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Selective catalytic oxidation of benzyl alcohol to benzaldehyde by a mononuclear oxovanadium(V) complex of a bis(phenolate) ligand containing bulky *tert*-butyl substituents

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Abstract A new mononuclear complex of vanadium(V), [V(O)(bp)(OCH_3)] (**1**) has been synthesized, where H_2bp is *N,N′*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N′,N′*-dimethylethylene-1,2-diamine. The complex was characterized by elemental analyses, spectroscopic methods and X-ray diffraction measurement. Single-crystal X-ray diffraction structure analysis of the complex revealed that the vanadium atom is octahedrally coordinated and that the bis(phenolate) ligand (bp^{2-}) is N_2O_2-bonded to the vanadium(V) center in a tetradentate dinegative fashion.

Introduction

Vanadium is an important element in biology, inorganic chemistry and organic syntheses [1–3]. The interest in coordination chemistry of vanadium has increased in the last decades because the active sites of some enzymes such as haloperoxidases consist of vanadate moieties which are able to catalyze oxidation reactions [4, 5]. Many vanadium complexes show activity in oxidation and oxo transfer reactions [6, 7]. Another important impetus to the coordination chemistry of vanadium is the catalytic oxidation of organic compounds such as olefins, sulfides, alcohols, etc. [8–10].

The oxidation of alcohols to their corresponding carbonyl compounds is one of the most important and fundamental reactions in organic synthesis [11, 12]. A number of methods are known for alcohol oxidations, but oxidation over metal catalysts using hydrogen peroxide are preferred now for their economic benefits and environmental acceptability, which depends mainly on the nature of the by-product, i.e. water [13]. Recently, catalytic oxidation of alcohols employing transition metal complexes, such as Fe [14], Cu [15], Co [16], Mo [17], Pd [18], Mn [19], V [20], etc., using H_2O_2 has been developed. Oxovanadium complexes are active catalysts in oxidation reactions using H_2O_2, and some of them have been used for enantioselective oxidation of prochiral substrates [21]. They can catalyze oxidation of benzyl alcohol to benzaldehyde with high selectivity in the presence of H_2O_2 [22].

On the other hand, the bis(phenolate)-based ligands obtained in the reaction of amines with phenols in the presence of formaldehyde are interesting N-, O-donor systems. Their metal complexes are good candidates for catalytic oxidation studies because of their resistance to oxidation in oxo transfer reactions [23]. Also, bis(phenolate)-based ligands are able to stabilize vanadium in high oxidation state of 5+ [24, 25]. Bis(phenolate) ligands bearing bulky *tert*-butyl groups may be useful in the selective oxidation reactions, because the incorporation of bulky substituents at the *ortho*-positions with respect to the phenolic O-donor atom directs the substrate toward the metal center, giving rise to improved selectivity [26–28].

In this work, we report the synthesis, characterization, crystal structure and catalytic reactivity of a new vanadium(V) complex of a tetradentate ligand including two

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phenolic rings bearing bulky *tert*-butyl substitutents in *ortho*- and *para*- positions with respect to the phenolic oxygen. The catalytic reactivity of this complex has been investigated in the selective oxidation of primary alcohols in the presence of H_2O_2.

Experimental

Materials and instrumentation

All starting chemicals were commercially available reagents and were used without further purification. IR spectra were recorded in KBr disks with a Bruker FT-IR spectrophotometer. UV–Vis solution spectra were recorded using a thermo-spectronic Helios Alpha spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Spectrospin spectrometer at 250 and 62.5 MHz, respectively. The reaction products of oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (phenyl methyl siloxane 30 μm × 320 μm × 0.25 μm) and gas chromatograph–mass spectrometry (Hewlett-Packard 5973 Series MS-HP gas chromatograph with a mass-selective detector). The elemental analyses (carbon, hydrogen and nitrogen) were obtained using a Carlo ERBA Model EA 1108 analyzer. Vanadium percentage of the complex was measured by a Varian spectrometer AA 220 instrument.

Synthesis of *N,N*′-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-*N*′,*N*′-dimethylethylene-1,2-diamine (H_2bp)

For synthesis of the amine-bis(phenolate) ligand, H_2bp, methanol (35 mL) was added to *N,N*-dimethylethane-1,2-diamine (4.40 mL, 0.05 mol) and the rapidly stirred solution was cooled to 0 °C after which aqueous formaldehyde solution (37 wt% in H_2O, containing 10 % methanol as stabilizer) (8 mL, 0.1 mol) was added dropwise. The mixture was stirred for 15 min, then 2,4-di-*tert*-butylphenol (20.63 g, 0.1 mol) was added, and the mixture was refluxed for 48 h. At the end, the solution was evaporated on a steam bath to 5 mL and cooled to room temperature. The resulting white precipitate was separated and filtered off, washed with 20 mL of cooled methanol and re-crystallized. Yield 80 % (20.99 g). M.p. 131–133 °C. Anal. Calc. for $C_{34}H_{56}N_2O_2$ (MW = 524.82): C, 77.8; H, 10.7; N, 5.3. Found: C, 77.8; H, 10.8; N, 5.3. FT-IR (KBr, cm^{-1}): 3,188 (s, br), 2,950 (m,br), 2,865(m, br), 1,768(s), 1,605(m), 1,592(w), 1,571(s), 1,506(m), 1,483(s), 1,467(m), 1,417(m), 1,388(m), 1,374(m), 1,360(m), 1,303(m), 1,285(m), 1,256(m), 1,224(w), 1,202(w), 1,160(m), 1,121(m), 1,105(s), 1,086(w), 1,057(w), 1,043(s), 1,024(m), 987(s), 948(m), 938(m), 923(s), 910(w), 891(w), 879(s), 824(m), 813(m), 800(w), 782(m), 756(m), 725(m), 681(m), 665(w), 649(m), 540(m). ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS, ppm): $\delta = 1.27$ (m, 18 H, CH_3 of *t-Bu*), 1.38 (m, 18 H, CH_3 of *t-Bu*), 2.30 (s, 6H, CH_3 of $N(CH_3)_2$), 2.57 (m, 4 H, N–CH_2), 3.65 (m, 2H, Ar–CH_2), 6.93 (d, 2H, $^{4}J_{HH} = 2.0$ Hz, aryl), 7.20 (d, 2H, $^{4}J_{HH} = 2.0$ Hz, aryl). ^{13}C NMR (62.19 MHz, $CDCl_3$, 25 °C, TMS, ppm): $\delta = 29.50$ (CH_3 of *t-Bu*), 31.7 (CH_3 of *t-Bu*), 34.0 (C of *t-Bu*), 35.0 (C of *t-Bu*), 44.8 (CH_3 of $N(CH_3)_2$), 49.0 (CH_2–N), 56.6 (Ar–CH_2), 56.9 (CH_2–$N(CH_3)_2$), 123.3, 124.8 (4CH of arom), 121.6, 136.0, 140.1, 153.3(8C of arom). UV–Vis (5×10^{-5} M, CH_3OH): λ_{max} (ε, M^{-1} cm^{-1}) = 216 (33 000), 279 nm (9 100).

Synthesis of [V(O)(bp)(OCH_3)]

The appropriate amount of ligand H_2bp (0.524 g, 1.0 mmol) was dissolved in CH_3OH (30 mL containing 3 % (v/v) H_2O) in association with $VO(acac)_2$ (0.265 g, 1.0 mmol). The solution was gently refluxed for 6 h. After cooling, the resulting solid was filtered off, washed with cooled absolute ethanol and dried at 100 °C. Single crystals of [V(O)(bp)(OCH_3)] were obtained by thermal gradient method. Yield 87 % (0.54 g). Anal. Calc. for $C_{35}H_{57}N_2O_4V$ (MW = 620.77): C, 67.7; H, 9.2; N, 4.5; V, 8.2. Found: C, 67.8; H, 9.4; N, 4.5; V, 8.2 %. FT-IR (KBr, cm^{-1}): 3,413(OH, w, br), 2,953(CH alif, s), 2,904(s), 2,867(m), 2,835(w), 2,810(w), 1,603(w), 1,467(s), 1,440(s), 1,411(m), 1,389(m), 1,359(s), 1,256(s), 1,241(s), 1,204(m), 1,070(s), 1,025(w), 958 (vs), 912(s), 871(w), 771(m), 761(m), 747(w), 648(w), 641(w), 589(m), 552(m). UV–Vis (5×10^{-5} M, CH_3OH): λ_{max} (ε, M^{-1} cm^{-1}) = 221 (32 000), 282 (15 500), 360 nm (2 600).

X-ray crystallography

Data collection for X-ray structure determination was performed on an Xcalibur R four-circle diffractometer with a Ruby CCD detector with graphite monochromatized Mo*Kα* radiation. The data were collected at 100(2) K using an Oxford Cryosystems cooler. Data collection, cell refinement, data reduction and analysis and absorption correction were carried out with the Xcalibur R software, CrysAlis^{Pro} [29]. The structure was solved by direct methods with SHELXS [30] and refined by full-matrix least-squares techniques on F^2 using SHELXL-2013 [30] with anisotropic thermal parameters for the non-H atoms (except for the atoms of low-occupied positions of disordered ligand). The H atoms were included from geometry and were refined using a riding model, with C–H = 0.95–0.99 Å, and with $U_{iso}(H) = 1.2U_{eq}(CH, CH_2)$

Table 1 Crystallographic data of **1**

	Complex 1
CCDC No.	946551
Formula	$C_{35}H_{57}N_2O_4V$
Mr/g mol^{-1}	620.76
Crystal size/mm	0.20 × 0.08 × 0.02
Crystal shape, color	Plate, dark yellow
T/K	100(2)
Radiation	MoKα ($\lambda = 0.71073$ Å)
Crystal system, space group	Monoclinic, $P2_1/n$
a/Å	15.268(6)
b/Å	21.931(8)
c/Å	21.810(8)
β/°	107.68(3)
V/Å^3	6,958(5)
Z	8
Calc. density/g cm^{-3}	1.185
F(000)	2,688
μ/mm^{-1}	0.32
Absorption correction	Empirical (multi-scan)
T_{min}, T_{max}	0.984, 1.000
Measured reflections	41,364
R_{int}	0.187
h, k, l	−18 → 18, −26 → 24, −26 → 23
Θ range	2.33–25.50
Independent reflections	12,957
Observed reflections	5,826
Data/parameters/restraints	1,2957/912/451
$R1(F_{obs})$	0.096
$wR2(F^2)$	0.203
GooF = S	1.09
Shift/error$_{max}$	0.000
$\Delta\rho_{max}/\Delta\rho_{min}$/e Å^{-3}	0.81/−0.72

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \sqrt{\sum \left[w(F_o^2 - F_c^2)^2\right] / \sum \left[w(F_o^2)^2\right]}$; Detailed information on the weighting scheme (w) is given in the crystallographic information file (CIF)

or $1.5U_{eq}(CH_3)$. Since the crystals of **1** were small and the quality of the diffraction pattern was low, the presented structure should be treated only as a model. The asymmetric unit of **1** contains two crystallographically independent complex molecules denoted as **1*A*** and **1*B***. The bp ligand in molecule **1*B*** is disordered and refined in two sites with s.o.f. = 0.830(5) and 0.170(5). In the refinement procedure of the disordered region, some geometrical restrains and constraints/restrains on the fractional coordinates and anisotropic displacement parameters (SAME, FLAT, EXYZ, EADP, SIMU instructions in SHELXL-2013) were applied, for details see the CIF file. The structure plots were prepared with DIAMOND [31]. The crystal data and refinement parameters are presented in Table 1. CCDC 946551 contains the supplementary crystallographic data for complex **1**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental setup for catalytic oxidation

Liquid phase catalytic oxidations of benzyl alcohol were carried out under air (atmospheric pressure) in a 25-mL round-bottom flask equipped with a magnetic stirrer. In a typical experiment, H_2O_2 was added to a flask containing the catalyst (1.6×10^{-3} mmol) and benzyl alcohol (1 mmol) in a 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 TLC, ^{1}H NMR and GC–Mass analyses.

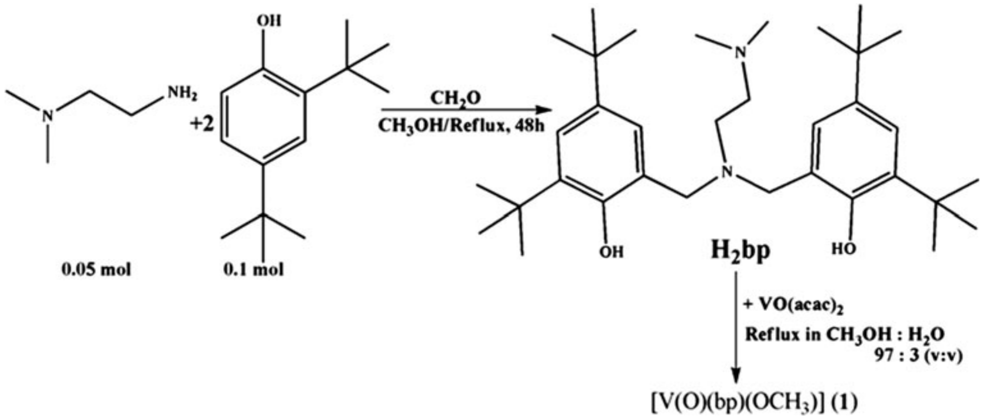
Results and discussion

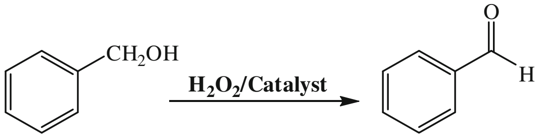
Synthesis of ligand and V-complex

The reaction of *N*,*N*′-dimethylethane-1,2-diamine with 2,4-di-*tert*-butylphenol in the presence of formaldehyde (37 %) gave the desired tetradentate bis(phenolate) ligand, H_2bp, in excellent yield and purity (Scheme 1). Complex $[V(O)(bp)(OCH_3)]$ (**1**) was synthesized by the reaction of $H_2bp/VO(acac)_2$ in 1:1 molar ratio in methanol (Scheme 1). The formation of the ligand, H_2bp, has been confirmed by NMR and infrared spectroscopy. In the IR spectrum of the ligand, the bands at 3,188, 1,592 and 1,256 cm^{-1} are due to O–H, C=C and C–O$_{phenolic}$ stretches, respectively [32, 33]. The elemental analysis is in good accordance with the proposed structure. The complex **1** is slowly formed by the reaction of H_2bp with $VO(acac)_2$ in methanol as solvent. During the reaction, vanadium(IV) is oxidized to vanadium(V) by air. On complexation, the shift of C–O$_{phenolic}$ and C–N bands shows coordination of H_2bp as a tetradentate dianionic ligand. In the IR spectrum of complex **1**, the band at 958 cm^{-1} is assigned to ν(V=O) [34, 35], and this band is observed as a new peak for the complex that is not present in the spectrum of the free ligand.

The electronic spectra of complex **1** (brown) and H_2bp (colorless) in MeOH solutions are shown in Fig. 1. The bis(phenolate) ligand displays two absorption bands at 216 and 278 nm. Based on their extinction coefficients, they are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The electronic spectrum of the complex is very similar to

Scheme 1 The synthesis pathway of ligand H_2bp and complex **1**





Scheme 2 Catalytic oxidation of benzyl alcohol in the presence of V(V) complex

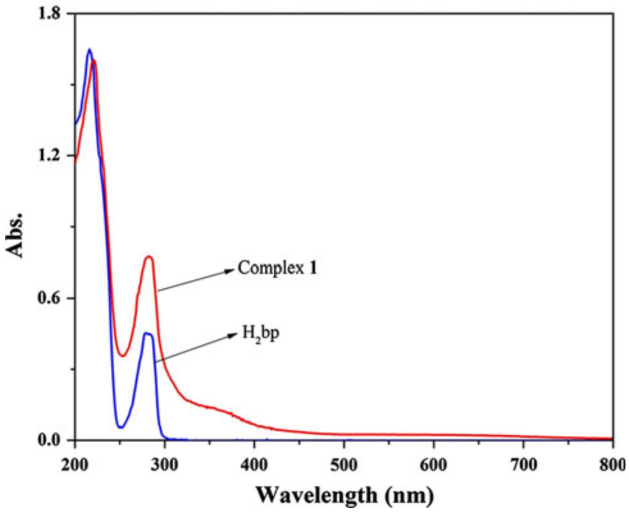


Fig. 1 The electronic spectra of H_2bp (*blue*), complex **1** (*red*) in the methanol. (Color figure online)

that of the free ligand, but is red shift in both absorption peaks. These peaks are attributed to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, and the shifts indicate the coordination of the ligand to the V(V) ion. For the complex, the broad band at higher energy of ~360 nm is due to the ligand to metal charge transfer (LMCT) transition.

X-ray structure of complex 1

The molecular structure of the complex [V(O)(bp)(OCH_3)] (**1**) was determined by X-ray diffraction analysis. The selected bond lengths and angles are tabulated in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) in complex **1**

Bond	Å	Angle	°
V1*A*–O3*A*	1.585(4)	O1*M*–V1*A*–O1*A*	97.46(17)
V1*A*–O1 *M*	1.767(4)	O2*A*–V1*A*–O1*A*	159.23(16)
V1*A*–O2*A*	1.886(4)	O3*A*–V1*A*–N1*A*	94.23(18)
V1*A*–O1*A*	1.895(4)	O1 *M*–V1*A*–N1*A*	160.27(19)
V1*A*–N1*A*	2.242(5)	O2*A*–V1*A*–N1*A*	79.04(16)
V1*A*–N2*A*	2.396(5)	O1*A*–V1*A*–N1*A*	83.09(16)
Angle		O3*A*–V1*A*–N2*A*	170.72(19)
O3*A*–V1*A*–O1*M*	105.3(2)	O1 *M*–V1*A*–N2*A*	83.97(18)
O3*A*–V1*A*–O2*A*	95.9(2)	O2*A*–V1*A*–N2*A*	82.39(17)
O1 *M*–V1*A*–O2*A*	95.84(18)	O1*A*–V1*A*–N2*A*	83.21(17)
O3*A*–V1*A*–O1*A*	95.9(2)	N1*A*–V1*A*–N2*A*	76.49(16)

The asymmetric unit of **1** contains two crystallographically independent complex molecules denoted as **1*A*** and **1*B*** (Fig. 2, Fig. S1). The bp ligand in molecule **1*B*** is disordered and refined in two sites: **1*B*** with s.o.f. = 0.830(5) and **1*C*** with s.o.f. = 0.170(5). The two independent molecules **1*A*** and **1*B*** are very similar (Fig. S1), and in the following description, only molecule **1*A*** will be discussed. In particular, the conformation of the organic ligand in the high-occupied position of **1*B*** is almost identical with that of **1*A***, while the other position of **1*B*** is slightly different in the orientation of three N1-bonded methylene groups.

X-ray analysis reveals that the complex **1** is a neutral mononuclear complex of oxovanadium(V). The coordination environment around the vanadium centers is best described as a distorted octahedral [VO_4N_2] with nitrogen atoms from the –NMe_2 moiety, tertiary nitrogen, two oxygen atoms provided by the bis(phenolate) ligand and two oxygen atoms from methoxy and oxido ligands. In complex **1**, two phenolate donor atoms provided by the bis(phenolate) ligand are located in a *trans* mode toward each other. The tertiary nitrogen and two phenolate oxygen atoms together with oxygen atom of methanol form the basal plane (with r.m.s. deviation of fitted atoms = 0.060 Å). Relative to this

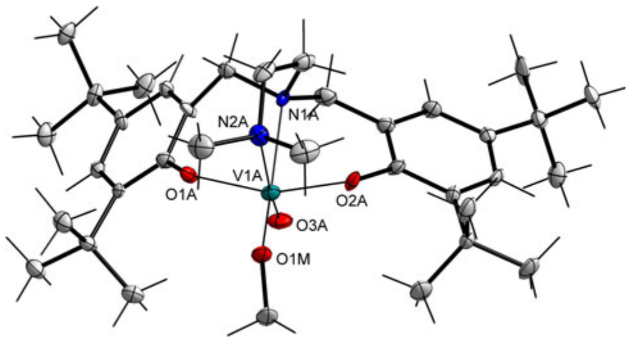


Fig. 2 The molecular structure of one of two crystallographically independent complex molecules (**1*A***) present in **1**. Displacement ellipsoids are drawn at the 40 % probability level

plane, the vanadium atom is displaced toward the apical oxygen atom O3 by 0.27 Å. The terminal V=O-type oxygen atom O3*A* occupies an axial position at a distance of 1.585(4) Å. The remaining axial position in the complex is occupied by the nitrogen of the *N,N′*-dimethyl moiety with the V–N_2 bond length of 2.396(5) Å. This bond is longer than the others, which can be attributed to the *trans* influence of the oxido group. The V–O and V–N bond lengths are similar with other vanadium complexes with bis(phenolate) ligands reported in CSD databases [36].

The intermolecular interactions in the crystal of **1** are provided by weak C–H···O and C–H···π contacts, in which the methylene groups from molecule **1*A*** and O3 atoms and phenyl rings from **1*B*** are involved (Table S1, Fig. S2).

Catalytic activity studies

Oxidation of benzyl alcohol

The catalytic activity of the complex **1** was tested in the oxidation of alcohols. The catalytic oxidation of benzyl alcohol (scheme 2) as a representative substrate with hydrogen peroxide was studied in the presence of complex **1**. Aqueous hydrogen peroxide (30 %) was selected as oxidant by considering its high selectivity, atom economy and environmentally benign properties. The results of control experiments revealed that the presence of catalyst and oxidant (H_2O_2) is essential for the oxidation. To achieve the maximum oxidation of alcohols, the effective parameters for suitable reaction conditions such as the oxidant concentration (moles of oxidant per moles of substrate), solvent and temperature of the reaction were investigated. The results of these studies are summarized in Table 3. In all these reactions, benzyl alcohol gave the benzaldehyde with 100 % selectivity by catalyst and there was no other product. The effect of oxidant concentration on the oxidation of benzyl alcohol by complex **1** is illustrated in Fig. 3. Different oxidant/substrate molar ratios (1:1, 2:1, 3:1 and 4:1) were considered, while the ratio of benzyl alcohol (1.0 mmol) to catalyst (1.6 μmol, 0.001 g) in 3 mL of acetonitrile was constant. The conversion of benzyl alcohol increased with increasing the amount of hydrogen peroxide in the reaction mixture. When H_2O_2/substrate mole ratio was 3:1, the maximum conversion of 59 % was obtained at 60 ± 1 °C.

In order to get the best reaction temperature, oxidation of alcohols was studied at 25 (room temperature), 40, 60 and 70 °C and the results are shown in Fig. 4. At room temperature, the oxidation of benzyl alcohol was low. Increasing the reaction temperature from 25 to 70 °C increased the conversion of benzyl alcohol, and 62 % conversion was obtained at 70 °C. The influence of the solvent nature in the catalytic oxidation of benzyl alcohol was investigated (Table 3, entries 7–14). Methanol, acetone, dichloromethane, chloroform, toluene, DMSO, THF and acetonitrile were used as solvents. Of the various

Table 3 Comparison of the catalytic activities of catalyst **1** in the oxidation of benzyl alcohol with hydrogen peroxide in different conditions

Entry	Catalyst	H_2O_2 (mmol)	Solvent	Temp. (°C)	Yield^A	Selectivity (%)	TON	TOF (h^{-1})
1	**1**	1	CH_3CN	60	30	100	188	47
2	**1**	2	CH_3CN	60	57	100	356	89
3	**1**	3	CH_3CN	60	59	100	368	92
4	**1**	4	CH_3CN	60	55	100	344	86
5	**1**	3	CH_3CN	25	13	100	81	20
6	**1**	3	CH_3CN	40	31	100	194	48
7	**1**	3	CH_3CN	70	62	100	388	97
8	**1**	3	$(CH_3)_2CO$	70	49	100	306	77
9	**1**	3	Toluene	70	51	100	816	204
10	**1**	3	$CHCl_3$	70	25	100	156	39
11	**1**	3	CH_2Cl_2	70	14	100	88	22
12	**1**	3	THF	70	29	100	181	45
13	**1**	3	CH_3OH	70	45	100	281	70
14	**1**	3	DMSO	70	2	100	12	3

Reaction conditions: catalyst, 1.6 μmol; benzyl alcohol, 1 mmol; solvent, 3 mL; time, 4 h

[A] Yields are based on the starting benzyl alcohol

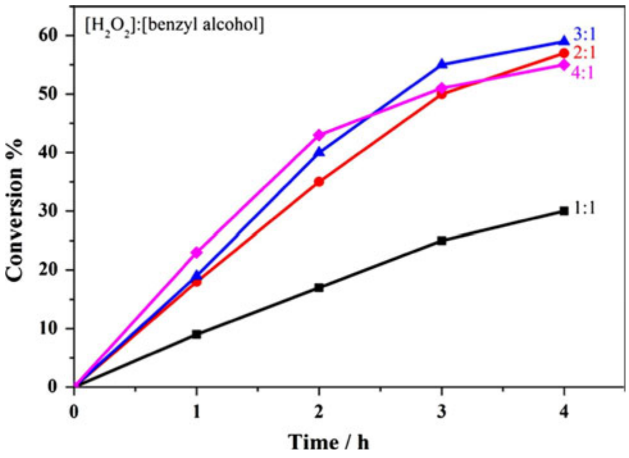


Fig. 3 Effect of H_2O_2 concentration on the oxidation of benzyl alcohol by **1**. Reaction conditions: catalyst, complex **1**, 1.6 μmol (0.001 g); CH_3CN, 3 mL; benzyl alcohol, 1 mmol; temperature, 60 ± 2 °C

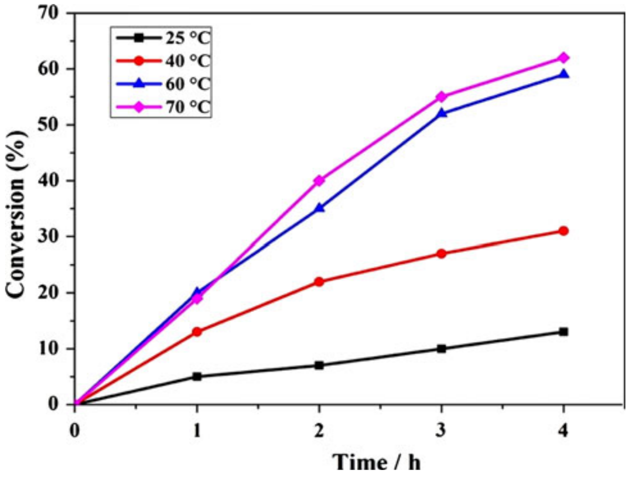


Fig. 4 Effect of the reaction temperature on the oxidation of benzyl alcohol by **1**. Reaction conditions: catalyst, complex **1**, 1.6 μmol (0.001 g); CH_3CN, 3 mL; benzyl alcohol, 1 mmol; H_2O_2, 3 mmol

solvents examined, acetonitrile was found to be the most suitable solvent for the reaction and this is in agreement with the known activities of vanadium complexes in oxidation reactions [8]. It was observed that the catalytic activity of the catalyst decreased with respect to acetonitrile (dielectric constants $\varepsilon = 37.5$ [37], donor number $D = 14.1$ [38]) >toluene ($\varepsilon = 2.38$, $D = 0$) >acetone ($\varepsilon = 20.7$, $D = 17$) >methanol ($\varepsilon = 32.7$, $D = 19$) >THF ($\varepsilon = 7.3$, $D = 20$) >chloroform ($\varepsilon = 4.9$, $D = 0$) >dichloromethane ($\varepsilon = 8.93$, $D = 0$) > DMSO ($\varepsilon = 46.7$, $D = 29.8$). Overall, the reactivity of catalyst in other solvents was very much lower than acetonitrile. This may be due to the high relative dielectric constant and low coordination ability of this solvent. Solvents with high donor ability decrease the reactivity of the catalyst, and the lowest conversion in DMSO is due to the highest coordinating ability of this solvent. High reactivity in toluene is due to high solubility of the catalyst in this solvent.

Conclusion

A new vanadium(V) complex of a tetradentate bis(phenolate) ligand was synthesized and characterized by spectroscopic and single-crystal X-ray analyses. The catalytic ability of this complex was investigated by using the environmentally benign and clean oxidant H_2O_2 for oxidation of benzyl alcohol. The effects of various parameters including the molar ratio of oxidant to substrate, the temperature and the solvent have been studied, and the optimized conditions were obtained. This complex is a selective catalyst for oxidation of benzyl alcohol to benzaldehyde.

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