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Synthesis, Crystal Structure, and Catalytic Property of a Vanadium(V) Complex with Mixed Ligands[1]

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Abstract—With a tridentate hydrazone ligand *N*'-(3-bromo-2-hydroxybenzylidene)-2-methylbenzohydrazide (H_2L) and a bidentate ligand benzohydroxamic acid (HL') with $VO(Acac)_2$, a mononuclear vanadium(V) complex was prepared and characterized by elemental analysis, IR spectroscopy and X-ray structure determination (CIF file CCDC no. 1029909). The complex crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions $a = 27.870(2)$, $b = 11.4893(5)$, $c = 18.467(2)$ Å, $\beta = 131.444(1)°$, $V = 4432.6(6)$ Å^3, $Z = 8$, $R_1 = 0.0350$, and $wR_2 = 0.0749$. Single crystal X-ray diffraction analysis reveals that the V atom is coordinated by the phenolate O, imino N and enolate O atoms of the hydrazone ligand, and the carbonyl O and hydroxy O atoms of benzohydroxamate ligand, and one oxo O group, in an octahedral coordination. Catalytic oxidation of the complex on some olefins was performed.

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INTRODUCTION

In recent years, the catalytic oxidation of olefins has aroused much attention in the production of chemicals and fine chemicals since epoxides are key starting materials for a wide variety of oily products [1–5]. Because of the environment friendly nature, H_2O_2 has been regarded as the first selected oxidant in the oxidation of olefins. Transition metal complexes with various ligands have presented interesting catalytic properties [6–10]. Among the complexes, vanadium species show efficient catalytic oxidation properties [11–16]. In this paper, a new vanadium(V) complex with mixed ligands *N*'-(3-bromo-2-hydroxybenzylidene)-2-methylbenzohydrazide (H_2L) and a bidentate ligand benzohydroxamic acid (HL') was prepared and its catalytic oxidation property was performed.

EXPERIMENTAL

Materials and methods. 3-Bromosalicylaldehyde, 2-methylbenzohydrazide and benzohydroxamic acid were purchased from Alfa Aesar. $VO(Acac)_2$ and solvents are commercially available and were used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL. Infrared spectra were measured on KBr disks with a Hitachi I-5040 FT-IR spectrophotometer. ^{1}H NMR data were recorded on a Bruker NMR 300 MHz instrument.

Synthesis of H_2L. 3-Bromosalicylaldehyde (2.01 g, 10 mmol) and 2-methylbenzohydrazide (1.50 g, 10 mmol) were dissolved in methanol (30 mL). The mixture was refluxed for 30 min and the solvent was evaporated by distillation. Colorless solid was recrysallized from methanol to give pure product of H_2L. The yield was 83%.

For $C_{15}H_{13}BrN_2O_2$

anal. calcd., %:	C, 54.07;	H, 3.93;	N, 8.41.
Found, %:	C, 53.89;	H, 4.02;	N, 8.50.

IR (KBr; ν, cm^{-1}): 3440 ν(O–H); 3241 ν(N–H); 1646 ν(C=O); 1608 ν(C=N); 1175 ν(C–OH).
^{1}H NMR (300 MHz; DMSO-d$_6$): δ 12.71 (s., 1H), 12.22 (s., 1H), 8.63 (s., 1H), 7.2–7.7 (m., 5H), 6.93 (t., 1H), 2.51 (s., 3H).

Synthesis of the complex. Equimolar quantities (1.0 mmol each) of H_2L (0.333 g), HL' (0.137 g) and $VO(Acac)_2$ (0.265 g) were dissolved in methanol (20 mL). The mixture was refluxed for 30 min and cooled to room temperature to give a deep brown solution. The solution was kept still in air for a week to slow evaporate to give brown block-shaped single crystals of the complex. The yield was 61%.

For $C_{22}H_{17}BrN_3O_5V$

anal. calcd., %:	C, 49.46;	H, 3.21;	N, 7.87.
Found, %:	C, 49.32;	H, 3.15;	N, 8.02.

IR (KBr; ν, cm^{-1}): 3445 ν(O–H); 3196 ν(N–H); 1602 ν(C=N); 976 ν(VO).

Catalytic oxidation experiment was carried out in a 50 mL glass round-bottom flask fitted with a reflux

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Table 1. Crystallographic data and and structure refinement for the complex

Parameter	Value
Formula weight	534.2
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	27.870(2)
b, Å	11.4893(5)
c, Å	18.467(2)
β, deg	131.444(1)
V, Å^3	4432.6(6)
Z	8
ρ_{calcd}, g cm^{-3}	1.601
F(000)	2144
μ, mm^{-1}	2.289
θ Range, deg	2.86–26.06
Index ranges hkl	$-32 \le h \le 34$, $-13 \le k \le 14$, $-22 \le l \le 22$
Reflections collected/unique	18693/4373
R_{int}	0.0279
Observed with $I > 2\sigma(I)$	3500
Parameters	293
Rastraints refined	1
Final R index ($I > 2\sigma(I)$)	0.0350, 0.0749
R index (all data)	0.0506, 0.0835
Goodness-of-fit on F^2	1.040
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.442/–0.361

condenser and placed in an oil bath at prearranged temperature under continuous stirring. The oxidation was carried out as follows: the complex (0.032 mmol) was dissolved in 10 mL 1,2-dichloroethane. Then 10 mmol alkene was added to the reaction mixture and 30 mmol 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).

X-ray structure determination. Data collection for the complex was performed with a Bruker Apex II CCD diffractometer at 298 K. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least squares (SHELXL-97) on F^2 [17]. All non-hydrogens were refined anisotropically. The hydrogen atom of N(3) was located from a difference Fourier map and refined isotropically, with N–H distance restrained to 0.90(1) Å. The remaining hydrogens were placed geometrically and refined with a riding model, with isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C). Crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material for complex has been deposited with the Cambridge Crystallographic Data Centre (no. 1029909; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The vanadium complex was prepared by reaction of equimolar quantities of the hydrazone ligand, benzohydroxamic acid and VO(Acac)$_2$ in methanol. Crystals of the complex are stable in air, and soluble in methanol, ethanol, DMF and DMSO, insoluble in water. The hydrazone ligand and the complex have been characterized by infrared spectroscopy. In the spectra

Table 2. Selected bond distances (Å) and angles (deg) for the complex

Bond	d, Å	Bond	d, Å
V(1)–O(1)	1.8697(18)	V(1)–O(2)	1.9755(17)
V(1)–O(3)	2.1904(19)	V(1)–O(4)	1.8655(17)
V(1)–O(5)	1.5855(19)	V(1)–N(1)	2.057(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(5)V(1)O(4)	95.00(9)	O(5)V(1)O(1)	98.99(9)
O(4)V(1)O(1)	107.93(8)	O(5)V(1)O(2)	100.76(9)
O(4)V(1)O(2)	88.95(7)	O(1)V(1)O(2)	152.70(8)
O(5)V(1)N(1)	96.27(9)	O(4)V(1)N(1)	161.51(8)
O(1)V(1)N(1)	84.72(8)	O(2)V(1)N(1)	74.58(8)
O(5)V(1)O(3)	170.93(9)	O(4)V(1)O(3)	76.16(7)
O(1)V(1)O(3)	82.16(8)	O(2)V(1)O(3)	81.30(7)
N(1)V(1)O(3)	92.79(8)		

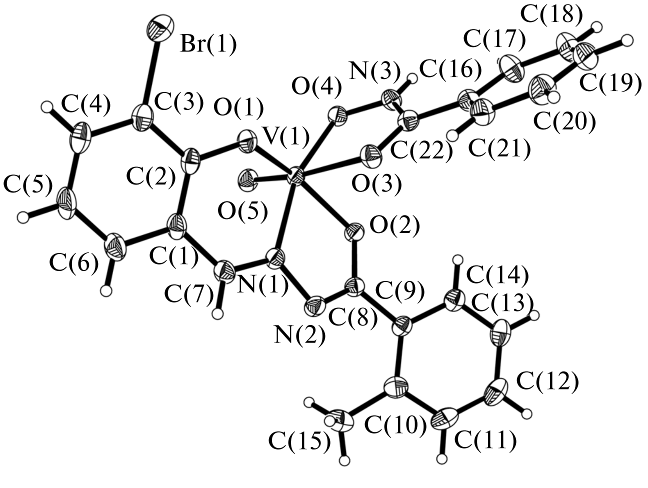


Fig. 1. The molecular structure of the complex with 30% probability thermal ellipsoids.

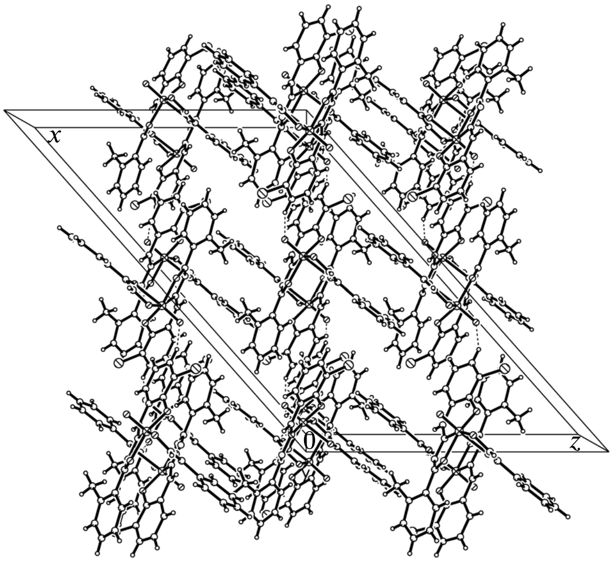
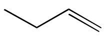
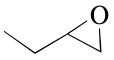
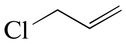
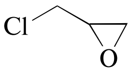
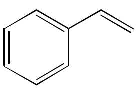
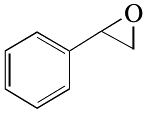
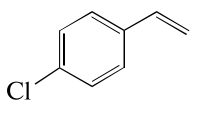
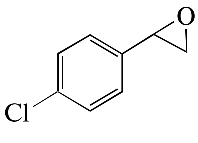
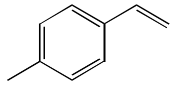
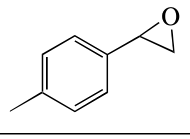


Fig. 2. Molecular packing structure of the complex, viewed along the *y* axis. Hydrogen bonds are shown as dashed lines.

of both H_2L and the complex, the broad bands centered at about 3440 cm^{-1} are assigned to the O–H vibrations of the water molecules. In the spectra of H_2L and the complex, the typical bands due to the N–H vibrations are observed at 3241 and 3196 cm^{-1}, respectively. In the infrared spectrum of H_2L, absorption bands appear attributed to N–H, C=O, C=N, and C–OH at 3241, 1646, 1608, and 1175 cm^{-1}, respectively. As a comparison, in the spectrum of the complex, the strong band indicative of the C=N group is observed at 1602 cm^{-1} [18], and the C=O absorption in the spectrum of H_2L is disappeared in that of the complex. The V=O stretching mode occur as a single sharp band at 976 cm^{-1} [19].

The molecular structure of the complex is shown in Fig. 1. The coordination geometry around vanadium

Table 3. Catalytic oxidation results*

Substrate	Product	Conversion, %**
		69
Cl 	Cl 	77
		86
		93
		82

* 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.

can be described as octahedral with the phenolate O, imine N and enolate O atoms of the hydrazone ligand, and the hydroxy O atom of the benzohydroxamate ligand in the equatorial plane, and with the carbonyl O atom of the benzohydroxamate ligand and one oxo O group in the axial positions. The O(5)=V(1)–O(3) axis is almost linear with bond angle of 170.93(9)°. Because of the *trans* influence of the oxo O group, the distance of V(1)–O(3) is much longer than the other bonds. Such elongation has previously been observed in other complexes with similar structures [20, 21]. The V atom deviates from the equatorial plane by 0.255(1) Å. All the bond values are in good agreement with those observed in vanadium(V) complexes with hydrazone ligands [20–23].

In the crystal structure of the complex, molecules are linked through intermolecular hydrogen bonds of N(3)–H(3)···O(2)^{i} (N(3)–H(3) 0.90(1), H(3)···O(2)^{i} 2.05(2), N(3)···O(2)^{i} 2.915(3) Å, N(3)–H(3)···O(2)^{i} 160(3)°; symmetry code: ^{i} $-x$, $1 - y$, $-z$) and C(4)–H(4)···O(5)^{ii} (C(4)–H(4) 0.93, H(4)···O(5)^{ii} 2.56(2), C(4)···O(5)^{ii} 3.253(3) Å, C(4)–H(4)···O(5)^{ii} 131(3)°; symmetry code: ^{ii} $-1/2 - x$, $-1/2 + y$, $-1/2 - z$) to form 1D chains, as shown in Fig. 2.

The catalytic results are given 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 82% yields, while in the oxidation of aliphatic substrates, the conversion is lower than 77%. Based on this consideration, it can be observed that the isolated double bonds are less reactive than the conjugated ones. For both aliphatic and aromatic substrates, the conversion for the chloro-substituted species is higher than the methyl or no substituted ones.

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