



# Investigation of synthesized new vanadium(III) complexes of ditolyldithiophosphate ligands by spectroscopic, cyclic voltammetric, DFT, antimicrobial and cytotoxic studies



Sandeep Kumar <sup>a</sup>, Atiya Syed <sup>a</sup>, Savit Andotra <sup>a</sup>, Ramanpreet Kaur <sup>b</sup>, Vikas <sup>b</sup>,  
Sushil K. Pandey <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Jammu, Jammu, 180006 India

<sup>b</sup> Quantum Chemistry Group, Department of Chemistry & Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh, 160014, India

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## ABSTRACT

Vanadium(III) complexes with sulfur donor dithiophosphate ligands corresponding to  $[(ArO)_2PS_2]_3V$  and  $[(ArO)_2PS_2]_2VCl.L$  ( $Ar = o-, m-, p-CH_3C_6H_4$  and  $p-Cl-m-CH_3C_6H_3$ ;  $L = NC_5H_5, P(C_6H_5)_3$ ), have been synthesized and characterized by various physico-chemical techniques like elemental analyses, magnetic studies, ESI-Mass, IR, UV and heteronuclear NMR ( $^1H, ^{13}C$  and  $^{31}P$ ) spectral studies. These analyses have contributed to the prediction of structure: by exhibiting significant  $\nu(P-S)$  and  $\nu(P=S)$  band shifting in comparative IR spectra; shifting of resonance signal in comparative  $^{31}P$  NMR spectra of ligands and complexes and stability of V(III) ion in the complexed state is confirmed by magnetic and UV studies. Therefore, the six coordinated geometry stabilizing the trivalent vanadium atom in the complexes and adducts, respectively has been confirmed. The cyclic voltammetric analyses presented the redox aptitude of the complex under analysis which can be utilized as catalyst in organic synthesis. The geometry of ligands and complexes has been optimized using density functional theory (DFT). The structural parameters, vibrational bands and energy gaps of frontier orbitals (HOMO–LUMO) have also been calculated. The calculated geometric and spectral results reproduced the experimental data with well agreement. The DFT computed frontier molecular orbitals (HOMO–LUMO) and their energies suggest charge transfer occurs within the complexes. Antimicrobial screening of the complexes against two bacterial strains: Gram–positive, *Enterococcus faecalis* and Gram–negative, *Escherichia coli* and fungus *Fusarium oxysporum* have shown potential bioactivity. A preliminary cytotoxic analysis has been carried out using the cultivated human cell lines: lung adeno carcinoma cell line **A-549**, leukemia cell line **THP-1**, prostate cancer cell line **PC3** and colorectal cancer cell line **HCT-116**.

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## 1. Introduction

In the past decade vanadium has encompassed the new arena of alternatives to insulin as antidiabetic drugs [1]. A variety of vanadium compounds are termed as insulinomimetics, insulin-mimetics or insulin enhancers. Clinical trials with such vanadium based antidiabetics have shown encouraging results but the main barriers in reaching the status of industrially commercialised drugs are two major problems-poor absorption from the gastrointestinal tract into the blood stream and the gastrointestinal stress, the

principle sign of vanadium toxicity [2–4]. Therefore, the development of vanadium-based antidiabetic oral drugs now focuses on the identifying organic ligands with enhanced properties so as to improve target selectivity, vanadium complex stabilities and ligand exchanges, facilitation of membrane passages and tissue distributions. It has also been recognized that the putative anticancer activity of vanadium based drugs goes hand in hand with the antidiabetic research [5]. Another important role of vanadium complexes is to understand the past and present nitrogen cycle. Vanadium nitrogenase is known as alternative to the principle nitrogen fixer-molybdenum nitrogenase. But now it is advocated that vanadium nitrogenase is the primary nitrogenase of evolutionary significance [6]. A range of oxidation states from +5 to –1 exhibited by vanadium in its complexes and fascinating structural novelties

\* Corresponding author.

E-mail address: [kpsushil@rediffmail.com](mailto:kpsushil@rediffmail.com) (S.K. Pandey).

and complexities displayed in their biological [7–9], industrial [10,11] and medicinal application [12,13] make them an interesting area of research. Therefore, in this research paper, an initiative has been made in the field of synthesizing vanadium complexes with sulfur donor dithiophosphate ligands and also involving coordination of pyridine and triphenylphosphine to obtain greater insight.

## 2. Experimental

A challenge in the preparation of V(III) complexes with dithiophosphates is the hydrolytic instability of the precursor reagents, therefore, inert atmosphere has to be maintained. The entire synthetic process is conducted under N<sub>2</sub> atmosphere conditions using Schlenk line techniques. Distillation of *ortho*-, *meta*- and *para*-hydroxytoluene (cresols) was carried out before use. Vanadium trichloride (Himedia) was used as received. The solvents used (toluene, hexane, tetrahydrofuran, chloroform and methanol) were purified and dried by standard methods before use. Elemental analyses of C, H, N and S were done on Vario EL III and CHNS-932 Leco elemental analyzer and their results were in good agreement ( $\pm 0.3\%$ ) with the calculated values. Volhard's method was used to estimate chlorine volumetrically. Vanadium was estimated gravimetrically as silver orthovanadate (Ag<sub>3</sub>VO<sub>4</sub>) [14]. The mass spectra were recorded on ESQUIRE3000\_00037 spectrophotometer. IR spectra were recorded using KBr pellet in the range of 4000–200 cm<sup>-1</sup> on a Perkin Elmer Spectrum 400-I FTIR spectrophotometer. The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Avance II and III 400 (400 MHz) spectrometer using TMS as internal reference for <sup>1</sup>H and <sup>13</sup>C NMR and H<sub>3</sub>PO<sub>4</sub> (85%) as external reference for <sup>31</sup>P NMR. The electronic spectra of the complexes were recorded in a range of 200–800 nm on a T90 + UV/VIS spectrophotometer using a pair of matched quartz cells of 10 mm path length at an ambient temperature. The room temperature magnetic susceptibility measurements have been carried out by vibrating sample magnetometer (VSM). The cyclic

voltammogram was recorded on Metrohm Autolab. The potential is applied between the reference electrode (Ag/AgCl) and the working electrode (Gold electrode) and the current is measured between the working electrode and the counter electrode (Platinum wire). 0.1 M phosphate buffer solution (pH = 7.0) was used.

### 2.1. Synthesis of ligands

The ligands (*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (**L1**), (*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (**L2**), (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (**L3**) and (*p*-Cl-*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>PS<sub>2</sub>Na (**L4**) acids were prepared by literature method [15].

### 2.2. Synthesis of complexes

#### 2.2.1. Synthesis of tris-*O,O'*-*o*-ditolyldithiophosphatovanadium(III) [((*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>V] (1)

Vanadium trichloride (0.16 g, 1.04 mmol) dissolved in tetrahydrofuran (~10 cm<sup>3</sup>) was added to a tetrahydrofuran solution (~20 cm<sup>3</sup>) of sodium *O,O'*-*o*-ditolyldithiophosphate (1.0 g, mmol) with constant stirring at room temperature for 2 h under nitrogen atmosphere. The reaction mixture was refluxed with continuous stirring for 5 h; white turbidity appeared due to the formation of sodium chloride. The contents were cooled and then sodium chloride was separated by filtration using alkoxy funnel fitted with G-4 disc. The product [((*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>V] (**1**) was obtained as green solid from the filtrate after removal of excess of tetrahydrofuran *in vacuo*.

The complexes **2–4** were prepared by the same procedure. The synthetic and analytical details of complexes **1–4** are listed in Table 1.

#### 2.2.2. Synthesis of Chlorobis-*O,O'*-*o*-ditolyldithiophosphatopyridinovanadium(III) [((*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>V(Cl)·NC<sub>5</sub>H<sub>5</sub>] (5)

Vanadium trichloride (0.13 g, 0.82 mmol) was dissolved in tetrahydrofuran solution (~10 cm<sup>3</sup>) and added to a tetrahydrofuran

**Table 1**  
Synthetic and analytical data of ditolyldithiophosphates of vanadium(III) (**1–12**).

S. No.	Reactants g (mmol)			Molar ratio	Reflux time (h)	Product (Physical state)	Yield (%)	Analysis (%) Found (Calcd.)					
	L	VCl <sub>3</sub>	Donor					C	H	N	S	Cl	V
1.	1.00 (3.01)	0.16 (1.04)	–	1:1	5	[(( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>3</sub> V] (Green solid)	89	51.42 (51.53)	4.21 (4.32)	–	19.56 (19.65)	–	5.11 (5.20)
2.	1.00 (3.01)	0.16 (1.04)	–	1:1	5	[(( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>3</sub> V] (Green solid)	85	51.31 (51.53)	4.11 (4.32)	–	19.42 (19.65)	–	5.06 (5.20)
3.	1.00 (3.01)	0.16 (1.04)	–	1:1	5	[(( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>3</sub> V] (Green solid)	89	51.27 (51.53)	4.17 (4.32)	–	19.50 (19.65)	–	5.01 (5.20)
4.	1.00 (2.49)	0.24 (1.04)	–	1:1	5	[(( <i>p</i> -Cl- <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>3</sub> V] (Green solid)	90	42.42 (42.54)	3.01 (3.06)	–	16.11 (16.23)	17.85 (17.94)	4.23 (4.30)
5.	0.54 (1.62)	0.13 (0.82)	0.21 (0.80)	2:1:1	5	[(( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·NC <sub>5</sub> H <sub>5</sub> ] (Light green solid)	90	50.40 (50.54)	4.11 (4.24)	1.70 (1.79)	16.25 (16.36)	4.48 (4.52)	6.42 (6.50)
6.	0.54 (1.62)	0.13 (0.82)	0.13 (0.82)	2:1:1	5	[(( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·NC <sub>5</sub> H <sub>5</sub> ] (Light green solid)	88	50.49 (50.54)	4.21 (4.24)	1.60 (1.79)	16.20 (16.36)	4.44 (4.52)	6.45 (6.50)
7.	0.54 (1.62)	0.13 (0.82)	0.13 (0.82)	2:1:1	5	[(( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·NC <sub>5</sub> H <sub>5</sub> ] (Light green solid)	89	50.39 (50.54)	4.19 (4.24)	1.65 (1.79)	16.30 (16.36)	4.38 (4.52)	6.39 (6.50)
8.	1.07 (2.64)	0.21 (1.33)	0.35 (1.33)	2:1:1	5	[(( <i>p</i> -Cl- <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·NC <sub>5</sub> H <sub>5</sub> ] (Light green solid)	90	42.81 (42.99)	3.11 (3.17)	1.49 (1.52)	13.82 (13.91)	19.18 (19.23)	5.46 (5.53)
9.	0.54 (1.62)	0.13 (0.82)	0.21 (0.80)	2:1:1	5	[(( <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] (Light green solid)	90	56.99 (57.11)	4.37 (4.48)	–	13.12 (13.26)	3.55 (3.66)	5.11 (5.27)
10.	0.54 (1.62)	0.13 (0.82)	0.13 (0.82)	2:1:1	5	[(( <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] (Light green solid)	88	56.99 (57.11)	4.37 (4.48)	–	13.12 (13.26)	3.55 (3.66)	5.11 (5.27)
11.	0.54 (1.62)	0.13 (0.82)	0.13 (0.82)	2:1:1	5	[(( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] (Light green solid)	89	56.90 (57.11)	4.25 (4.48)	–	13.19 (13.26)	3.58 (3.66)	5.21 (5.27)
12.	1.07 (2.64)	0.21 (1.33)	0.35 (1.33)	2:1:1	5	[(( <i>p</i> -Cl- <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> ) <sub>2</sub> V(Cl)·P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] (Light green solid)	90	49.87 (49.99)	3.45 (3.56)	–	11.54 (11.61)	15.96 (16.04)	4.56 (4.61)

L = (*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (1,5,9), (*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (2,6,10), (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (3,7,11), (*p*-Cl-*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>PS<sub>2</sub>Na (4,8,12).  
Donor = NC<sub>5</sub>H<sub>5</sub> (5–8), P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (9–12).

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