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Synthesis, Crystal Structures, and Catalytic Properties of Two Oxidovanadium(V) Complexes with Tridentate Schiff Bases[1]

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Abstract—Two new oxidovanadium(V) complexes, [VO_2L^1] (**I**) and [VO_2L^2] (**II**), where L^1 and L^2 are the deprotonated forms of 4-methyl-2-[(2-morpholin-4-ylethylimino)methyl]phenol (HL^1) and 2-[(2-isopropylaminoethylimino)methyl]-4-trifluoromethoxyphenol (HL^2), respectively, have been prepared and characterized by physico chemical methods and single crystal X-ray diffraction (CIF files CCDC nos. 1443671 (**I**), 1443672 (**II**)). The V atom in each complex is coordinated by the phenolate oxygen, imino nitrogen and amino nitrogen of the Schiff base ligand, and two oxo groups, forming trigonal-bipyramidal geometry. The oxidation of olefins with the complexes as catalyst was evaluated, which indicated that both complexes showed effective catalytic efficiency in oxidation of several aliphatic and aromatic substrates by using *tert*-butyl hydrogen peroxide as oxidant.

Keywords: Schiff base, oxidovanadium complex, X-ray diffraction, catalytic property

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INTRODUCTION

The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals since epoxides are key starting materials for a wide variety of oily products [1–3]. Much work has been carried out to explore new and efficient catalysts for these reactions. H_2O_2 has been used as the first selected oxidant in these reactions because of its environment-friendly characteristic. The vanadium enzymes such as vanadium-nitrogenases and vanadate-dependent haloperoxidases, have been found in nature [4–6]. In recent years, vanadium complexes with various organic ligands have shown interesting catalytic properties in many organic reactions [7–10]. Schiff bases are a kind of versatile ligands in coordination chemistry. The synthesis, characterization and reactivity studies of a number of vanadium complexes with Schiff bases have been reported [11–14]. Some of the complexes have shown interesting catalytic properties [15–17]. In order to further study the catalytic potentiality of vanadium complexes, in this paper, two new oxidovanadium(V) complexes, [VO_2L^1] (**I**) and [VO_2L^2] (**II**), where L^1 and L^2 are the deprotonated form of 4-methyl-2-[(2-morpholin-4-ylethylimino)methyl]phenol (HL^1) and 2-[(2-isopropylaminoethylimino)methyl]-4-trifluoromethoxyphenol (HL^2), respectively, are presented.

EXPERIMENTAL

Materials and methods. All the reagents and solvents used in the synthesis were procured commercially and used without subsequent purification. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were carried out using the JASCO FT-IR model 420 spectrophotometer with KBr disk in the region 4000–400 cm^{-1}. Electronic absorption spectra measurement in acetonitrile was measured using a Labda 900 spectrometer. ^1H NMR spectra were measured in DMSO-d^6 on Bruker 300 MHz spectrometer.

Synthesis of I. HL^1 (0.248 g, 1.0 mmol) and $VO(Acac)_2$ (0.265 g, 1.0 mmol) were dissolved and mixed in methanol (20 mL). The mixture was stirred at room temperature for 30 min to give yellow solution. After leaving the solution for a few days at room temperature, fine yellow crystals were formed. The product was filtered and washed with methanol. The yield was 53%.

IR (KBr; ν_{max}, cm^{-1}): 1627 m ν(C=N), 950 s and 853 s ν(V=O). Absorption spectrum in acetonitrile

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(λ_{max}, nm (ε, L mol^{-1} cm^{-1})): 267 (15130), 322 (8210), 413 (2350).

For $C_{14}H_{19}N_2O_4V$

anal. calcd., %: C, 50.92; H, 5.80; N, 8.48.
Found, %: C, 50.71; H, 5.89; N, 8.37.

Synthesis of II. HL^2 (0.290 g, 1.0 mmol) and VO(Acac)$_2$ (0.265 g, 1.0 mmol) were dissolved and mixed in methanol (20 mL). The mixture was stirred at room temperature for 30 min to give yellow solution. After leaving the solution for a few days at room temperature, fine yellow crystals were formed. The product was filtered and washed with methanol. The yield was 65%.

IR (KBr; ν_{max}, cm^{-1}): 3111 w ν(NH), 1645 m, ν(C=N), 950 s and 859 s ν(V=O). Absorption spectrum in acetonitrile (λ_{max}, nm (ε, L mol^{-1} cm^{-1})): 270 (14320), 325 (9780), 425 (2160).

For $C_{13}H_{16}N_2F_3O_4V$

anal. calcd., %: C, 41.95; H, 4.33; N, 7.53.
Found, %: C, 42.10; H, 4.41; N, 7.45.

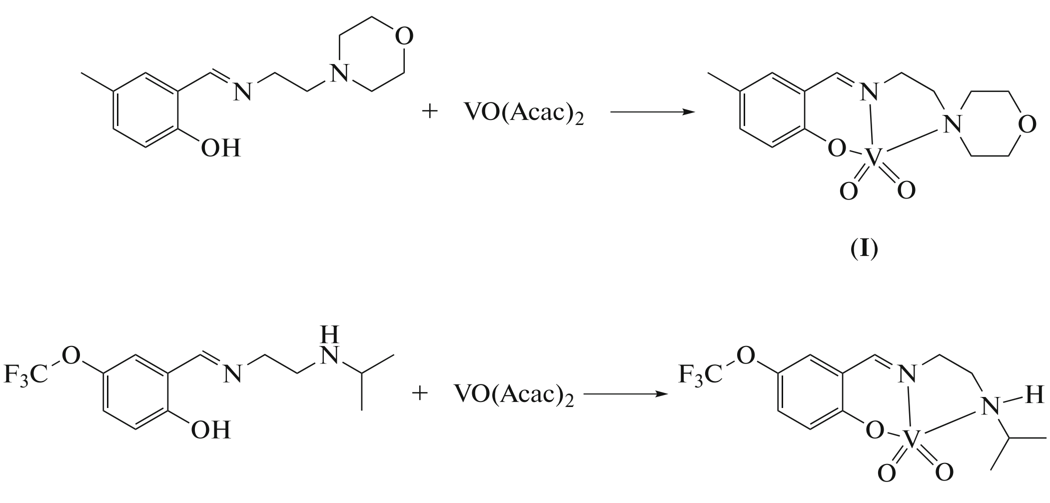
X-ray structure determination. X-ray data for the compounds were collected on a Bruker SMART APEX II diffractometer equipped with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). A preliminary orientation matrix and cell parameters were determined from three sets of ω scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s frame^{-1}. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS [18]. The structures were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-H atoms with the SHELXTL program [19]. The amino hydrogen atom in complex **II** was located from a difference Fourier map and refined isotropically with N–H distance restrained to 0.90(1) Å. The remaining H atoms were calculated at idealized positions and refined with the riding models. Crystallographic data for the compounds are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1443671 (**I**), 1443672 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Catalytic epoxidation of olefins. Catalytic experiments were carried out in a 50 mL glass round-bottom flask fitted with a reflux condenser and placed in an oil bath at prearranged temperature under continuous stirring. The oxidation was carried out as follows. The complexes (0.032 mmol) were dissolved 10 mL of 1,2-dichloroethane. Then alkene (10 mmol) was added to the reaction mixture and TBHP (30 mmol) was added. The reaction mixture was refluxed for 1 h. 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).

RESULTS AND DISCUSSION

The Schiff bases were reacted with VO(Acac)$_2$ in methanol followed by slow vaporization to generate fine yellow crystalline complexes, as shown in Scheme 1:



(I)

(II)

Table 1. Crystallographic data and refinement parameters for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	330.25	372.22
Crystal size, mm	0.15 × 0.13 × 0.13	0.20 × 0.20 × 0.17
Temperature, °C	298(2)	298(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pca2_1$
a, Å	21.017(2)	10.995(2)
b, Å	6.0710(6)	14.595(3)
c, Å	11.4094(11)	10.155(2)
β, deg	97.855(2)	
V, Å	1442.1(2)	1629.7(6)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.521	1.517
$\mu(MoK_\alpha)$, mm^{-1}	0.705	0.659
$F(000)$	688	760
Number of measured reflections	7208	8095
Number of observations ($I > 2\sigma(I)$)	2438	2261
Unique reflections	2685	2416
Refinement parameters	191	214
Number of restraints	0	2
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0277, 0.0790	0.0437, 0.1135
R_1, wR_2 (all data)*	0.0310, 0.0811	0.0472, 0.1193
Goodness of fit of F^2	1.110	1.084

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

Crystals of the complexes are stabilized in air at room temperature, and soluble in methanol, ethanol, and acetonitrile.

Molecular structures of complexes **I** and **II** are shown in Fig. 1. The Schiff bases coordinate to the V atoms through the phenolate oxygen, imino nitrogen, and amino nitrogen. The coordination geometry around the V atom can be described as distorted trigonal bipyramidal with the imino nitrogen of the Schiff base ligand and two oxo groups defining the basal plane, and with the phenolate oxygen and the amino nitrogen of the Schiff base ligand occupying the axial positions. The Schiff base ligand coordinates to the V atom forming a five- and a sixmembered chelate rings with bite angles of 75.15(5)° and 83.15(5)° for **I**, and 77.50(11)° and 83.38(12)° for **II**, which are similar to those observed in similar vanadium complexes [20, 21]. The displacement of the V atoms from the basal mean planes toward the phenolate oxygen are 0.132(2) Å for **I** and 0.086(2) Å for **II**. The V–O, V–N, and V=O bonds in the complexes are within normal ranges and similar to those observed in oxidovanadium complexes [22, 23].

In the crystal structure of complex **I**, molecules are linked through C–H···O hydrogen bonds to form dimers along the x axis. The dimers are futher linked

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
V(1)–O(1)	1.9085(13)	V(1)–O(3)	1.6091(13)
V(1)–O(4)	1.6248(14)	V(1)–N(1)	2.1419(13)
V(1)–N(2)	2.1594(14)		
	II		
V(1)–O(1)	1.933(3)	V(1)–O(2)	1.626(3)
V(1)–O(3)	1.622(3)	V(1)–N(1)	2.138(3)
V(1)–N(2)	2.170(3)		
Angle	ω, deg	Angle	ω, deg
	I		
O(3)V(1)O(4)	109.42(8)	O(3)V(1)O(1)	102.78(7)
O(4)V(1)O(1)	98.80(7)	O(3)V(1)N(1)	116.83(7)
O(4)V(1)N(1)	132.07(6)	O(1)V(1)N(1)	83.15(5)
O(3)V(1)N(2)	94.81(6)	O(4)V(1)N(2)	89.57(6)
O(1)V(1)N(2)	156.62(5)	N(1)V(1)N(2)	75.15(5)
	II		
O(3)V(1)O(2)	110.28(18)	O(3)V(1)O(1)	100.60(15)
O(2)V(1)O(1)	95.98(15)	O(3)V(1)N(1)	117.93(15)
O(2)V(1)N(1)	131.08(16)	O(1)V(1)N(1)	83.38(12)
O(3)V(1)N(2)	94.51(14)	O(2)V(1)N(2)	91.42(14)
O(1)V(1)N(2)	159.65(13)	N(1)V(1)N(2)	77.50(11)

Table 3. Hydrogen bond distances (Å) and bond angles (deg) for complexes **I** and **II***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
		I		
C(8)–H(8)···O(1)^{i}	0.93	2.48(3)	3.222(3)	137(4)
C(11)–H(11*A*)···O(4)	0.97	2.47(3)	2.981(3)	113(3)
C(12)–(H12*B*)···O(2)^{ii}	0.97	2.57(3)	3.483(4)	156(4)
		II		
N(2)–H(2)···O(2)^{iii}	0.90	2.03(2)	2.896(3)	161(3)
C(7)–H(7)···O(1)^{iv}	0.93	2.54(3)	3.224(3)	130(4)
C(7)–H(7)···O(3)^{iv}	0.93	2.52(3)	3.379(3)	154(4)
C(8)–H(8*A*)···O(1)^{iii}	0.97	2.54(3)	3.422(4)	151(5)
C(12)–H(12*C*)···O(2)	0.96	2.55(2)	3.182(3)	123(4)

* Symmetry codes: ^{i} $x, 1/2 - y, -1/2 + z$; ^{ii} $1 - x, 1/2 + y, 1/2 - z$; ^{iii} $1/2 - x, y, 1/2 + z$; ^{iv} $-1/2 + x, 1 - y, z$.

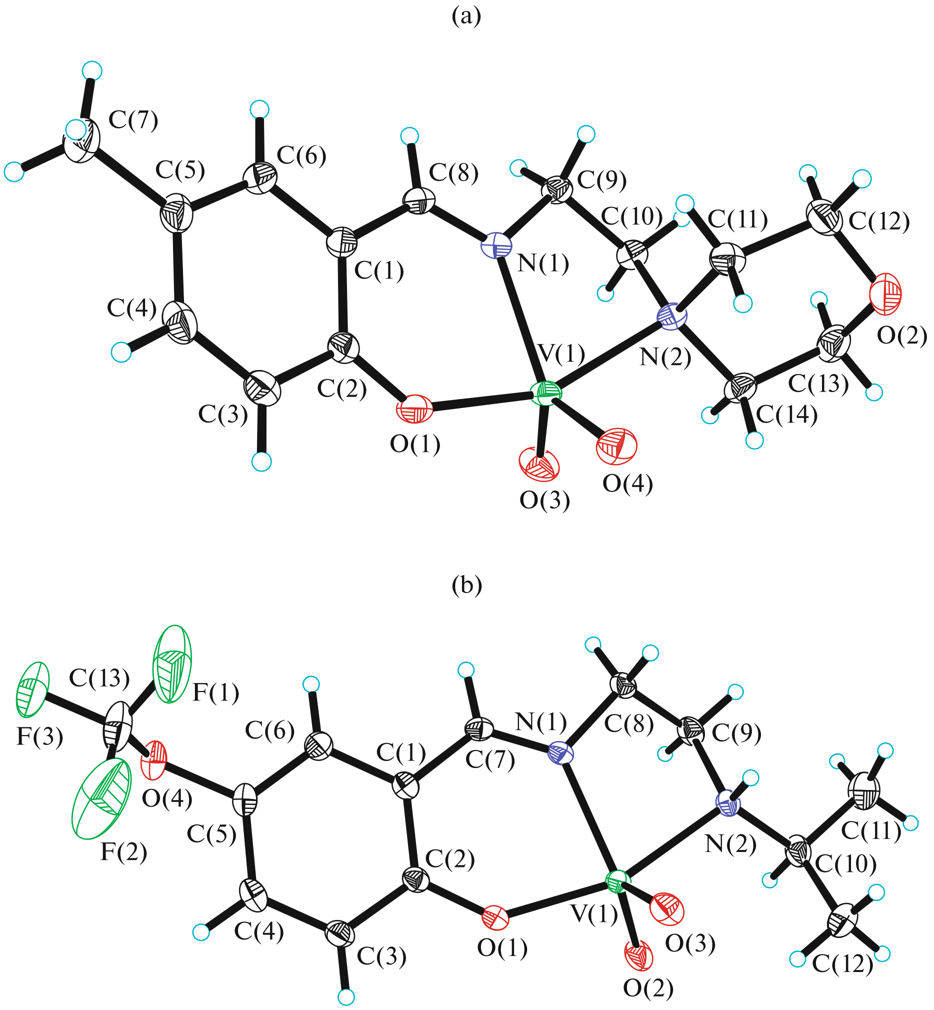


Fig. 1. Molecular structure of complex **I** (a) and **II** (b) with 30% probability thermal ellipsoids.

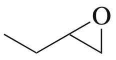
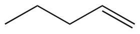
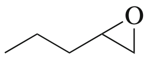
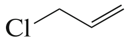
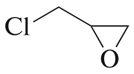
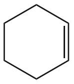
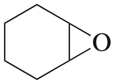
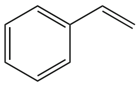
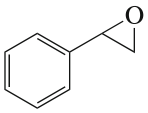
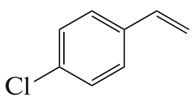
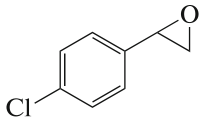
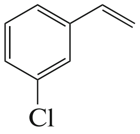
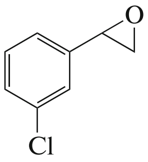
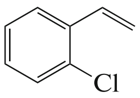
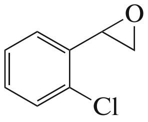
through C–H···O hydrogen bonds to form one-dimensional bands along the *z* axis (Table 3, Fig. 2a). In the crystal structure of complex **II**, molecules are linked through C–H···O hydrogen bonds, to form one-dimensional bands along the *x* axis (Table 3, Fig. 2b).

The weak and sharp band at 3111 cm^{-1} for **II** is assigned to the ν(NH) vibration. The V=O stretching modes occur as a pair of sharp strong bands at 950 and 853 cm^{-1} for **I** and 950 and 859 cm^{-1} for **II**, which are assigned to the antisymmetric and symmetric stretching modes of the dioxovanadium(V) moieties [24]. The strong bands indicative of the C=N groups in the complexes are observed at 1627 cm^{-1} for **I** and 1645 cm^{-1} for **II** [25]. The new weak peaks observed in the range 400–800 cm^{-1} may be attributed to the V–O and V–N vibrations in the complexes. The IR spectra of the complexes are similar to each other, indicating the complexes are similar structures, as evidenced by the single crystal X-ray determination.

In the electronic spectra of the complexes, the bands at about 420 nm are attributed to ligand-to-metal charge transfer [26]. The bands at about 325 nm are assigned to n–π^* transitions [27]. The intense bands at about 270 nm are assigned to intraligand π–π^* transitions [27].

The catalytic results are listed in Table 4. Effective epoxide yields and 100% selectivity were observed for all aliphatic and aromatic substrates. In general, oxidation of aromatic substrates gave the corresponding epoxides in over 90% yields, while in the oxidation of aliphatic substrates, the conversion is lower than 82%. Based on this consideration, it can be observed that the isolated double bonds are less reactive than the conjugated ones. For the aliphatic substrates, the conversion for the chloro-substituted methyloxirane is higher than the methyl or ethyl substituted species. For the aromatic substrates, the same phenomenon was observed. Thus, it may be concluded that the com-

Table 4. Detailed information of the catalytic oxidation of olefins catalyzed by the complexes*

Substrate	Product	Conversion, %**	
		I	**II**
		69	73
		63	65
		82	78
		80	85
		91	88
		93	92
		98	94
		95	97

* The molar ratio of catalyst : substrate : TBHP is 1 : 300 : 1000. The reactions were performed in mixture of $CH_3OH–CH_2Cl_2$ ($V : V =$ 6 : 4; 1.5 mL).

** The GC conversion (%) was measured relative to the starting substrate after 1 h.

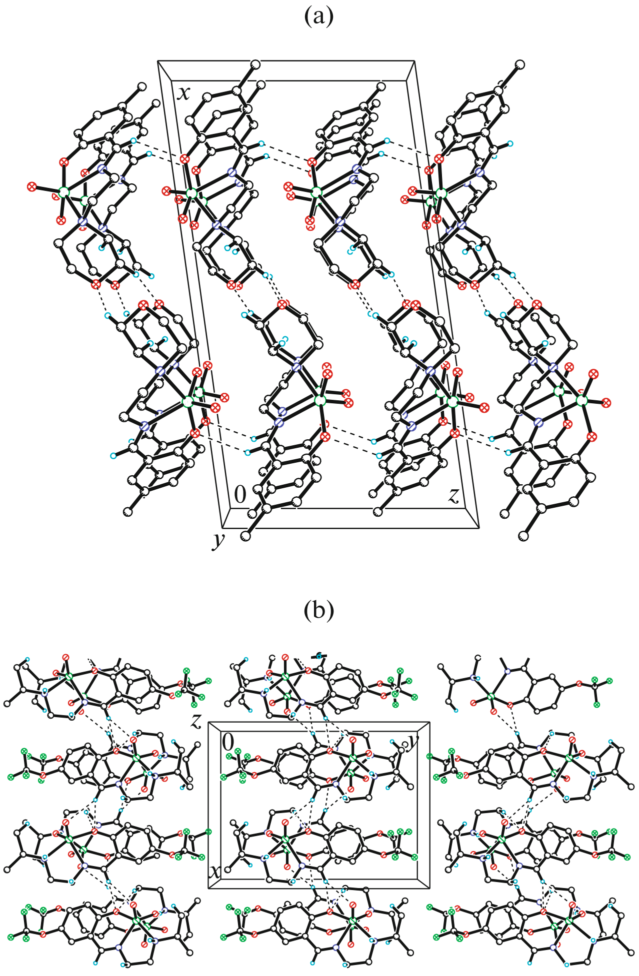


Fig. 2. Molecular packing of complex **I** (a) and **II** (b). Hydrogen bonds are drawn as thin dashed lines.

plexes have good catalytic property on the chloro substituted substrates.

In summary, a pair of new oxidovanadium(V) complexes with similar tridentate Schiff base ligands have been synthesized and characterized by infrared and electronic spectra, as well as single crystal X-ray determination. The Schiff base ligands coordinate to the V atoms through the phenolate oxygen, imino nitrogen and amino nitrogen atoms. The V atoms in the complexes are coordinated by the Schiff base ligands and two oxo groups, forming trigonal-bipyramidal geometry. The complexes are effective catalyst for the oxidation of various aliphatic and aromatic olefins, especially for the chloro-substituted substrates.

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