1}$, indicating the non-electronic nature [16]. The infrared spectrum of the complex was recorded within the 4000–400 cm⁻¹ region. The benzohydrazone ligand has stretching bands attributed to C=O, C=N, C-OH, and NH at 1647, 1614, 1163 and 1221, and 3241 cm⁻¹, respectively. The complex exhibits typical bands at 969 cm⁻¹, which is assigned to the V=O vibration [17]. The band due to v(C=O) was



Fig. 1. UV-Vis spectra of H_2L and complex I.

absent in the spectrum of complex I, and new C-O stretch appeared at 1260 cm⁻¹. This suggests occurrence of keto-imine tautomerization of the ligand during complexation. The v(C=N) absorption observed at 1614 cm⁻¹ in the free benzohydrazone ligand shifted to 1608 cm^{-1} for complex I upon coordination to the V atom. The weak peaks in the low wave numbers at 492 and 589 cm^{-1} may be attributed to V–O and V–N bonds in the complex. The electronic spectral data for the complex in acetonitrile were recorded in the range of 200–800 nm. UV-Vis spectra of H₂L and complex I are shown in Fig. 1. The intense absorption bands at 240 nm for H_2L and 225 nm for the complex may be assigned to intra-ligand $\pi \to \pi^*$ transitions. The absorption band centered at 445 nm in complex I may be assigned to the ligand-to-metal charge transfer transition. The remaining absorption bands can be assigned to the $n \rightarrow \pi^*$ transitions.

An ORTEP representation of the complex with atom numbering scheme is depicted in Fig. 2. X-ray crystallography reveals that the asymmetric unit of the complex contains a mononuclear oxovanadium(V) species and a methanol molecule. The V centre is six coordinated by three donor atoms (NO_2) of the coordinated benzohydrazone ligand L, two oxygen atoms of the coordinated benzohyroxamate ligand, and one oxo oxygen atom. In the octahedral coordination, O(4) and O(6) are the axial ligand atoms, and O(1), O(2), N(1), and O(5) form the equatorial plane. The coordination environment of the V atom is slightly distorted, as evidenced from the bond lengths and angles. In the equatorial plane, the metal-ligand bond distance involving the imine nitrogen (V(1)-N(1))2.084(3) Å is longer than the bond lengths involving oxygens (V(1)-O(1) 1.909(3), V(1)-O(2) 1.961(3), V(1)-O(5) 1.858(2) Å). As expected due to Jahn-Teller distortion, the bond distances involving the axial donor atoms (V(1)–O(4) 2.204(3), V(1)–O(6)



Fig. 2. A perspective view of the molecular structure of complex **I** with atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bond is shown as a dashed line.

1.572(3) Å) significantly longer or shorter than the bond lengths involving the equatorial atoms. The *trans* angles $(152.9(1)^{\circ}, 165.3(1)^{\circ}, \text{ and } 168.5(1)^{\circ})$ and the *cis* angles $(74.7(1)^{\circ}-103.8(1)^{\circ})$ deviate much from the ideal values. The coordinate bond values are in agreement with those observed in vanadium(V) complexes with hydrazones [18, 19]. The average deviation (0.0597 Å) of the equatorial donor atoms and the disdplacement (0.248 Å) of the metal center from the least-squares plane defined by the equatorial donor atoms indicates that the NO₃ cavity affords an almost perfect plane to the metal center. The benzohydrazone ligand is approximate planar with dihedral angel between the two benzene rings of $2.0(5)^{\circ}$.

In the crystal structure of I, mononuclear oxovanadium complex molecules are linked by methanol molecules through intermolecular $O(3)-H(3A)\cdots O(6)^{i}$, $O(7)-H(7)\cdots O(1)^{ii}$, $O(7)-H(7)\cdots Br(1)^{ii}$, and N(3)- $H(3)\cdots O(7)^{iii}$ hydrogen bonds (O(3)-H(3A) 0.82, $H(3A)\cdots O(6)^{i}$ 2.59, $O(3)\cdots O(6)^{i}$ 3.088(4) Å, O(3)- $H(3A)\cdots O(6)^{i}$ 121°; O(7)-H(7) 0.82, H(7) $\cdots O(1)^{ii}$ 2.19, $O(7)\cdots O(1)^{ii}$ 2.974(4) Å, $O(7)-H(7)\cdots O(1)^{ii}$ 160°: H(7)····Br(1)ⁱⁱ O(7)–H(7) 0.82, 2.84, O(7)...Br(1)ⁱⁱ 3.385(4) Å, O(7)-H(7)...Br(1)ⁱⁱ 126°; $H(3)\cdots O(7)^{iii}$ N(3) - H(3)0.90(1).1.89(2). $N(3) \cdots O(7)^{iii}$ 2.742(5) Å, $N(3) - H(3) - O(7)^{iii}$ $159(4)^{\circ}$; symmetry codes: ⁱ -x, 1 - y, 2 - z; ⁱⁱ 1 - x, 1 - y, 2 - z;ⁱⁱⁱ x, 1 + y, z) to form 2D layers parallel to the xy plane (Fig. 3).

Epoxidation of styrene was carried out at room temperature with complex I, as the catalyst and PhIO or NaOCl as the oxidant. The brown solution containing complex I and the substrate was intensified after the addition of oxidant indicating the formation of oxo-metallic intermediates of the catalyst. After completion of oxidation reaction of the alkene, the solution regains its initial color which suggests that the regeneration of the catalyst takes place. The percentage of conversion of styrene, selectivity for styrene oxide, vield of styrene oxide for complex I and reaction time to obtain maximum vield using both oxidants are listed in Table 3. The data reveal that the complex as a catalyst converts styrene efficiently in the presence of both oxidants. The catalyst is selective towards the formation of styrene epoxide despite of the formation of byproducts which have been identified by GC-MS as benzaldehyde, phenylacetaldehyde, styrene epoxide derivative, alcohols, etc. When the reactions are carried out with PhIO, styrene conversions are 95%. With NaOCl as oxidant, styrene conversion dropped to 82%. It is evident that PhIO acts as a better oxidant with respect to both styrene conversion and styrene epoxide selectivity.

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Fig. 3. Molecular packing diagram of complex I, viewed along the x axis direction. Hydrogen bonds are shown as dashed lines.

Time, h Oxidant	Conversion %	Epovide vield %	Selectivity, %		
	Oxidant		Liponiae yiela, /	epoxide	other
2.0	PhIO	95	81	87	13
2.5	NaOCl	82	62	82	18

Table 3. Epoxidation of styrene catalyzed by complex I

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