

## Short communication

# A novel anionic di-oxido vanadium(V) Schiff base complex: Synthesis, spectral characterization, X ray crystal structure, catalytic activity for the preparation of tetrahydro-4H-chromene derivatives and antibacterial properties

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## ABSTRACT

In this work, a tridentate ONO Schiff base ligand, 1-[[((2-hydroxyphenyl)imino)methyl)naphthalen-2-yl] [H<sub>2</sub>L] and its di-oxido vanadium(V) complex [(VO<sub>2</sub>(L))(NHET<sub>3</sub>)] have been synthesized and fully characterized using elemental analysis, molar conductivity and FT-IR, UV-Vis, and <sup>1</sup>HNMR spectroscopies. Single crystal X-ray diffraction was also used to accomplish the crystal structure of di-oxido vanadium(V) complex. The catalytic activity of the complex was also evaluated for the synthesis of tetrahydro-4H-chromene derivatives. The synthesized [(VO<sub>2</sub>(L))(NHET<sub>3</sub>)] complex showed superior catalytic characteristics in comparison to the previously reported catalysts. Furthermore, the antimicrobial properties of the complex against both gram-positive and gram-negative pathogens were evaluated, that an enhanced antibacterial activity was obtained with MIC values in the range of 100–200 µg/ml.

## 1. Introduction

Schiff bases derived from the reaction of primary amines and aldehydes have gained extensive interest due to their widespread applications. Schiff bases as polydentate ligands can form stable complexes with transition metals with versatile and tunable structures which have distinct catalytic and biologic activities [1–4]. The presence of azomethine (—N=CH) bond in Schiff bases is the crucial factor for the formation of stable complexes with transition metals [5]. An extensive library of Schiff bases have been synthesized and complexed with transition metal ions with potential applications in medicine and industry (catalysis and anticorrosion) [6–17]. Among the studied metals, vanadium complexes have gained much attention not only for their catalytic activities but also due to their antibacterial, anticancer, and other medicinal applications [8,18–21]. Vanadium complexes can act as the catalyst in several industrially important oxidation, epoxidation, and hydroxylation processes [22,23]. Also, it has crucial roles in many immune-related pathways in biological systems [24–26]. It is believed that the ability of vanadium to exist in three different forms and oxidation states is responsible for its physiological characteristics [27].

Recognizing the importance of both biological and industrial aspects, herein, we reported a di-oxido vanadium(V) Schiff base-complex using 1-[[((2-hydroxyphenyl)imino)methyl)naphthalen-2-yl] [H<sub>2</sub>L] as the ligand. [H<sub>2</sub>L] and the [(VO<sub>2</sub>(L))(NHET<sub>3</sub>)] complex have been synthesized and characterized using UV-Vis, FT-IR, and <sup>1</sup>HNMR spectroscopies while the crystal structure of complex was evaluated using X-ray crystal diffraction. Finally, the catalytic performance of the [(VO<sub>2</sub>(L))(NHET<sub>3</sub>)] complex was evaluated in the synthesis process of tetrahydro-4H-chromenes. In addition, the biological activity of the parent ligand and the vanadium complex were evaluated against four different gram-positive and gram-negative pathogens. The synthesized compounds are stable at room temperature. They are soluble in most organic solvents including DMSO, DMF, methanol and ethanol and less soluble in other common solvents like dichloromethane, acetonitrile and insoluble in toluene, benzene and *n*-hexane. The molar conductivity value of the synthesized complex in EtOH shows that it is an 1:1 type electrolyte. In the asymmetric unit of the complex, two [(VO<sub>2</sub>(L))(NHET<sub>3</sub>)] species exist. Figs. 1 and S1 depict the perspective view of these species and the asymmetric unit of the crystal, respectively. Also, Table S2 represents some selected bond distances and interbond angles. To determine the

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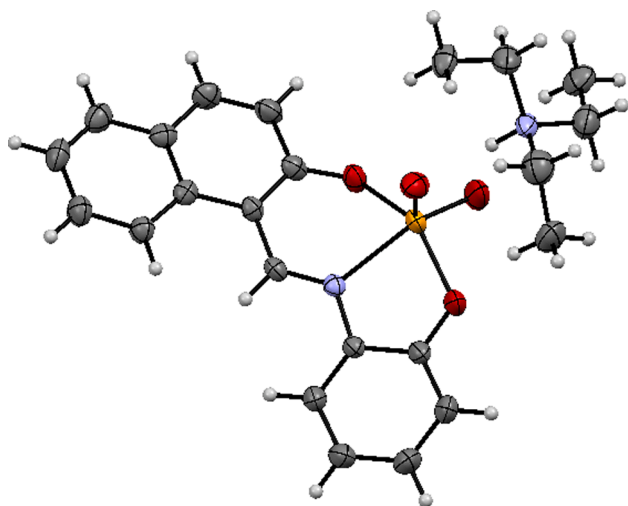


Fig. 1. Perspective view of  $[\text{VO}_2(\text{L})](\text{NHET}_3)$ .

geometry of the pentacoordinated complexes, trigonality index ( $\tau_5$ ) described by Addison et al. is calculated [28].  $\tau_5 = 0$  indicates an ideal square-pyramid while  $\tau_5 = 1$  indicates an ideal trigonal bipyramid. The values of  $\tau_5$  for  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  (1) and  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  (2) were calculated to be 0.21 and 0.14, respectively, confirming the distorted square pyramidal geometry of both molecules in the asymmetric unit. In the structure of the complex, the coordination sphere of the vanadium ion are occupied by two oxido groups (in *cis*-position) and ONO donor atoms of the dianionic Schiff base ligand. The nitrogen atom of the imino group and the oxygen atoms of the naphtholate and phenolate groups are the donor atoms of the deprotonated Schiff base  $[\text{L}^{2-}]$ .

In the complex structure, the triethylammonium cation is strongly bonded to the apical oxygen atom via hydrogen bonding. According to the obtained results (Fig. S2), the FT-IR spectrum of  $[\text{H}_2\text{L}]$  ligand showed a vibrational band at  $1630\text{ cm}^{-1}$ , which can be attributed to the  $\text{C}=\text{N}$  group and approved the formation of a Schiff base ligand. The tensile vibration of OH and vibration band of  $\text{C}=\text{C}$  in the aromatic rings can be seen at  $3447\text{ cm}^{-1}$  and  $1406\text{--}1459\text{ cm}^{-1}$ , respectively. After complexation, the frequency of the mentioned azomethine ( $\text{C}=\text{N}$ ) band at  $1630\text{ cm}^{-1}$  decreased to  $1615\text{ cm}^{-1}$  [8]. Two absorption bands observed at  $987\text{ cm}^{-1}$  and  $824\text{ cm}^{-1}$  are attributed to the symmetric and asymmetric stretching vibration bands of *cis*- $\text{VO}_2$ , respectively [18]. In addition, the vibrations appeared at  $459\text{ cm}^{-1}$ ,  $506\text{ cm}^{-1}$  and  $2977\text{ cm}^{-1}$  can be related to the  $\text{V}-\text{N}$ ,  $\text{V}-\text{O}$ , and  $\text{N}-\text{H}$  bonds, respectively. Two absorption bands at  $2496\text{ cm}^{-1}$  and  $2602\text{ cm}^{-1}$  were also ascribed to  $\text{CH}_2$  and  $\text{CH}_3$  groups of triethyl amine, respectively [29]. According to the  $^1\text{H}$  NMR measurements (Fig. S3), three singlet signals were observed at 8.3 ppm, 10.8 ppm, and 12.0 ppm, which can be assigned to the protons of  $\text{CH}=\text{N}$ , amine OH, and aldehyde  $\text{O}-\text{H}$ , respectively [9]. The presence of the azomethine proton confirms the formation of the ligand, while the protons of the aromatic rings are observed in the range of 7.2–8.1 ppm [2]. In title V(V) complex, the protons of the azomethine moiety and aromatic rings were spotted at 10.1 and 6.7–9.3 ppm respectively. The triplet and quaternary peaks observed at 1.2 ppm and 3.1 ppm are assigned to the  $\text{CH}_3$  and  $\text{CH}_2$  groups of triethylamine [30]. In the UV-Vis spectrum of the  $[\text{H}_2\text{L}]$  ligand (Fig. S4), three absorption bands appeared at 320 nm, 450 nm, and 470 nm can be attributed to  $\pi \rightarrow \pi^*$  transition in the aromatic rings,  $\pi \rightarrow \pi^*$  transition in the azomethine, and  $n \rightarrow \pi^*$  transition in azomethine, respectively. In the case of the V(V) complex, the absorption band corresponded to the  $\pi \rightarrow \pi^*$  transition is observed at 345 nm. The absorption peak appeared at 455 nm is related to the charge transfer from the ligand to the metal (LMCT) [2,6].

The title complex was used in the synthesis process of tetrahydro-4H-chromene derivatives in order to evaluate its catalytic activity. At first,

Table 1

Three component reaction of dimesone, malononitrile and aromatic aldehydes.

Entry	Ar	Time (min)	Yield (%)	M.p. ( $^{\circ}\text{C}$ )	
				Found	Reported
1a	$\text{C}_6\text{H}_5$	45	97	231–233	231–232 [29]
1b	4-Cl- $\text{C}_6\text{H}_4$	45	95	214–216	215–217 [29]
1c	3-NO <sub>2</sub> - $\text{C}_6\text{H}_4$	50	87	216–218	217–219 [31]
1d	2,4-(Cl) <sub>2</sub> - $\text{C}_6\text{H}_3$	55	88	176–178	175–178 [29]
1e	4-CH <sub>3</sub> - $\text{C}_6\text{H}_4$	50	85	217–219	218–220 [29]

Table 2

Comparison between previous catalysts used for the synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile and  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  used in this study.

Catalyst	Reaction conditions	Time (min)	Yield (%)	Reference
$[\text{VO}(\text{L})(\text{phen})]$	EtOH, reflux	20	90	[29]
Triethylbenzylammonium chloride	$\text{H}_2\text{O}$ , $90\text{ }^{\circ}\text{C}$	240	90	[32]
$\text{K}_3\text{PO}_4$	EtOH, stirred	45	94	[31]
$[\text{Cu}(\text{L}')(\text{Imi})]$ (8%mol) <sup>a</sup>	EtOH, $50\text{ }^{\circ}\text{C}$	20	92	[2]
Tetrabutylammonium bromide	EtOH, reflux	20	92	[33]
$[\text{VO}_2(\text{L})](\text{NHET}_3)$	Acetonitrile, $50\text{ }^{\circ}\text{C}$	45	97	This work

an initial optimization was conducted on the reaction conditions (temperature, solvent, and catalyst loading). Three different solvents (DI water, acetonitrile, and ethanol), three different levels of catalyst loading (5, 10, and 20 mol%), and four levels of temperature (30, 50, 80,  $100\text{ }^{\circ}\text{C}$ ) were used in this optimization. The title V(V) complex acted as a homogenous catalyst and finally column chromatography was used for the purification of the product. For a complete list of the results obtained from this optimization, one can refer to Tables S3–S5. As one can see, the di-oxido vanadium(V) complex shows an optimum catalytic performance (97% yield and the reaction time of 45 min) in acetonitrile at  $50\text{ }^{\circ}\text{C}$ , using 10 mol% catalyst loading for the synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1a). Using the optimal conditions, various tetrahydro-4H-chromene derivatives were synthesized [29,31]. Table 1 reports the obtained reaction time and yield for the synthesis of tetrahydro-4H-chromenes using the aromatic aldehydes. According to the obtained results, the nature and position of the substituents on the aromatic ring have no discernible impact on the success of the reaction. In addition, the recyclability of the di-oxido vanadium(V) complex was studied by monitoring the efficiency of the catalyst after three consecutive runs under the optimal conditions (1a: 97%, 95%, 93%). The efficiency of the catalyst was reduced by only 4% after three consecutive runs, which demonstrated the ability of the catalyst for multiple uses.

In order to compare the performance of  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  complex, the obtained results in this study were compared with those of the previously catalysts used in the catalytic synthesis of 1a. As can be seen in Table 2, the yield, reaction time, and temperature of the reaction are superior or comparable with the other catalysts [2,29,32–33]. The possible mechanism proposed for the synthesis of tetrahydro-4H-chromene derivatives catalyzed by the di-oxido-vanadium(V) complex is shown in Fig. 2.

The antibacterial activity of  $[\text{H}_2\text{L}]$  and  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  complex against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Bacillus cereus* bacteria were evaluated using inhibition zone and MIC assays (Fig. 3). According to the obtained results (Table 3),  $[\text{H}_2\text{L}]$  ligand is effective on all of the studied bacteria, except *E. coli*. However, the  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  complex have higher antibacterial activity against both gram-negative and gram-positive bacteria, especially *Staphylococcus aureus*. Interestingly, this complex shows a considerable

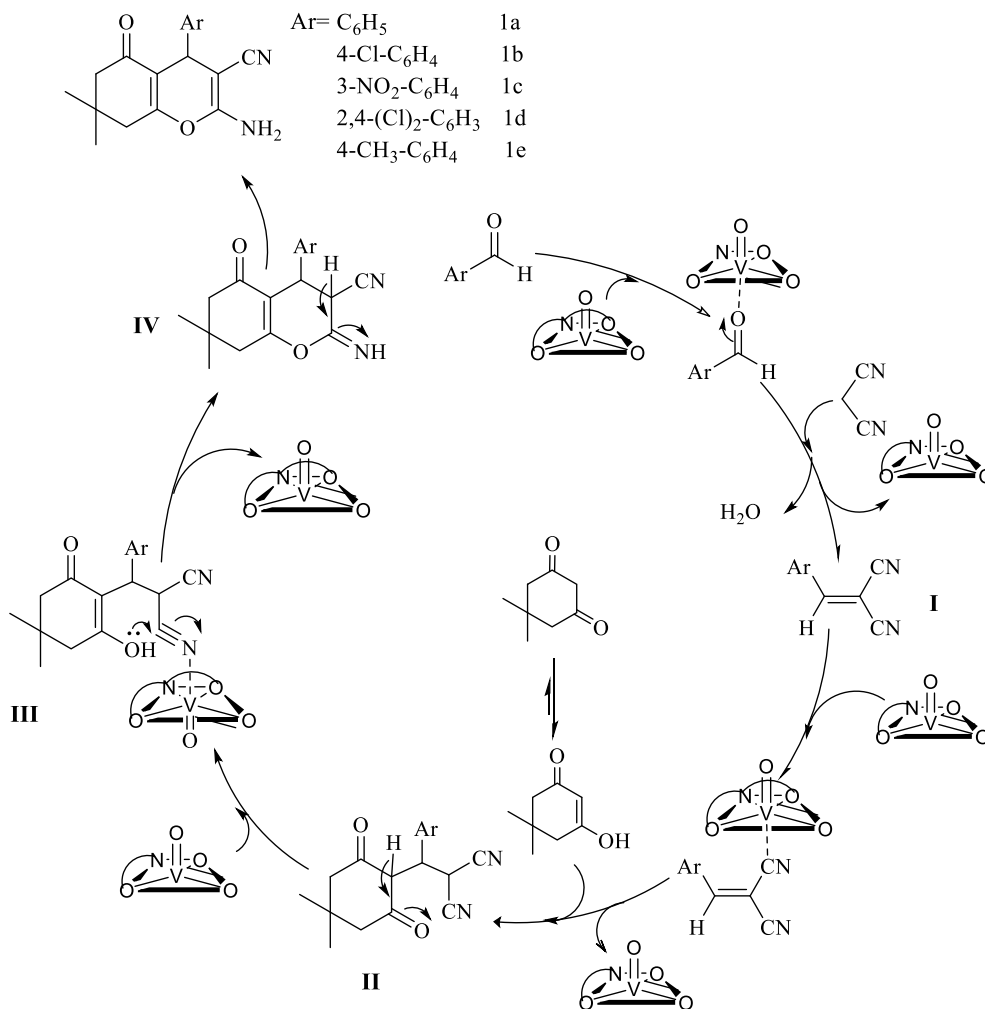


Fig. 2. Proposed mechanism for the synthesis of tetrahydro-4H-chromene derivatives catalyzed by di-oxido vanadium(V) complex.

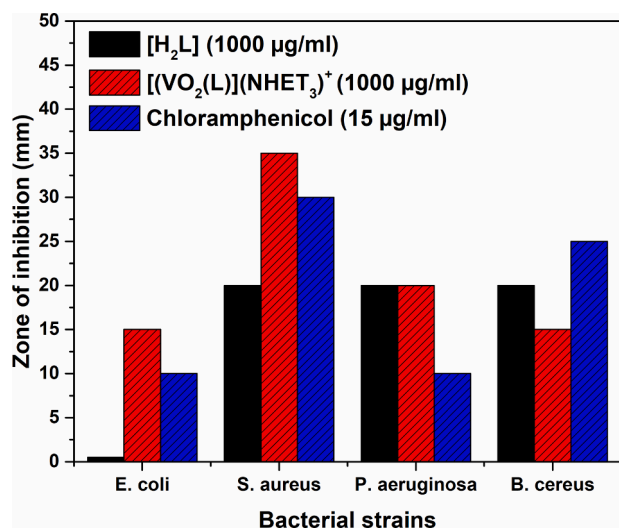


Fig. 3. The measured zone of inhibition (mm) of [H<sub>2</sub>L] (1000 µg/ml), [VO<sub>2</sub>(L)](NHET<sub>3</sub>)<sup>+</sup> (1000 µg/ml) and chloramphenicol antibiotic (15 µg/ml) as positive control against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus cereus* bacteria.

Table 3

Antimicrobial activities of [H<sub>2</sub>L] and [VO<sub>2</sub>(L)](NHET<sub>3</sub>)<sup>+</sup> complex against gram-positive and gram-negative bacteria determined by the inhibition zone method.

	[H <sub>2</sub> L]		[VO <sub>2</sub> (L)](NHET <sub>3</sub> )		Positive control (Chloramphenicol 15 µg/ml)
	500 µg/ ml	1000 µg/ml	500 µg/ ml	1000 µg/ml	
<i>Escherichia coli</i>	0	0	25	15	10
<i>Staphylococcus aureus</i>	20	20	35	35	30
<i>Pseudomonas aeruginosa</i>	10	20	15	20	10
<i>Bacillus cereus</i>	10	20	25	15	25

Table 4

The MIC values (µg/ml) of [H<sub>2</sub>L] and [VO<sub>2</sub>(L)](NHET<sub>3</sub>)<sup>+</sup> complex against studied microorganisms.

	<i>E. coli</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>B. cereus</i>
[H <sub>2</sub> L]	250	7.8	250	31.2
[VO <sub>2</sub> (L)](NHET <sub>3</sub> ) <sup>+</sup>	250	250	125	125

antibacterial activity against *E. coli*, even though this bacteria is resistant to the parent ligand. The obtained MIC values for [H<sub>2</sub>L] and [VO<sub>2</sub>(L)](NHET<sub>3</sub>)<sup>+</sup> complex are reported in Table 4, and it can be inferred that the

antibacterial activity of  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  complex against *P. aeruginosa* bacteria is considerably higher (125  $\mu\text{g}/\text{ml}$ ) than that of  $[\text{H}_2\text{L}]$  (250  $\mu\text{g}/\text{ml}$ ).

Based on the previous studies [6,30], the enhanced activity of  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  complex against microorganisms can be attributed to the delocalization of the  $\pi$ -electrons in chelate moiety and also the positive charge of the central atom in the complex. The two mentioned phenomena have a significant impact on the lipophilicity of the complex, which will facilitate its penetration into the microorganism membranes and, eventually result in the cell death.

In conclusion, a tridentate ONO Schiff base ligand; 1-(((2-hydroxyphenyl)imino)methyl)naphthalen-2-ol  $[\text{H}_2\text{L}]$  and its di-oxido vanadium(V) complex  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  were successfully synthesized and fully characterized. The di-oxido vanadium(V) complex showed enhanced antibacterial activity against all of the studied microorganisms (especially *Staphylococcus aureus*), which confirmed the antibacterial activity of the synthesized complex. The efficiency of the  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  complex as the catalyst remains more than 90% even after three consecutive runs. High yield, mild temperature reaction, and the possibility to use the  $[\text{VO}_2(\text{L})](\text{NHET}_3)$  catalyst several times are the advantages of the synthesized complex in comparison to the previously reported catalysts for the synthesis of tetrahydro-4H-chromene derivatives.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

The synthesis and characterization of the ligand  $[\text{H}_2\text{L}]$  and its di-oxido vanadium(V) complex, Crystal structure determination, Catalytic activity, Parameters optimization, Biological activity and related figures and tables are in Supporting information. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2033464. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data to this article can be found online at <https://doi.org/10.1016/j.inoche.2021.108561>.

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