

# A novel oxido-vanadium(V) Schiff base complex: synthesis, spectral characterization, crystal structure, electrochemical evaluation, and biological activity

S. Yousef Ebrahimipour<sup>1</sup> · Maryam Mohamadi<sup>2</sup> ·  
Iran Sheikhshoaei<sup>1</sup> · Sebastián Suárez<sup>3</sup> ·  
Ricardo Baggio<sup>4</sup> · Moj Khaleghi<sup>5</sup>

Received: 10 November 2014 / Accepted: 2 April 2015  
© Springer Science+Business Media Dordrecht 2015

**Abstract** A new oxido-vanadium(V) complex,  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$  ( $\text{L} = [(3\text{-methoxy-2oxidobenzylidene)benzohydrazidato}]$ ,  $\text{PrOH} = \text{propanol}$ ,  $\text{OPr} = \text{propanolato}$ ) has been synthesized and characterized by means of elemental analysis, Fourier transform infrared (FTIR), proton nuclear magnetic resonance ( $^1\text{H NMR}$ ), ultraviolet-visible (UV-Vis) spectroscopy, voltammetry and molar conductivity measurement. The structure of the complex has also determined using single crystal X-ray diffraction. The geometric structure around the V(V) ion has been found to be octahedral in which the positions around the central ion are occupied by ONO ligand donors, oxido groups, and oxygen atoms of coordinated propanol and propoxide group. Electrochemical behavior of this complex is also discussed in more details. In vitro antimicrobial effect of the title complex has investigated exhibiting significant activities against some Gram-positive (*Staphylococcus aureus*, *Micrococcus luteus*, *Bacillus cereus*, *Eterococcus faecalis*) and Gram-negative bacteria (*Pseudomonas aeruginosa*, *Escherichia coli*, *Klebsiella* sp, *Pseudomonas* sp) and fungus strain (*Candida albicans*).

---

✉ S. Yousef Ebrahimipour  
Ebrahimipour@ymail.com; Ebrahimipour@uk.ac.ir

<sup>1</sup> Department of Chemistry, Faculty of Science, Shahid Bahonar University of Kerman, 76169-14111 Kerman, Iran

<sup>2</sup> Department of Chemistry, Payame Noor University (PNU), 19395-4697, Tehran, Iran

<sup>3</sup> Departamento de Química Inorgánica, Analítica y Química, Física/INQUIMAE-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina

<sup>4</sup> Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

<sup>5</sup> Department of Biology, Faculty of Science, Shahid Bahonar University of Kerman, Kerman, Iran

**Keywords** Schiff base ligand · V(V) complex · Electrochemical behavior · Antimicrobial activity · Biofilm formation

## Introduction

In coordination chemistry, Schiff bases are versatile ligands due to their ease of synthesis, multi-denticity and their combining of donor atoms [1]. Also, Schiff base complexes possess high stability in different oxidation states, resulting in wide application of these compounds [2].

The interest in coordination chemistry of vanadium has increased in the last decades because of its catalytic and medicinal importance. Different enzymes, including nitrogenases and haloperoxidases [3–5], phosphate-metabolizing enzymes [6] and phosphomutases [7], are in close relationship to vanadium. Vanadium compounds participate in a variety of non-enzymatic, industrially important reactions like oxidation of sulfides and thioethers [8, 9], epoxidation of allylic alcohols, phenols and catechol [10–12], and hydroxylation of alkenes [13]. One of the most important impetuses to the coordination chemistry of vanadium in the context of medical applications has arisen from the ability of vanadium complexes to promote insulin mimetic activity in the pathophysiological state of diabetes mellitus in humans [14–16]. Also, some oxido-vanadium complexes have been found to exhibit important anticancer properties [17, 18].

The wide spectrum of physiological effects of vanadium is concentrated on the biologically relevant oxidation states (IV and V) and is associated with the interactions in which it is involved with physiological ligands [19]. The rich chemistry of vanadium(V) is probably due to its ability to exist in three different forms: viz. mononuclear  $\text{VO}^{3+}$  and  $\text{VO}^{2+}$  motifs, and dinuclear  $\text{V}_2\text{O}_3^{4+}$  motif.

Herein, a tridentate ONO hydrazine Schiff base ligand [HL] and its oxido-vanadium(V) complex  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$  have been synthesized and fully characterized by means of physico-chemical and spectroscopic methods. The electrochemical behavior of the oxido-vanadium(V) complex has also discussed. Furthermore, the antimicrobial activities of [HL] and  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$  have been investigated against microorganisms.

## Experimental

### Materials and instrumentation

All chemicals and solvents used were of analytical reagent grade and were used as received. Micro analyses for C, H and N were determined on a Thermo Finnigan Flash Elemental Analyzer 1112EA. Melting points were measured on an Electrothermal-9100 apparatus and were uncorrected. FTIR spectra were recorded on a Shimadzu FTIR-8400S with KBr discs in the range of 400–4000  $\text{cm}^{-1}$ . Molar conductance measurements were made by means of a Metrohm 712 Conductometer in EtOH.  $^1\text{H-NMR}$  spectra were recorded at 25 °C on Bruker AVANCE III 500 and

100 MHz spectrometers using dimethyl sulfoxide (DMSO)- $d_6$  or  $CDCl_3$  as solvents and tetramethylsilane (TMS) as the internal standard. Electronic spectra in ethanolic solutions of the compounds were recorded with a Cary 50 UV–Vis spectrophotometer.

### Synthesis of [(2-hydroxy-3-methoxybenzylidene)benzohydrazide] [HL]

An ethanolic solution (5 ml) of benzohydrazide (0.14 g, 1 mmol) was added drop wise to 5 ml of ethanolic solution of 3-methoxy-2 hydroxy benzaldehyde (0.15 g, 1 mmol) with constant stirring. After 15 min, the resulted precipitate was filtered, washed with cold ethanol and dried in vacuum over silica gel.

Yield: 0.224 g, 83 %. m.p.: 116 °C. Anal. Calc. for  $C_{15}H_{14}N_2O_3$  (270.28 g mol<sup>-1</sup>): C, 66.66; H, 5.22; N, 10.36. Found: C, 66.18; H, 5.30; N, 10.53 %. FT-IR (KBr), cm<sup>-1</sup>:  $\nu(NH)$  3571,  $\nu(OH)$  3367,  $\nu(CH_{ar})$  2839–3062,  $\nu(C=O)$  1647,  $\nu(C=N)$  1610,  $\nu(C=C_{ring})$  1470,  $\nu(C-O)$  1296,  $\nu(N-N)$  1149,  $\delta_{oopb}(OH)$  733. <sup>1</sup>H-NMR (500 MHz, DMSO- $d_6$ , 25 °C, ppm):  $\delta$  = 12.10 (*s*, 1H; NH), 11.03 (*s*, 1H; OH), 8.67 (*s*, 1H; CH=N), 6.85–7.96 (*m*, 8H, rings), 3.82 (*s*, 3H, OCH<sub>3</sub>). UV/Vis (EtOH)  $\lambda_{max}$ , nm (log $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>): 225 (4.53), 305 (4.60), 343 (4.07).

### Synthesis of [(3-methoxy-2oxidobenzylidene)benzohydrazidato] propanol propanolato oxido-vanadium(V) [VO(L)(PrOH)(OPr)] (1)

VO(acac)<sub>2</sub> (0.1 mmol, 0.03 g) and HL (0.1 mmol, 0.03 g) were added to 5 ml of propanol and the mixture was refluxed at 100 °C for 30 min. After 3 days, suitable single crystals appeared due to slow evaporation of the solvent. The resultant product was isolated, and dried in a vacuum desiccator over silica gel.

Yield: 61 %. m.p.: 201 °C. Molar conductivity (1.0 × 10<sup>-3</sup> M, EtOH): 7  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calc. for  $C_{21}H_{27}N_2O_6V$  (454.39 g mol<sup>-1</sup>): C, 55.51; H, 5.99; N, 6.17. Found: C, 55.65; H, 5.89; N 6.09 %. FT-IR (KBr), cm<sup>-1</sup>:  $\nu(OH)$  3447,  $\nu(CH_{ar})$  2868–3060,  $\nu(C=N)$  1601,  $\nu(C=C_{ring})$  1452,  $\nu(C-O)$  1284,  $\nu(N-N)$  1173,  $\nu(V=O)$  972,  $\delta_{oopb}(OH)$  733,  $\nu(V-O)$  600,  $\nu(V-N)$  429. <sup>1</sup>H-NMR (100 MHz,  $CDCl_3$ , 25 °C, ppm):  $\delta$  = 8.9 (*s*, 1H; CH=N), 6.9–8.02 (*m*, 8H, rings), 3.82 (*s*, 3H, OCH<sub>3</sub>), 5.3 (*s*, 1H, OH), 0.8–2.4 (*m*, 14H, C<sup>16</sup>H<sub>2</sub>, C<sup>17</sup>H<sub>2</sub>, C<sup>18</sup>H<sub>3</sub>, C<sup>19</sup>H<sub>2</sub>, C<sup>20</sup>H<sub>2</sub>, C<sup>21</sup>H<sub>3</sub>). UV/Vis (EtOH),  $\lambda_{max}$ , nm (log( $\epsilon$ ), L mol<sup>-1</sup> cm<sup>-1</sup>): 271 (4.51), 319 (4.39), 340 (4.34), 422 (3.80).

### Crystal structure determination

Single-crystal X-ray diffraction data were collected at 294(2) K on an Oxford Diffraction CCD diffractometer using Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) with  $\omega$  scan technique. An empirical absorption correction was applied to the raw intensities [20].

The structures were solved by direct methods (SHELXS-97) [21] and refined with a full-matrix least-squares technique on F<sup>2</sup> using SHELXL-2014 [21]. On refinement, the large propanol/propoxy tails showed a pronounced vibration, with

large anisotropic displacement parameters leading to unrealistic C–C distances due to libration. Attempts to refine them as disordered moieties proved unsuccessful.

Hydrogen atoms were spotted in a difference map; those attached to carbon were further idealized, riding in coordinates and thermal factors on their host atoms; those attached to the oxygen of propoxy were refined with restrained O–H = 0.85(1) Å. Full details of crystallographic data and structure refinement parameters can be found in Table 1.

## Electrochemical measurements

Cyclic voltammetry measurements were performed using a Sama-500 electrochemical system (Isfahan, Iran) in conjunction with a personal computer for data storage and processing. A three-electrode system composed of an Ag/AgCl/3 M KCl reference electrode, a Pt wire as a counter electrode and a glassy carbon electrode as a working electrode were employed for the electrochemical studies.

**Table 1** Crystal, collection and refinement data for (I)

Crystal data	
Chemical formula	C <sub>21</sub> H <sub>27</sub> N <sub>2</sub> O <sub>6</sub> V
$M_r$	454.38
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
$a, b, c$ (Å)	10.8345 (3), 18.4298 (6), 22.7242 (6)
$\beta$ (°)	93.167 (2)
$V$ (Å <sup>3</sup> )	4530.6 (2)
$Z, Z'$	8, 2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.48
<i>Data collection</i>	
Diffractometer	Oxford Diffraction Gemini CCD S Ultra Diffractometer
Absorption correction	Multi-scan <i>CrysAlis PRO</i> [1], Oxford diffraction (2009)
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	30214, 10642, 5737
$R_{int}$	0.057
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.688
<i>Refinement</i>	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.063, 0.180, 0.98
No. of reflections	10,642
No. of parameters	555
No. of restraints	50
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.55, -0.47

## Microorganism strains and culture

In this study, we used five standard bacteria (*Pseudomonas aeruginosa* ATCC 27853; *Staphylococcus aureus* PTCC 1112; *Micrococcus luteus* PTCC 1110, *Bacillus cereus* PTCC 1015 and *Escherichia coli* PTCC 1330) that three of them were isolated from clinical samples (*Pseudomonas* sp; *Klebsiella* sp and *Eterococcus faecalis*) and one from yeast (*Candida albicans* PTCC 5027). Brain-heart infusion medium (BHI-Merck) was used for *E. faecalis*, whereas other bacteria were cultured on Mueller–Hinton medium (Merck). Also, yeast extract glucose chloramphenicol (YGC) medium (Merck) for the yeast strain was used as the test medium.

## Determination of antimicrobial activity

Antimicrobial assays were performed using the agar well diffusion method [22] for [HL] and [VO(L)(PrOH)(OPr)]. The agar media were inoculated with 100  $\mu$ l of the inoculums which were prepared using an overnight culture of each bacterium, and yeast strain (18–24 h) adjusted to a turbidity equivalent to a 0.5-McFarland standard [23]. Wells were cut and then 50  $\mu$ l of the synthesized compounds (50 mg/ml; DMSO was used as the solvent) was added. The plates were then incubated at 37 °C for 24–48 h. The antibacterial activity was assayed by measuring the diameter of the inhibition zone in millimeter (mm) formed around the well. DMSO, as solvent, was used as a negative control, whereas ciprofloxacin (standard antibiotic) and fluconazole (standard antifungal drug) were used as the positive controls. The experiments were performed in triplicate.

## Determination of minimum inhibitory and bactericidal concentration

Microtiter minimum inhibitory concentration (MIC) and minimal bactericidal concentration (MBC) tests were carried out according to standard techniques (NCCLS, 2008). Briefly, serial two-fold dilutions of each compound were performed in media broth. A suspension of each organism was added to wells at a concentration of  $5 \times 10^5$  CFU/ml, and the microtiter plates were incubated aerobically at 37 °C for 24 h. The MIC was defined as the lowest concentration of antibiotic in which there was no visible growth after overnight incubation. In the wells in which no visible growth was observed, 10  $\mu$ l of the compound was sub-cultured and the agar plate was incubated aerobically at 37 °C for the colony count. MBC was defined as the highest dilution showing a  $\geq 99.9$  % kill rate after 24 h of incubation. Serial dilutions ranging from 100 mg/ml to 0.39 mg/ml were prepared in the medium.

## Biofilm formation assessment

Those bacteria that have good adhesion to the surface are appropriate for biofilm production. For detection of the microbial adhesion to the surface in the presence of the vanadium complex, the microtitre plates were prepared as described previously

[24]. Briefly, a culture of the bacteria and yeast were grown overnight in the broth media. Then, the overnight cultures were diluted 1:100 into fresh medium for biofilm assays. 200  $\mu\text{l}$  of the diluted solution was added to a 96-well dish. After the growth phase, the medium was carefully removed with a pipette, the wells of the microtitre plates were then rinsed three times with 200  $\mu\text{l}$  of sterile PBS. After washing, wells were filled with 96 % ethanol for 15 min. The microtitre plates were dried in air and then, 200  $\mu\text{l}$  of 1 % crystal violet were added for 5 min. Then, the microtitre plates were washed with distilled water, and then dried. Finally, 200  $\mu\text{l}$  of 33 % glacial acetic acid were added to the wells and absorbance was measured at 540 nm with an ELISA reader.

Data for biofilm formation of all strains were compared with the data obtained for the negative control. *S. aureus* PTCC 1431 was used as positive control and microbial medium without microorganisms was used as the negative control.

## Results and discussion

A new oxido-vanadium(V) complex,  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$ , containing tridentate ONO hydrazone ligand HL was synthesized in propanol as the solvent. This complex was stable in air and soluble in most common solvents, except *n*-hexane, diethyl ether and water. The molar conductivity value of this complex was consistent with its non-electrolyte nature.

### Spectral characterization

Selected frequencies and vibrational assignments of [HL] and its oxido-vanadium(V) complex are listed in the experimental section. In the free ligand spectrum, the bands observed at 3367 and 734  $\text{cm}^{-1}$  are corresponded to stretching and out-of-plane vibrations of OH, respectively while in the spectrum of the complex, these bands appeared at 3447 and 733  $\text{cm}^{-1}$ , respectively. Disappearance of C=O and NH vibrations in the FTIR spectrum of  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$  indicates HL contributes an *enolic* form on complexation [25]. After coordination, the red shift of ( $-\text{C}=\text{N}$ ) from 1610  $\text{cm}^{-1}$  to 1601  $\text{cm}^{-1}$  shows that the azomethine nitrogen atom coordinates to the metal center [26–29]. A shift in C-O bond energy of the complex from 1296  $\text{cm}^{-1}$  in HL to a lower frequency (1284  $\text{cm}^{-1}$ ) indicates the ligand coordinates to the metal through the phenolic oxygen atom [30]. The strong band at 972  $\text{cm}^{-1}$  is ascribed to stretching vibration of the the vanadyl moiety [31, 32].

The electronic spectra of the compounds were recorded in EtOH. In the UV–Vis spectrum of HL, the band observed at 225 nm is ascribed to  $\pi \rightarrow \pi^*$  transitions of the aromatic rings. Two bands at 305 and 343 nm can be assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  of the azomethine and carbonyl moieties [33]. In the electronic spectrum of the V(V) complex, intra-ligand transitions show a red shift in comparison with free ligand, indicating enolization followed by deprotonation of the ligand. Moreover, the band at about 422 nm is assignable to  $\text{N}(p)/\text{O}(p) \rightarrow \text{V}(d)$  charge transfer (LMCT) [30].

## X-ray structure characterization

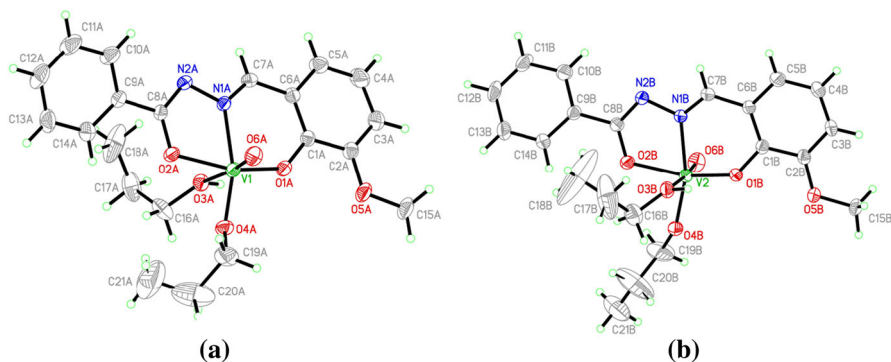
The crystal and molecular structure of [(3-methoxy-2-oxidobenzylidene)benzohydrazidato] propanol propanolato oxido-vanadium(V) was determined using single crystal X-ray diffraction. The asymmetric unit is composed of two independent moieties (**Ia** and **Ib**), which are identical in formulation [VO(L)(PrOH)(OPr)], but show inverted configurations. Figure 1a, b show ellipsoid plots of both independent moieties **Ia** and **Ib**. The coordination geometry around the vanadium(V) ion shows a distorted octahedral environment with an NO<sub>5</sub> chromophore. Some selected bond distances and angles are also listed in Table 2.

Searching in Cambridge structural database, (CSD, V5.34 [34]) we found two oxido-vanadium(V) alcohol-alkoxy complexes [35, 36] similar to the title synthesized complex, Scheme 1 depicts the structures of these complexes along with the complex synthesized here.

In spite of differences in the alcohol chain, the coordination sphere around vanadium(V) ion is extremely similar in the complexes **I**, **II** and **III**. A comparison of the selected bond distances and angles of the complexes are given in Table 2. Moreover, Fig. 2 presents an L.S. fit of the four molecules (**Ia**, **Ib**, **II** and **III**) showing an identical coordination sphere around the central ion.

In the title complex, V=O6 and V-O3 bonds which are trans to each other and occupy the apical sites, are the shortest and longest VO bonds, respectively. While the basal plane is determined by the donor atoms of the tridentate L<sup>2-</sup> (O1, O2, and N1) and the oxygen atom of the coordinated propoxy (O4). The basic descriptors of this geometry are (in **Ia/Ib** sequence): max. deviation from the basal L.S. plane, 0.020(2)/0.019(2) Å for N1 and 0.306(3)/0.323(4) Å for vanadium ion deviated towards O6.

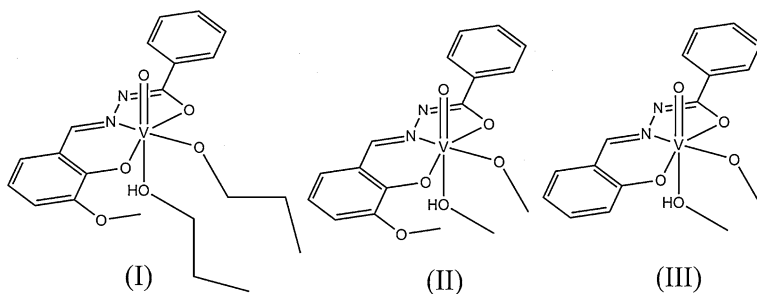
There are few intermolecular H-bonding interactions in the structure. All of them are presented in Table 3. Entries #1 and #2 described O-H...N type and entries #3 and #4 described C-H...O type, define chains running along “a” (Fig. 3a). These chains, in turn, are weakly linked to dual-chain slabs (Fig. 3a) by the remaining C-H...O bond (entry #5 in Table 3). As shown in Fig. 3b, these slabs are almost non-interacting.



**Fig. 1** Ellipsoid plots of both independent moieties **Ia** and **Ib**

**Table 2** Selected geometric parameters (Å, °) for **Ia**, **Ib**, **II** and **III**

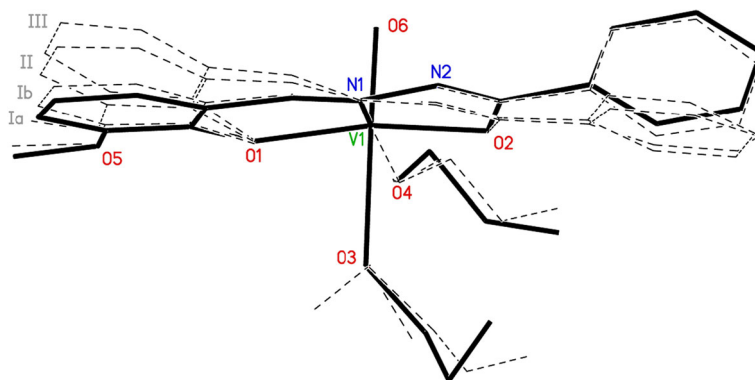
Bond/angle	Ia	Ib	II <sup>(30)</sup>	III <sup>(31)</sup>
V1—O6A	1.592 (2)	1.575 (3)	1.578 (4)	1.580 (3)
V1—O4A	1.761 (2)	1.768 (2)	1.769 (3)	1.761 (3)
V1—O1A	1.847 (2)	1.836 (2)	1.839 (3)	1.850 (3)
V1—O2A	1.946 (2)	1.957 (2)	1.966 (2)	1.954 (3)
V1—N1A	2.118 (3)	2.111 (3)	2.109 (4)	2.122 (3)
V1—O3A	2.338 (2)	2.396 (3)	2.346 (4)	2.367 (3)
O6A—V1—O4A	103.44 (12)	103.77 (14)	104.17 (19)	103.23 (14)
O6A—V1—O1A	100.86 (12)	101.58 (13)	100.97 (17)	100.22 (16)
O4A—V1—O1A	101.42 (10)	102.77 (10)	103.20 (15)	101.65 (12)
O6A—V1—O2A	95.45 (11)	96.56 (12)	96.48 (17)	97.38 (16)
O4A—V1—O2A	94.29 (10)	91.76 (10)	91.66 (16)	94.21 (12)
O1A—V1—O2A	153.95 (10)	153.19 (10)	153.41 (13)	152.84 (13)
O6A—V1—N1A	95.57 (11)	96.72 (13)	96.11 (18)	96.49 (13)
O4A—V1—N1A	158.75 (12)	156.42 (12)	156.54 (17)	158.23 (12)
O1A—V1—N1A	83.96 (9)	84.12 (10)	84.05 (14)	83.58 (13)
O2A—V1—N1A	74.29 (9)	74.22 (10)	74.22 (14)	73.97 (12)
O6A—V1—O3A	174.05 (10)	174.94 (11)	173.89 (18)	175.37 (14)
O4A—V1—O3A	82.12 (10)	80.60 (11)	80.39 (15)	80.75 (11)
O1A—V1—O3A	79.86 (10)	79.72 (10)	81.71 (13)	81.11 (11)
O2A—V1—O3A	81.89 (9)	80.62 (9)	79.17 (13)	79.84 (10)
N1A—V1—O3A	78.60 (9)	78.50 (10)	78.63 (15)	79.21 (11)

**Scheme 1** The structures of the synthesized complex **(I)** and two similar vanadium(V) alcohol-alkoxy complexes **(II and III)**

### Electrochemical activity

Cyclic voltammograms of  $10^{-3}$  M of the  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$  were recorded in DMSO containing 0.1 M tetra-*n*-butylammonium bromide (TBAB) as the supporting electrolyte by scanning the potential from  $-0.8$  to  $0.7$  V. Figure 4 reveals the



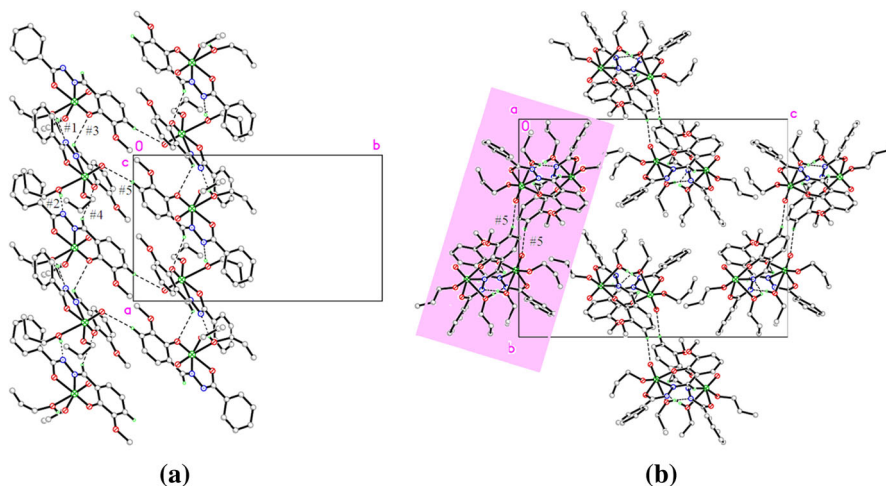


**Fig. 2** L.S. fit of the four molecules (**Ia**, **Ib**, **II** and **III**)

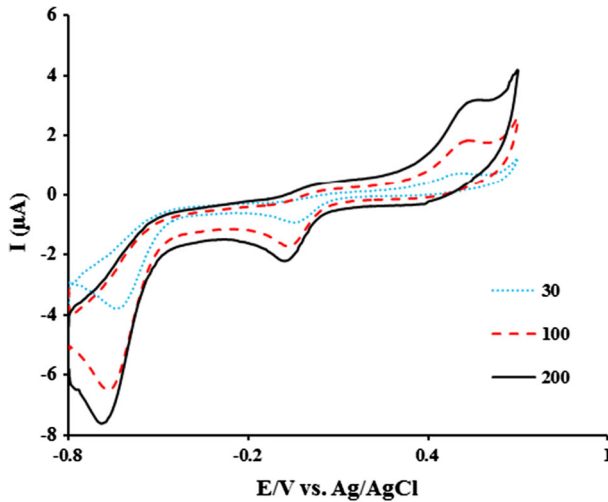
**Table 3** Hydrogen-bond geometry (Å, °) for (**I**)

Code	<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
#1	O3A—H3AO...N2B	0.84 (3)	1.99 (3)	2.824 (3)	170 (3)
#2	O3B—H3BO...N2A <sup>a</sup>	0.85 (4)	2.10 (4)	2.824 (3)	143 (4)
#3	C7A—H7AA...O1B <sup>b</sup>	0.93	2.55	3.059 (4)	115
#4	C7B—H7BA...O1A	0.93	2.57	3.181 (4)	124
#5	C3B—H3BA...O6A <sup>c</sup>	0.93	2.56	3.470 (4)	166

Symmetry codes: <sup>a</sup>  $x + 1, y, z$ ; <sup>b</sup>  $x - 1, y, z$ ; <sup>c</sup>  $-x + 1, -y + 2, -z + 1$



**Fig. 3** Representation of intermolecular H-bonding interactions



**Fig. 4** Cyclic voltammograms of the title V(V) complex at scan rates of 30, 100 and 200 mV/s

corresponding voltammograms obtained at scan rates of 30, 100 and 200 mV/s. An irreversible oxidation peak is observed at 500 mV corresponded to the ligand. Two separate peaks obtained in the reverse direction of the scan at -41 and -641 mV, are assigned to V(V)/V(IV) and V(IV)/V(III). Investigation of the effect of scan rate indicates that with increasing the scan rate from 30 to 200 mV, the currents of both cathodic peaks increase accompanied with negative shifts in their peak potentials, as expected for irreversible electrode processes [37].

### Antimicrobial activity

Antimicrobial activities of [VO(L)(PrOH)(OPr)] and free ligand [HL] against *Pseudomonas* sp; *Klebsiella* sp, *E. faecalis*, isolated from a clinical sample, *P. aeruginosa* ATCC 27853, *S. aureus* PTCC 1112, *M. luteus* PTCC 1110, *B. cereus* PTCC 1015, *E. coli* PTCC 1330, and *C. albicans* PTCC 5027, were assessed by evaluating the presence of inhibition zone (IZ), MIC and MBC values. The results obtained are reported in Table 4. As seen the oxido-vanadium(V) complex possessed a great potential of antibacterial activity, while [HL] didn't show any antimicrobial effects. Also, the antibacterial effect of the complex on Gram-positive bacteria was more than its effect on Gram-negative ones. In addition, the complex was found to be effective on *C. albicans* PTCC 5027. However, according to the obtained results, the bacteria isolated from clinical samples were resistant to [VO(L)(PrOH)(OPr)] and ciprofloxacin antibiotic.

The MIC and MBC values for the title complex were in the range of 100–0.39 mg/ml. The results of our study showed that the title oxido-vanadium(V) complex was effective on Gram-positive bacteria and yeast. It was observed that the complex not only inhibited the growth of the microorganisms, but also killed *C. albicans* PTCC

**Table 4** In vitro antimicrobial activity of the compounds, 50 mg/mL (IZ)

Microorganism	[VO(L)(PrOH)(OPr)] dia. of clear zone (mm)	[HL] dia. of clear zone (mm)	Ciprofloxacin dia. of clear zone (mm)	Fluconazol dia. of clear zone (mm)
<i>P. aeruginosa</i> ATCC 27853	0	0	22	0
<i>S. aureus</i> PTCC 1112	24	0	25	0
<i>M. luteus</i> PTCC 1110	20	0	31	0
<i>B. cereus</i> PTCC 1015	24	0	24	0
<i>E. coli</i> PTCC1330	0	0	27	0
<i>Pseudomonas</i> sp*	0	0	0	0
<i>Klebsiella</i> sp*	0	0	0	0
<i>E. faecalis</i> *	0	0	0	0
<i>C. albicans</i> PTCC 5027	22	0	0	35

\* Clinical bacteria

**Table 5** In vitro antimicrobial activity of [VO(L)(PrOH)(OPr)] (MIC and MBC, mg/mL)

Microorganism	[VO(L)(PrOH)(OPr)]	
	MIC	MBC
<i>S. aureus</i> PTCC 1112	–	1.563
<i>M. luteus</i> PTCC 1110	–	6.25
<i>B. cereus</i> PTCC 1015	–	6.25
<i>C. albicans</i> PTCC 5027	6.25	12.5

**Table 6** Comparison of anti-biofilm formation effect, MIC and MBC of [VO(L)(PrOH)(OPr)], (mg/ml)

Compound	Microorganisms							
	<i>S. aureus</i> PTCC 1112		<i>M. luteus</i> PTCC 1110		<i>B. cereus</i> PTCC 1015		<i>C. albicans</i> PTCC 5027	
	ABF*	MBC	ABF	MBC	ABF	MBC	ABF	MIC
[VO(L)(PrOH)(OPr)]	0.39	1.563	3.125	6.25	1.563	6.25	3.125	6.25

\* Anti-biofilm formation effect

5027. We found that the V(V) complex is a bactericidal compound, capable of killing bacteria at a minimum lethal concentration (Table 5).

According to the biofilm formation results, it was found that the title complex repressed biofilm formation in *S. aureus* PTCC 1112 (0.39 mg/mL), *M. luteus* PTCC 1110 (3.125 mg/mL), *B. cereus* PTCC 1015 (1.563 mg/mL) and *C. albicans* PTCC 5027 (3.125 mg/mL). Moreover, the formation of the biofilm was inhibited by the complex at a concentration lower than minimum lethal and inhibitory concentration (Table 6).

## Conclusion

A new oxido-vanadium(V) complex containing a tridentate ONO Schiff base ligand (2-hydroxy-3-methoxybenzylidene)benzoydrazide was synthesized and characterized using physico-chemical and spectroscopic methods of CHN, FTIR,  $^1\text{H}$ NMR, UV–Vis as well as voltammetry. The structure of the complex was also determined with single crystal X-ray diffraction. According to the obtained data, vanadium(V) ion was found to be coordinated by the di-negative and tridentate chelating agent through its oxygen and nitrogen moieties. Other positions around the central ion are occupied by oxygen atoms of oxido group, propanol and propoxide group. Antimicrobial assay showed that the  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$  complex possesses significant activities against both Gram-positive and Gram-negative bacteria as well as fungus species.

## Supplementary data

CCDC 1025915 contains the supplementary crystallographic data for  $[\text{VO}(\text{L})(\text{PrOH})(\text{OPr})]$ . A copy of this information may be obtained free of charge from: Director, CCDC, 12 Union Road, Cambridge, Cb2 1EZ, UK (fax: +44 1223 336 033); web page: <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>.

**Acknowledgments** The authors gratefully acknowledge the financial support provided for this work by the Shahid Bahonar University of Kerman.

## References

1. Z.K. Li, Y. Li, L. Lei, C.M. Che, X.G. Zhou, *Inorg. Chem. Commun.* **8**, 307 (2005)
2. A.H. Kianfar, M. Paliz, M. Roushani, M. Shamsipur, *Spectrochim. Acta A* **82**, 44 (2011)
3. J.N. Carter-Franklin, J.D. Parrish, R.A. Tschirret-Guth, R.D. Little, A. Butler, *J. Am. Chem. Soc.* **125**, 3688 (2003)
4. D. Rehder, G. Santoni, G.M. Licini, C. Schulzke, B. Meier, *Coord. Chem. Rev.* **237**, 53 (2003)
5. R. Eady, *Coord. Chem. Rev.* **237**, 23 (2003)
6. A. Sigel, H. Sigel, *Metal Ions in Biological Systems: Volume 31: Vanadium and its role for life*, CRC Press, 1995
7. M. Sutradhar, T. Roy Barman, S. Ghosh, M.G. Drew, *J. Mol. Struct.* **1020**, 148 (2012)
8. J. Sun, C. Zhu, Z. Dai, M. Yang, Y. Pan, H. Hu, *J. Org. Chem.* **69**, 8500 (2004)
9. S.A. Blum, R.G. Bergman, J.A. Ellman, *J. Org. Chem.* **68**, 150 (2003)
10. M. Buhl, R. Schurhammer, P. Imhof, *J. Am. Chem. Soc.* **126**, 3310 (2004)
11. P.M. Reis, J.A.L. Silva, J.J.R.F.D. Silva, A.J.L. Pombeiro, *J. Mol. Catal. A: Chem.* **224**, 189 (2004)
12. C.X. Yin, R.G. Finke, *J. Am. Chem. Soc.* **127**, 9003 (2005)
13. L. Gonzalez Cuervo, Y.N. Kozlov, G. Süß-Fink, G.B. Shul'pin, *J. Mol. Catal. A: Chem.* **218**, 171 (2004)
14. P. Zimmet, K.G. Alberti, J. Shaw, *Nature* **414**, 782 (2001)
15. H. Sakurai, Y. Kojima, Y. Yoshikawa, K. Kawabe, H. Yasui, *Coord. Chem. Rev.* **226**, 187 (2002)
16. S.I. Pillai, S.P. Subramanian, M. Kandaswamy, *Eur. J. Med. Chem.* **63**, 109 (2013)
17. O.Y. Abakumova, O. Podobed, N. Belayeva, A. Tochilkin, *Biochem. (Mosc.) Suppl. Ser. B Biomed. Chem.* **6**, 164 (2012)
18. L. Naso, M. Valcarcel, P. Villacé, M. Roura-Ferrer, C. Salado, E.G. Ferrer, P.A. Williams, *New J. Chem.* **38**, 2414 (2014)

19. D. Rehder, *Bioinorganic Vanadium Chemistry* (Wiley, New York, 2008)
20. Oxford Diffraction. CrysAlis PRO. Oxford Diffraction Ltd, E. Oxfordshire
21. G.M. Sheldrick, *Acta Crystallogr. A* **64**, 112 (2008)
22. S. Irshad, M. Mahmood, F. Perveen, *Res. J. Biol.* **2**, 1 (2012)
23. A. Cinarli, D. Gürbüz, A. Tavman, A. Seher Birteksöz, *Bull. Chem. Soc. Ethiop.* **25**, 407 (2011)
24. H. Kubota, S. Senda, N. Nomura, H. Tokuda, H. Uchiyama, *J. Biosci. Bioeng.* **106**, 381 (2008)
25. S.Y. Ebrahimipour, I. Sheikhshoae, A. Crochet, M. Khaleghi, K.M. Fromm, *J. Mol. Struct.* **1072**, 267 (2014)
26. R. Takjoo, J.T. Mague, A. Akbari, S.Y. Ebrahimipour, *J. Coord. Chem.* **66**, 2852 (2013)
27. S.Y. Ebrahimipour, I. Sheikhshoae, J. Castro, W. Haase, M. Mohamadi, S. Foro, M. Sheikhshoae, S. Esmaeili-Mahani, *Inorg. Chim. Acta* **430**, 245 (2015)
28. S.Y. Ebrahimipour, M. Mohamadi, J. Castro, N. Mollania, H. Amiri Rudbari, A. Saccá, *J. Coord. Chem.* **68**, 632 (2015)
29. S.Y. Ebrahimipour, Z. Rashid Ranjabr, E. Tavakolinejad Kermani, B. Pour Amiri, H. Amiri Rudbari, A. Saccá, F. Hoseinzade, *Transit. Metal Chem.* **40**, 39 (2015)
30. S.Y. Ebrahimipour, M. Abaszadeh, J. Castro, M. Seifi, *Polyhedron* **79**, 138 (2014)
31. S.Y. Ebrahimipour, J.T. Mague, A. Akbari, R. Takjoo, *J. Mol. Struct.* **1028**, 148 (2012)
32. I. Sheikhshoae, S.Y. Ebrahimipour, A. Crochet, K.M. Fromm, *Res. Chem. Intermediat.* **41**, 1881 (2015)
33. S.Y. Ebrahimipour, H. Khabazadeh, J. Castro, I. Sheikhshoae, A. Crochet, K.M. Fromm, *Inorg. Chim. Acta* **427**, 51 (2015)
34. F.H. Allen, *Acta Crystallogr. B* **58**, 380 (2002)
35. S. Gao, Z.Q. Weng, S.-X. Liu, *Polyhedron* **17**, 3595 (1998).
36. S.P. Rath, S. Mondal, A. Chakravorty, *Inorg. Chim. Acta* **263**, 247 (1997)
37. A. Radi, M. El Ries, S. Kandil, *Anal. Chim. Acta* **495**, 61 (2003)