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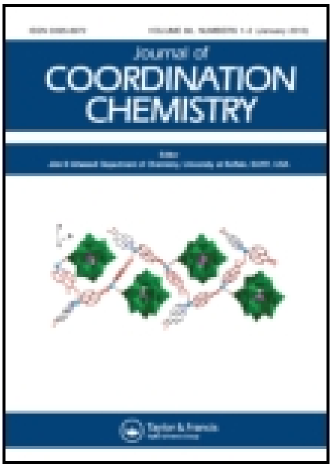

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Vanadium(V) complexes with hydrazone and benzohydroxamate ligands: synthesis, structures and catalytic epoxidation

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Vanadium(V) complexes with hydrazone and benzohydroxamate ligands: synthesis, structures and catalytic epoxidation

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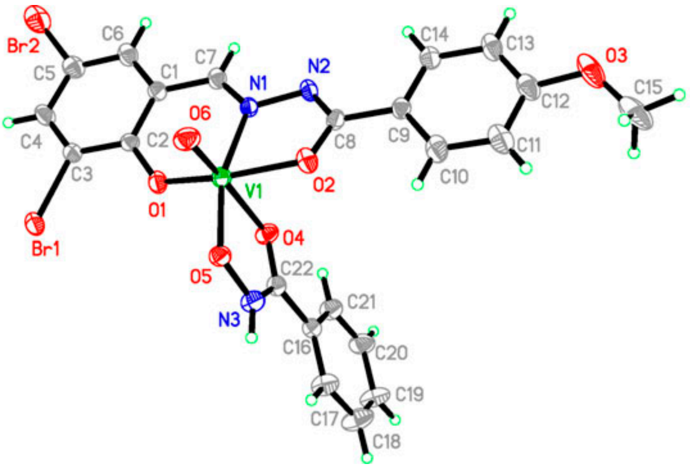

Two structurally similar vanadium(V) complexes, [VOL^{1}L] (**1**) and [VOL^{2}L] (**2**), where L^1 is the dianionic form of *N′*-(3,5-dibromo-2-hydroxybenzylidene)-4-methoxybenzohydrazide, L^2 is the dianionic form of *N′*-(3,5-dibromo-2-hydroxybenzylidene)nicotinohydrazide, and L is benzohydroxamate, were prepared and characterized by elemental analysis, infrared spectra, and single crystal X-ray diffraction. **1** crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions $a = 12.0262(7)$, $b = 16.5629(9)$, $c = 12.3449(8)$ Å, $\beta = 105.160(2)°$, $V = 2373.4(2)$ Å^3, $Z = 4$, $R_1 = 0.0376$, $wR_2 = 0.0844$, GOOF = 1.058; **2** crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions $a = 10.6439(7)$, $b = 16.1968(9)$, $c = 13.1108(8)$ Å, $\beta = 104.180(2)°$, $V = 2191.4(2)$ Å^3, $Z = 4$, $R_1 = 0.0521$, $wR_2 = 0.1142$, GOOF = 1.018. X-ray analysis indicates that vanadium in the complexes are coordinated by phenolate oxygen, imino nitrogen, and enolate oxygen of the hydrazone, two oxygens of the benzohydroxamate, and one oxo, generating octahedral coordination. Oxidations of olefins with the complexes as catalysts were evaluated. The complexes showed effective catalytic efficiency in oxidation of several aliphatic and aromatic substrates under mild conditions, using *tert*-butyl hydrogen peroxide as oxidant.

Keywords: Hydrazone ligand; Vanadium complex; Crystal structure; Catalytic epoxidation

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1. Introduction

The development of processes for oxidation of olefins is a goal that has long been pursued. The challenge is to make such processes environmental friendly using nontoxic reagents and energy-efficient catalytic methods [1]. Vanadium complexes are well known for use in organic synthesis, in particular for oxidations of various organic compounds [2–7]. Vanadium complexes have attracted attention for sulfoxidation and epoxidation of olefins [8–13]. The synthesis and catalytic properties of a number of vanadium complexes with Schiff bases have been reported [4, 7, 14–16]. However, the number of documented vanadium complexes catalyzing the peroxidic oxidation of sulfides is still limited and the structure-activity relationship is not clear. In this work, two new structurally similar vanadium(V) complexes, [VOL^{1}L] (**1**) and [VOL^{2}L] (**2**), where L^1 is the dianionic form of *N*′-(3,5-dibromo-2-hydroxybenzylidene)-4methoxybenzohydrazide (H$_2$L^1), L^2 is the dianionic form of *N*′-(3,5-dibromo-2-hydroxybenzylidene)nicotinohydrazide (H$_2$L^2), and L is benzohydroxamate, were prepared and studied for their structures and catalytic oxidation of olefins (scheme 1).

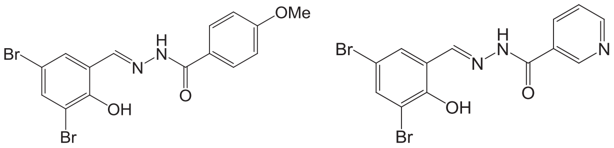
2. Experimental

2.1. *Materials and methods*

All chemicals and solvents were analytical reagent grade and purchased from Beijing Chemical Reagent Company. H$_2$L^1 and H$_2$L^2 were prepared according to the literature method [17]. 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 from 4000 to 400 cm^{-1}. GC analyses were performed on a Shimadzu GC-2014 gas chromatograph. UV–vis spectra were measured with a Perkin-Elmer Lambda 18 spectrophotometer.

2.2. *Syntheses of the complexes*

[VOL^{1}L] (**1**). A methanolic solution (15 mL) of VO(acac)$_2$ (0.26 g, 1.0 mM) was added to a methanolic solution (15 mL) of H$_2$L^1 (0.43 g, 1.0 mM) and benzohydroxamic acid (0.14 g, 1.0 mM). The mixture was stirred at room temperature for 1 h to give a brown solution. Single crystals of the complex, suitable for X-ray diffraction, were formed at the bottom of the vessel on slow evaporation of the solution in air for a few days. Yield: 54%. Anal. Calcd for $C_{22}H_{16}Br_2N_3O_6V$: C, 42.00; H, 2.56; N, 6.68. Found: C, 41.86; H, 2.67; N, 6.81%.



Scheme 1. The hydrazone ligands H$_2$L^1 (left) and H$_2$L^2 (right).

[VOL^2L] (**2**). This complex was prepared according to the same method as **1**, but with H_2L^1 replaced by H_2L^2 (0.40 g, 1.0 mM). Yield: 67%. Anal. Calcd for $C_{20}H_{13}Br_2N_4O_5V$: C, 40.03; H, 2.18; N, 9.34. Found: C, 40.22; H, 2.30; N, 9.17%.

2.3. *X-ray structure determination*

X-ray measurement was performed using a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan technique. Determination of the Laue class, orientation matrix, and cell dimensions were performed according to established procedures where Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles. The positions of non-hydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The amino hydrogens were located from difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90(1) Å. The remaining hydrogens were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with the aid of the SHELXS-97 and SHELXL-97 suite of codes [18, 19]. The crystallographic data for the complexes are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystal data for **1** and **2**.

	1	**2**
Chemical formula	$C_{22}H_{16}Br_2N_3O_6V$	$C_{20}H_{13}Br_2N_4O_5V$
Fw	629.1	600.1
Crystal shape/color	Block/deep brown	Block/deep brown
Crystal size (mm)	0.20 × 0.18 × 0.16	0.18 × 0.17 × 0.17
T (K)	298(2)	298(2)
λ (Mo Kα) (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.0262(7)	10.6439(7)
b (Å)	16.5629(9)	16.1968(9)
c (Å)	12.3449(8)	13.1108(8)
β (°)	105.160(2)	104.180(2)
V (Å^3)	2373.4(2)	2191.4(2)
Z	4	4
μ (Mo Kα) (cm^{-1})	3.829	4.140
T (min)	0.5148	0.5228
T (max)	0.5794	0.5396
D_{Calcd} (g cm^{-3})	1.761	1.819
F (000)	1240	1176
Collected reflections	25,139	21,696
Unique reflections	4402	4492
Observed reflections [$I \geq 2\sigma(I)$]	3523	3289
Parameters	311	292
Restraints	1	1
Goodness of fit on F^2	1.058	1.018
R_{int}	0.0431	0.0415
R_1 [$I \geq 2\sigma(I)$]	0.0376	0.0521
wR_2 [$I \geq 2\sigma(I)$]	0.0844	0.1142
R_1 (all data)	0.0551	0.0807
wR_2 (all data)	0.0923	0.1295

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Bond lengths			
V1–O1	1.873(2)	V1–O2	1.948(2)
V1–O5	1.855(2)	V1–O6	1.581(3)
V1–O4	2.168(3)	V1–N1	2.094(3)
Bond angles			
O6–V1–O5	97.24(13)	O6–V1–O1	98.68(14)
O5–V1–O1	102.76(11)	O6–V1–O2	97.85(14)
O5–V1–O2	93.51(11)	O1–V1–O2	155.06(11)
O6–V1–N1	100.11(13)	O5–V1–N1	160.29(11)
O1–V1–N1	83.84(11)	O2–V1–N1	74.95(10)
O6–V1–O4	173.67(12)	O5–V1–O4	76.69(10)
O1–V1–O4	84.57(11)	O2–V1–O4	80.91(11)
N1–V1–O4	85.61(10)		
2			
Bond lengths			
V1–O1	1.889(3)	V1–O2	1.944(3)
V1–O4	1.848(3)	V1–O5	1.583(3)
V1–O3	2.196(3)	V1–N1	2.073(3)
Bond angles			
O5–V1–O4	95.89(15)	O5–V1–O1	98.69(15)
O4–V1–O1	105.29(13)	O5–V1–O2	101.32(15)
O4–V1–O2	90.55(12)	O1–V1–O2	152.99(13)
O5–V1–N1	98.92(15)	O4–V1–N1	161.03(13)
O1–V1–N1	84.17(13)	O2–V1–N1	74.99(12)
O5–V1–O3	171.30(15)	O4–V1–O3	75.85(12)
O1–V1–O3	81.18(12)	O2–V1–O3	81.72(12)
N1–V1–O3	89.73(12)		

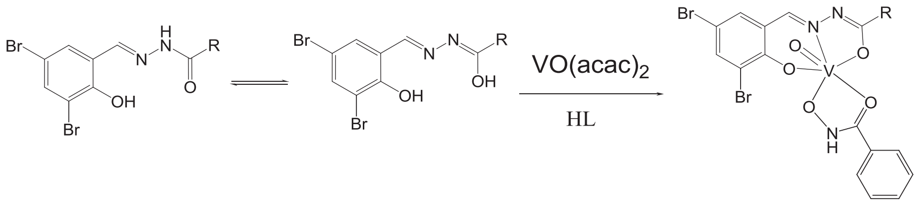
2.4. *Oxidation*

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 mM) were dissolved in 10 mL 1,2-dichloroethane. Then 10 mM alkene was added to the reaction mixture and 30 mM TBHP 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).

3. Results and discussion

3.1. *Synthesis*

The hydrazones were readily prepared by condensation of 3,5-dibromo-2-hydroxybenzohydrazide with 4-methylbenzohydrazide and nicotinohydrazide, respectively, in methanol. The vanadium complexes were synthesized by stirring equimolar quantities of the hydrazone ligands, benzohydroxamic acid and VO(acac)$_2$ in methanol at room temperature (scheme 2). The chemical formulas of the complexes have been confirmed by elemental analyses, IR spectra, and single crystal X-ray diffraction.



Scheme 2. Preparation of the complexes. **1**: R = *p*-OMePh; **2**: R = *m*-pyridine.

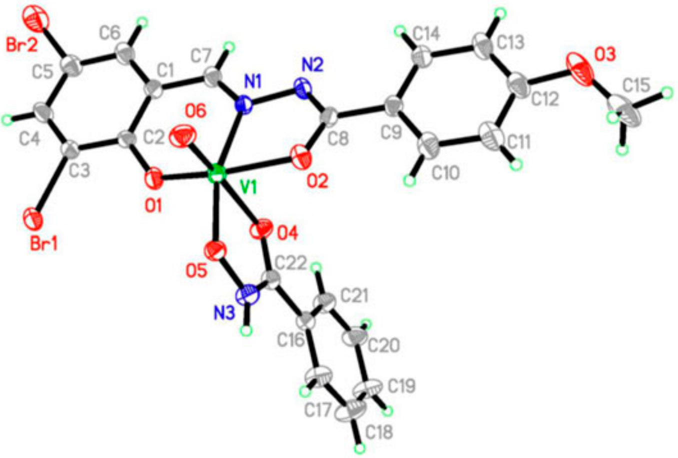


Figure 1. Molecular structure of **1** with 30% probability thermal ellipsoids.

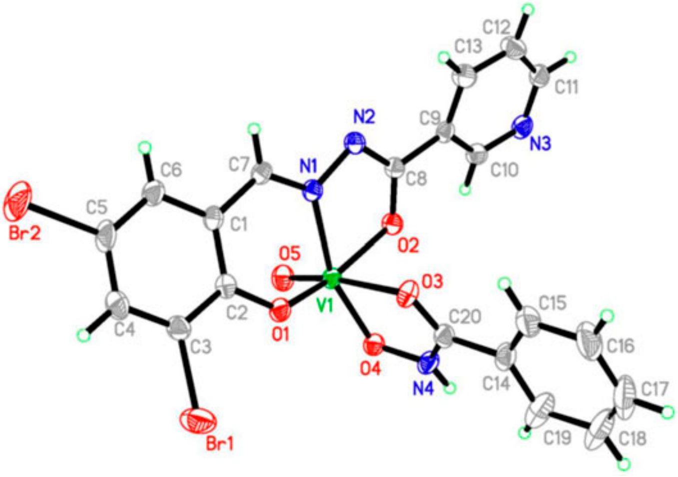


Figure 2. Molecular structure of **2** with 30% probability thermal ellipsoids.

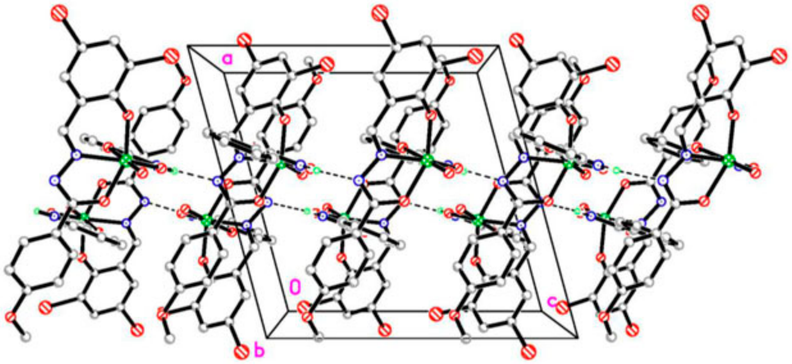


Figure 3. Molecular packing of **1** viewed along the *b* axis. Hydrogen bonds are drawn as thin dotted lines.

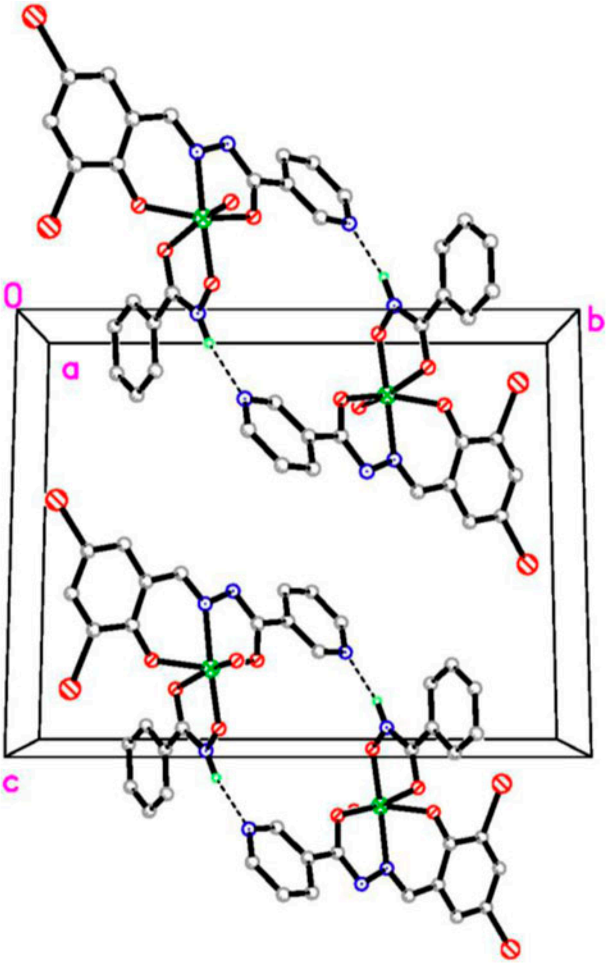


Figure 4. Molecular packing of **2**. Hydrogen bonds are drawn as thin dotted lines.

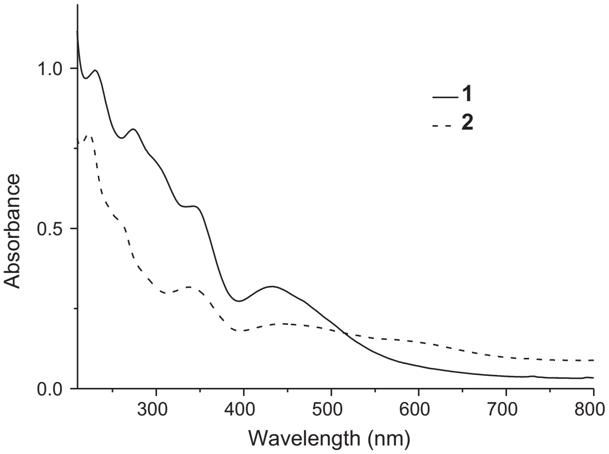


Figure 5. UV–vis spectra of the complexes.

3.2. *Structure description of the complexes*

The molecular structures of **1** and **2** are shown in figures 1 and 2, respectively. The coordination geometry around *V* can be described as distorted octahedral, with the phenolate oxygen, imino nitrogen, and enolate oxygen of the hydrazone, and one hydroxy oxygen of the benzohydroxamate defining the equatorial plane, and with the carbonyl oxygen of the benzohydroxamate and the oxo occupying axial positions. The hydrazone ligands coordinate to *V* in a meridional fashion forming five- and six-membered chelate rings with bite angles of 74.95(10)° and 83.84(11)° for **1**, and 74.99(12)° and 84.17(13)° for **2**. The dihedral angles between the aromatic rings of the hydrazone ligands are 1.9(2)° for **1** and 39.4(3)° for **2**. The displacements of *V* in **1** and **2** from the equatorial mean planes toward the apical oxo are 0.281(1) and 0.284(1) Å, respectively. The hydrazone ligands are coordinated in their dianionic form, which is evident from the N2–C8 and O2–C8 bond lengths. The abnormal bond values indicate the presence of the enolate form of the ligand amide groups. The V–O, V–N and V=O bonds are within normal ranges and are similar to those observed in similar vanadium complexes [20, 21]. The distances between *V* and the hydroxy oxygen are much longer than the other bonds, caused by the *trans* effect of the oxo.

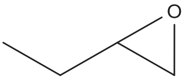
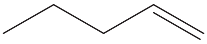
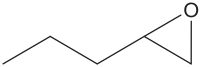
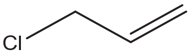
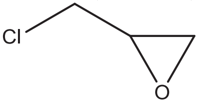
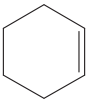
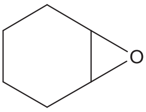
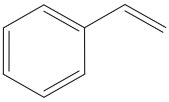
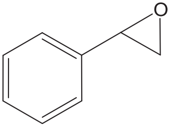
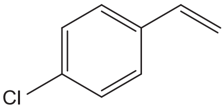
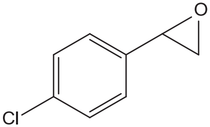
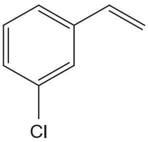
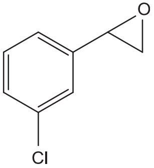
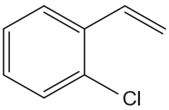
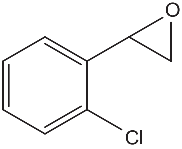
In the crystal structure of **1**, the molecules are linked through intermolecular N3–H3···N2 hydrogen bonds [N3–H3 = 0.90(1) Å, H3···N2^{i} = 2.09(1) Å, N3···N2^{i} = 2.990(4) Å, N3–H3···N2^{i} = 173(5)°; symmetry code for i: x, $1/2-y$, $-1/2+z$] to form chains along the *c*-axis (figure 3). In the crystal structure of **2**, adjacent molecules are linked through two intermolecular N–H4···N3 hydrogen bonds [N4–H4 = 0.90(1) Å, H4···N3^{ii} = 1.86(2) Å, N4···N3^{ii} = 2.749(5) Å, N4–H4···N3^{ii} = 168(6)°; symmetry code for ii: $2-x$, $-y$, $1-z$] (figure 4).

3.3. *IR and UV–vis spectra*

The hydrazones show stretching bands attributed to C=O, C=N, C–OH and NH at 1645–1672, 1619–1625, 1175–1183, and 3210–3230 cm^{-1}, respectively [22]. For the complexes, absence of the bands characteristic of N–H and C=O groups indicates enolization of the hydrazone ligands and coordination through deprotonated enolic oxygens. The V=O stretches occur as single sharp bands at 978 cm^{-1} for **1** and 973 cm^{-1} for **2** [23]. The strong bands indicative of C=N groups of the complexes are located at 1605 cm^{-1} for **1** and 1610 cm^{-1} for **2** [24]. The weak peaks observed at low wavenumbers (420–600 cm^{-1}) may be attributed to V–O and V–N vibrations.

The UV–vis spectra of the complexes were recorded in acetonitrile. In the UV–vis region, **1** shows bands at 230, 274, 346, and 433 nm, and **2** shows bands at 223, 262, 341, and 445 nm (figure 5). The weak bands at 390–500 nm were attributed to ligand-to-metal charge transfer (LMCT) from the p_π orbital on the phenolate oxygen to the empty *d* orbitals of the vanadium ion [25]. The bands at 310–350 nm were assigned to n–π^* transitions [26]. The intense bands at 250–280 nm were assigned to intra-ligand π–π^* transitions [26].

Table 3. Catalytic oxidation of olefins catalyzed by **1** and **2**.[a]

Substrate	Product		Conversion (%)[b]
		**1** **2**	72.0 75.4
		**1** **2**	68.2 65.3
		**1** **2**	77.8 82.0
		**1** **2**	87.2 90.3
		**1** **2**	85.5 88.0
		**1** **2**	92.7 95.6
		**1** **2**	98.3 99.1
		**1** **2**	95.5 93.0

[a] 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).

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

3.4. *Catalytic oxidation results*

Vanadium complexes often show interesting catalytic properties [27–30]. When compared to reported species, the present two complexes have excellent performance. The catalytic results are listed in table 3. 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 80% yields, while in oxidation of aliphatic substrates the conversion is lower than 80%. Based on this consideration, isolated double bonds are less reactive than the conjugated ones, in agreement with those reported previously [31–33]. When comparing the results of **1** and **2**, they are similar. This indicates that the slight difference of the hydrazone ligands is not essential for influence of the catalytic properties.

4. Conclusion

Two structurally similar vanadium complexes with hydrazone and benzohydroxamate ligands have been prepared and structurally characterized by single crystal X-ray structure determination and infrared spectra. The hydrazones coordinate to *V* through the phenolate oxygen, imino nitrogen, and enolate oxygen with vanadium in octahedral coordination geometry. The complexes are effective catalysts for oxidation of aliphatic and aromatic olefins.

Supplementary material

CCDC 988425 (**1**) and 988426 (**2**) contain the supplementary crystallographic data for the complex. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44)1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

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