



Synthesis, characterization, EPR spectroscopy and catalytic activity of a new oxidovanadium(IV) complex with N₂O₂-donor ligand



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ABSTRACT

A new oxidovanadium(IV) complex, 2[VOL(OH₂)] CH₃OH (**1**), was synthesized from the reaction of VO(acac)₂ with a symmetric N,O-donor Schiff base ligand (H₂L), in which H₂L is 6,6'-((1E,1'E)-((2-hydroxypropane-1,3-diyl)bis(azanilylidene))bis(methanylylidene))bis(2-methoxyphenol). The compounds were characterized by elemental analysis and spectroscopic methods. The molecular structure of complex was determined by single-crystal X-ray analysis which indicated that the crystal packing of complex contains two independent mononuclear vanadium complexes connected together by several strong hydrogen bonding interactions. The EPR spectrum of powdered complex **1** at liquid helium temperature showed two intensive octets which proved to be associated with V⁴⁺ ions with 3d¹ electronic configuration. From EPR spectrum the values of the parameters: $g_{\parallel} = 1.9454 \pm 0.0004$, $g_{\perp} = 1.9491 \pm 0.0004$, $A_{\parallel} = 0.0084 \pm 0.0008 \text{ cm}^{-1}$ and $A_{\perp} = 0.0033 \pm 0.0006 \text{ cm}^{-1}$ were calculated for this complex. Complex **1** was employed as catalyst for oxidation of cyclooctene in the presence of H₂O₂ as oxidant. In order to obtain the suitable condition of catalytic oxidation, the effect of various parameters including the amount of the catalyst, temperature and solvent was studied. The results of catalytic studies showed that complex **1** can provide an effective and selective catalytic system for epoxidation of cyclooctene.

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1. Introduction

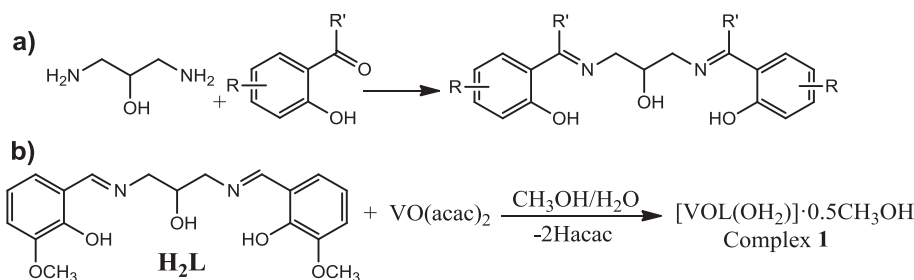
The coordination chemistry of vanadium has received increasing interest in the past years which can be attributed to its interesting biological and catalytic properties [1]. The importance of vanadium as bio-essential element is fine documented [2] since it is found in remarkably high concentration in vanadate-dependent haloperoxidases [3], in certain mushrooms, polychaete worms and marine environments (in a number of species of marine algae and ascidians) [4]. Vanadium plays a significant role in the reduction of N₂ to NH₃ [5], and its complexes show insulin-mimetic behavior [6]. Oxidovanadium complexes are found to be attractive and effective (pre)catalysts for oxidation reactions (like sulfoxidation [7], epoxidation of olefins [8], oxidation of alcohols [9], etc.) and oxidative coupling of phenolic compounds [10]. Although

vanadium is seen in a variety of oxidation states, the +4 and +5 oxidation states are the most stable ones under aerobic conditions [11]. The most commonly coordination compounds of vanadium(IV) exist as vanadyl derivatives, VO²⁺, which binds four other ligands strongly and one weakly (the one *trans* to the vanadyl center) [12]. Vanadium(IV) complexes with d¹ electronic configuration ($S = 1/2$) are interesting candidates to be studied by EPR spectroscopy [13].

The ligands obtained from the reaction of 1,3-diamino-2-propanol with *ortho*-hydroxybenzaldehyde derivatives (Scheme 1) are a class of interesting and versatile N- and O-donor ligands for construction of transition metal complexes [14]. Due to the presence of both alcoholic and phenolic oxygen donor atoms, these ligands can act as chelating and bridging ligands to form multinuclear complexes [15]. Some interesting multinuclear transition metal complexes and mixed metal complexes have been synthesized by this kind of ligands [16]. The central alcoholic functionality of such ligands plays a significant role in formation of multinuclear

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Scheme 1. (a) General formula of ligands obtained from the reaction of 1,3-diamino-2-propanol with *ortho*-hydroxybenzaldehyde and (b) structure of H₂L and synthesis of complex 1.

complexes and also in stabilizing the crystal packing of obtained compounds. This group can be coordinated to the metal cores [17] or can be involved in intermolecular or intramolecular hydrogen bonding interactions [18]. So, such ligands can be interesting candidates for structural studies.

Considering the applications of vanadium complexes in various fields of science and also the interesting structural properties of the ligands obtained from the reaction of 1,3-diamino-2-propanol with *ortho*-hydroxybenzaldehyde derivatives, in the present paper we report synthesis, spectroscopic studies and crystal structure of a new oxidovanadium(IV) complex by such ligands. Moreover, by considering our studies on catalytic properties of transition metal complexes [19] and also the fact that the epoxides are one of the important and relatively expensive intermediates in organic syntheses [20], the catalytic behavior of complex was studied in the oxidation of cyclooctene by H₂O₂ as a green oxidant.

2. Experimental

2.1. Materials and instrumentations

All starting materials were purchased from Acros and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. IR spectra were recorded as KBr pellets with a Nicolet iS10 FT-IR spectrophotometer in the range of 400–4000 cm⁻¹. The resolution of FT-IR instrument and the scan's numbers are 4 and 10, respectively. UV–Vis spectra of solutions were recorded on a thermo spectronic, Helios Alpha spectrophotometer. ¹H and ¹³C NMR spectra of ligand in CDCl₃ solution were measured on a Bruker 250 and 62.9 MHz spectrometer, respectively, and chemical shifts are indicated in ppm relative to tetramethylsilane. The atomic absorption analysis was carried out using Varian Spectra AA-220 equipment. The EPR spectrum was acquired by using a commercial Bruker EMX spectrometer operating at fixed 9.25 GHz frequency (X-band) with Oxford Instruments helium-flow cryostat. The reaction products of oxidation were determined and analyzed using an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm).

2.2. Synthesis of 6,6'-((1E,1'E)-((2-hydroxypropane-1,3-diyl)bis(azanilylidene))bis(methanylylidene))bis(2-methoxyphenol) (H₂L)

A methanol (10 mL) solution of 1,3-diamino-2-propanol (0.45 g, 5.00 mmol) was drop-wise added to a methanol solution (10 mL) of 2-Hydroxy-3-methoxybenzaldehyde (1.52 g, 10.00 mmol) and the mixture was refluxed for 4 h. Then the solution was evaporated on a steam bath to 5 mL and cooled to room temperature. Resulting white precipitate was separated and filtered off, washed with 5 mL of cooled methanol and recrystallized. Yield: 91% (1.63 g). *Anal.*

Calc. for C₁₉H₂₂N₂O₅ (MW = 358.39): C, 63.67; H, 6.19; N, 7.82. Found: C, 63.73; H, 6.22; N, 7.78. FT-IR (KBr, cm⁻¹): 3325 (m, br), 3016 (w), 2905 (w), 2839 (w), 1636 (vs, C=N), 1474 (s), 1256 (vs), 1079 (m), 734 (s), 519 (m), 459 (w). ¹H NMR (250.13 MHz, CDCl₃, TMS): δ = 13.2 (s, 2H, PhO–H), 8.24 (s, 2H, CH=N), 6.81 (d, 2H, J = 8.00 Hz), 6.76 (m, 2H), 6.68 (m, 2H), 5.19 (s, 1H, CH–OH), 4.16 (m, 1H), 3.80 (s, 6H, –OCH₃), 3.74 (d, 2H, J = 4.25 Hz), 3.66 (d, 2H, J = 5.75 Hz). ¹³C NMR (62.90 MHz, CDCl₃, TMS): δ = 55.93, 61.85, 69.97, 113.98, 117.60, 118.10, 123.18, 148.52, 152.95 and 167.20 ppm. UV–Vis (in CH₃OH, c = 5 × 10⁻⁵ mol dm⁻³, λ_{max} [nm] with ε [M⁻¹ cm⁻¹]): 222 (17 700), 265 (8900), 298 (5300), 339^{sh} (1 800), 423 nm (1 900).

2.3. Synthesis of complex 2[VOL(OH₂)] CH₃OH (1)

Complex 1 was synthesized by the reaction of ligand, H₂L (0.358 g, 1.00 mmol) and VO(acac)₂ (0.256 g, 1.00 mmol) using the

Table 1
Crystallographic data of complex 1.

	1
Net formula	C ₃₉ H ₄₈ N ₄ O ₁₅ V ₂
M _r /g mol ⁻¹	914.70
Crystal size/mm	0.17 × 0.11 × 0.04
T/K	173 (2)
Radiation	MoKα
Diffractionmeter	'KappaCCD'
Crystal system	Monoclinic
Space group	P2 ₁ /n
a/Å	13.4424 (3)
b/Å	12.6233 (2)
c/Å	23.8288 (4)
α/°	90
β/°	101.6360 (9)
γ/°	90
V/Å ³	3960.35 (13)
Z	4
Calc. density/g cm ⁻³	1.534 (1)
μ/mm ⁻¹	0.550
Refls. measured	22243
R _{int}	0.057
Mean σ(I)/I	0.0578
θ range	3.20–25.35
Observed refls.	4930
x, y (weighting scheme)	0.0766, 5.0347
Hydrogen refinement	mixed
Refls in refinement	7153
Parameters	561
Restraints	4
R (F _{obs})	0.058
R _w (F ²)	0.164
S	1.03
Shift/error _{max}	0.001
Max electron density/e Å ⁻³	0.97
Min electron density/e Å ⁻³	–0.77

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