



Synthesis and Characterization of *O*, *O*'-ditolyl and benzyl dithiophosphates complexes of Vanadium(V) Atom

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Abstract- Reaction of Vanadiumoxytrichloride, VOCl_3 with sodium salt of *O,O*-ditolyl and benzyl dithiophosphoric acid i.e (*o*-, *m*- and *p*- $\text{MeC}_6\text{H}_4\text{O}$) $_2\text{PS}_2\text{Na}$, $(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\text{Na}$, in different molar ratio of 1:1, 1:2 and 1:3, resulted in the synthesis of various coordinated complexes corresponding to [*o*-, *m*- or *p*- $\text{MeC}_6\text{H}_4\text{O}$] $_2\text{PS}_2\text{VOCl}_2$, [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}\text{VOCl}_2$], [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}_2\text{VOCl}$], [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}_3\text{VO}$] and [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}_3\text{VO}$]. These analyses have contributed to the prediction of structure: by exhibiting significant $\nu(\text{P-S})$ and $\nu(\text{P-S})$ band shifting in comparative IR spectra; shifting of resonance signal in comparative ^{31}P NMR spectra of ligands and complexes which indicates the bidentate linkage of dithiophosphate moieties leading to pentagonal bipyramidal and square bipyramidal geometry around the Vanadium(V) atom and stability of Vanadium(V) ion in the complexed state is confirmed by magnetic and UV studies. The calculated geometric and spectral results reproduced the experimental data with well agreement. Antimicrobial screening of the complexes against two bacterial strains: Grampositive, *Enterococcus faecalis* and Gramnegative, *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.

Key words: Dithiophosphates; Phosphordithioates, Phosphorous-Sulfur compounds.

1. INTRODUCTION

Vanadium is an unique element in view of its applicability in biological ¹⁻², industrial ³ and catalytical ⁴ processes. Vanadate acts as inhibitors ⁵⁻⁶ for a number of enzymes including ATP phosphohydrolase, phosphotyrosyl, protein phosphates and ribonucleases. Some compound of vanadium like sodium orthovanadate, vanadyl sulfate, peroxovanadium, bis(maltolato) oxovanadium(IV) etc acts as mimic agents in the treatment of diabetes. 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. Vanadium-sulfur chemistry has also found applications in various fields such as vanadium sulfur conducting materials, in oil industry for extraction of vanadium impurities from heavy crude oils ^{3,7}. Uses of $\text{V}^{\text{IV}}\text{O}$ and V^{VO} complexes as catalyst for conversion of sulfide to sulfoxide are known⁸. Dialkylphosphonates, dialkyldithiophosphonates, *O,O*'-dialkyldithiophosphates and *O,O*'-alkylenedithiophosphates are well known due to their versatile utility as active pesticides ⁹⁻¹⁰ and also for providing various aspects of bonding with several metals and metalloids ¹¹⁻¹⁴. These derivatives find

extensive application in agriculture ¹⁵⁻¹⁶, industries ¹⁷⁻¹⁸ and analytical studies ¹⁹⁻²⁰. Usually these ligands predominantly exhibited bidentate mode of bonding ²¹⁻²⁷. Moreover the less common monodentate linkages have also been observed in the case of nickel and tin ²⁸⁻²⁹. Recently, the synthesis and characterization of ditolyldithiophosphates added a new development in the area of dithiophosphate chemistry³⁰⁻³¹. Some metal complexes with the ditolyl/dibenzyl dithiophosphate ligands have also been reported^{23, 32-39}. Some interesting application of ditolyl and benzyl dithiophosphates has also been reported such as rubber vulcanizers ⁴⁰, aerofloats ³⁷, polymerization catalyst ⁴², oil additives ³⁹ and acaricides ⁴³. In view of the above interesting facets, it was thought worthy to investigate the chemistry of these elements with *o*-, *m*- and *p*-ditolyl and benzyl dithiophosphate and we report herein on the synthesis and characterization of some ditolyl and benzyl dithiophosphate complexes of vanadium (V).

Experimental

Moisture was carefully excluded throughout the experimental manipulations by using standard Schlenk's techniques. The sodium salt of *O,O*-bis(ortho- meta- and para- ditolyl) and benzyl phosphorodithioate were prepared by the literature methods ³²⁻³³. VOCl_3 was prepared ²⁵ by the reaction of V_2O_3 with SOCl_2 . Sulfur was estimated as BaSO_4



(Messenger's method) and vanadium was estimated as AgVO_4 . IR spectra was recorded in KBr mulls in the range of $4000\text{--}400\text{ cm}^{-1}$ on a perkin elmer 377 or brucker vector 22 spectrophotometer. The ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a brucker DRX 500 MHz spectrometer using TMS as the internal reference for ^1H NMR and 85% H_3PO_4 as an internal reference for ^{31}P NMR at University of Panjab, Chandigarh.

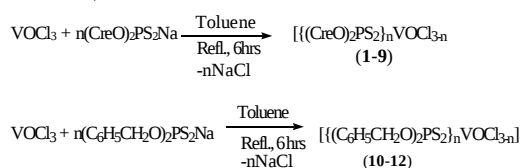
Synthesis of $[(o-, m- \text{ and } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]_n\text{VOCl}_{3-n}$, (where $n = 0, 1, 2$).

To a toluene solution (~ 25) of vanadyloxychloride, VOCl_3 , (0.285g; 3.30 mmol) was added in dropwise manner into the toluene suspension of sodium salt of *O,O'*-ditolyl and benzyl dithiophosphate (1.01g; 3.30 mmol) at room temperature in 1:1, 1:2 and 1:3 molar stoichiometry. The color of the content was changed quickly to light yellow. The content was then refluxed for ~ 6 hrs during which the yellow color was further deepened. The reaction mixture was cooled to room temperature and precipitated sodium chloride was separated by filtration by using sintered glass (G-4) funnel. Now, excess of toluene was evaporated under reduced pressure. Final drying of the product in vacuo for 3-4 hrs yields the compound as dark yellow sticky solid in 80-85% yield. Similar methodology was adapted for the synthesis of other complexes with different molar ratio i.e 1:2 and 1:3. The synthetic and analytical data are given in the table 1.

<Insert Table 1>

Results and Discussion

Reaction of VOCl_3 with sodium salt of ditolyl and benzyl dithiophosphonate, (*o*-, *m*- and *p*- $\text{MeC}_6\text{H}_4\text{O})_2\text{PS}_2\text{Na}$, $(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\text{Na}$, were carried out in 1:1, 1:2 and 1:3 molar ratio in refluxing toluene under anhydrous conditions, which yielded the complexes of the type $[(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\text{VOCl}_2]$, $[(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\text{VOCl}_2]$, $[(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]_2\text{VOCl}$, $[(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2]_2\text{VOCl}$, $[(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]_3\text{VO}$ and $[(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2]_3\text{VO}$ (scheme 1).



Scheme1. Reaction of VOCl_3 with $[(\text{CreO})_2\text{PS}_2\text{Na}]$; (where Cre = *o*-, *m*- or *p*- MeC_6H_4 - and $n=0,1,2$).

The feasibility of the reaction of sodium ditolyl and benzyl dithiophosphorodithioate was investigated by using 1:3 molar reactions. These reactions appears to be sluggish and need to reflux for 6-7 hrs. The complexes were obtained as viscous liquid or solid and were soluble in chloroform, dichloromethane and benzene, while insoluble in *n*-hexane and petroleum ether. These complexes were appeared to be moisture sensitive. However, these can be kept unchanged for long under anhydrous and inert atmosphere. These

compounds are non-volatile even under reduced pressure and get decomposed to a dark brown material, which could not be characterized. The outcome of the elemental analyses (C, H, S and V) has supported the composition of individual complexes.

Infrared spectra

The infrared spectra³⁴⁻³⁷ of these complexes have shown characteristics absorption of $\nu(\text{P})\text{-O-C}$ in the region $1190\text{--}1010\text{ cm}^{-1}$ and the appearance of the weak to medium intensity bands in the region $960\text{--}795\text{ cm}^{-1}$ were due to $\nu\text{P-O-(C)}$ ring vibrations. The characteristics absorption for $\nu\text{P=S}$ and $\nu\text{P-S}$ (symmetric and asymmetric vibrations) were observed with a slight shift to the parent dithiophosphate ligand in the region $783\text{--}648\text{ cm}^{-1}$ and $647\text{--}508\text{ cm}^{-1}$, which is indicative of complexation between metal and ligand. The appearance of new bands in the region $469\text{--}443\text{ cm}^{-1}$ is also suggestive of $\nu\text{V-S}$ bond formation. The $\nu\text{V=O}$ and $\nu\text{V-Cl}$ band was appeared in the region $972\text{--}918\text{ cm}^{-1}$ $546\text{--}509\text{ cm}^{-1}$ in the complexes. The relevant infrared spectra have been summarized in the table 2.

<Insert Table 2>

^1H NMR spectra

The ^1H NMR spectra³⁴⁻³⁷ of these complexes (in CDCl_3) has shown the characteristic resonance pattern for each proton. The chemical shift for the methyl protons (attached to the tolyl ring) was observed as singlet at 1.9 ppm in and another singlet was observed at 5.6-5.9 ppm due to the $-\text{CH}_2$ attached to the benzyl ring. There were two resonances for the ring protons of *para* complex whereas four resonances were observed for *ortho* and *meta* derivatives. The *ortho* proton of *ortho* derivative resonates at 6.7 ppm as a doublet with $J = 8.4\text{ Hz}$ while the *meta* protons resonate at 6.9 as a doublet with $J = 7.6\text{ Hz}$ and 7.0 ppm as a triplet with $J = 7.4\text{ Hz}$. The *para* protons of *ortho* derivatives resonate at 6.6 ppm as a triplet with $J = 8.4\text{ Hz}$. In case of *meta* derivative the *ortho* protons resonate at 6.6 as a singlet and 6.7 ppm as a doublet with $J = 8.4\text{ Hz}$. while the *meta* protons resonate at 7.0 ppm as a triplet with $J = 7.4\text{ Hz}$. The *para* derivatives exhibit two signals, one at 6.9 ppm as a doublet with $J = 8.4\text{ Hz}$ for *ortho* protons and second at 6.6 ppm as a doublet with $J = 8.4\text{ Hz}$ for *meta* protons. The benzyl derivatives shows three signals. The *ortho* protons resonate at 6.7 ppm as doublet with $J = 8.2$, *meta* protons resonate at 7.0 ppm with $J = 8.0$ and *para* proton resonate at 7.5 ppm as a triplet with $J = 7.8\text{ Hz}$. The resonance for individual protons is specified in the Table 3.

^{31}P NMR spectra

The ^{31}P NMR spectra³⁴⁻³⁷ (proton decoupled) of all the complexes have shown the presence of chemical shift as singlet in each case in with a downfield shift compared to the parent dithiophosphato ligand. The chemical shift for these compounds was found in the region $70.0\text{--}83.9\text{ ppm}$ respectively. Occurrence of singlet in each case might be correlated with the equivalent nature of phosphorus nucleus and

symmetric nature of the species as well. The ^{31}P NMR spectral data are given in the **Table 3**.

<Insert Table 3>

^{13}C NMR spectra

The ^{13}C NMR spectral³⁴⁻³⁷ data of few representative compounds have been recorded in CDCl_3 , the chemical shift for methyl carbon ($-\text{CH}_3$) attached to the tolyl ring was observed in the region 20.6-21 ppm and for methylene carbon ($-\text{CH}_2$) of benzyl derivatives appeared in the region 77.6-77.8 ppm. The carbon nuclei of the phenyl group ($-\text{C}_6\text{H}_4$) have displayed their resonance in the region 115.3-149.5 ppm. The chemical shifts for C-O carbon of *meta* and *para* derivatives were found in the downfield region 149.0-150.6 ppm as compared to the *ortho* derivative (144-145 ppm). The chemical shift for *ortho*, *meta* and *para* C-(CH_3) carbon was observed at 115.6 ppm, 120.2 ppm and 130.8 ppm respectively. The ^{13}C NMR spectral data are given in the **Table 4**.

<Insert table 4>

MASS SPECTRA

The mass spectra of few representative vanadium(III) complexes have been carried out and these have shown the molecular ion peak $[\text{M}^+]$ at 447.2 (m/z) (**1**, **10**), 756.7 (m/z) (**4**, **11**), and 1030 (m/z) (**7**, **12**). Similar molecular ion peak were shown by *meta*- and *para*-substituted derivatives. In addition to the molecular ion peak several other peaks were also observed, which are corresponding to the fragmented species after the consecutive removal of different groups. Moreover, the complex (**1**, **4** and **7**) contains chlorine atom in the dithiophosphate ligand moiety also contain chlorine atom that results in appearance of isotopic peaks in the mass spectrum. The masses of the fragmented ions, listed in the table, are calculated using one chlorine atom mass equal to 35 amu, as it is the most abundant isotope of chlorine atom. The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes. The mass spectra of these complexes are listed in the **Table 5**.

<Insert table 5>

Structural features

O,O'-Alkylenedithiophosphate and *O,O'*-ditolyldithiophosphate ligands mostly binds with the transition metal center in bidentate mode as illustrated by the literature survey³⁴⁻³⁷. Since the efforts to get the suitable crystals were not successful, so it would not be appropriate to predict a precise structure of these complexes without single crystal X-ray diffraction analysis. However, in conjunction with the literature reports and observations based on elemental analyses, IR, NMR (^1H , ^{13}C and ^{31}P) and mass spectra, a pentagonal bipyramidal (tpb-sp^3) geometry akin to $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_2(\text{L-L}')]\text{n}^{40}$ may tentatively be assigned for complexes $[\{(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}]$, whereas square pyramidal geometry, akin to $\text{exo}[\text{VO}_2\{\text{N}-(2\text{-oxidonaphthal)-His}\}]^{41}$, may be proposed for the complexes $[\{(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}]$.

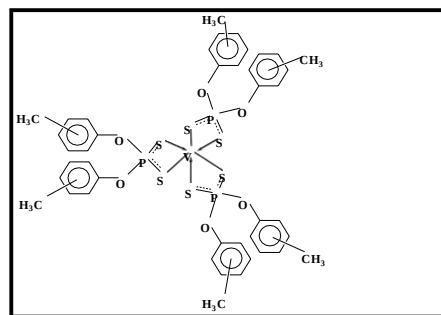


Figure 1: Proposed pentagonal bipyramidal structure of the complexes of the type $[\{(\text{CreO})_2 \text{PS}_2 \}_3 \text{VO}]$ (**7-9**); ($\text{Cre} = o-, m- \text{ or } p\text{-CH}_3\text{C}_6\text{H}_4-$)

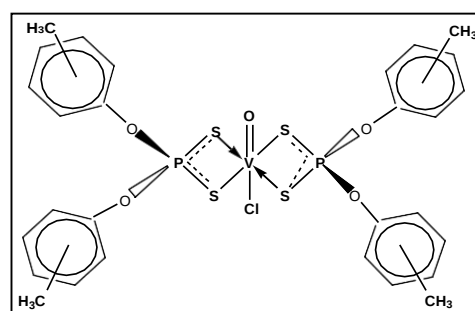


Figure 2: Proposed square bipyramidal structure of the complexes of the type $[\{(\text{CreO})_2 \text{PS}_2 \}_2 \text{VOCl}]$ (**4-6**); ($\text{Cre} = o-, m- \text{ or } p\text{-CH}_3\text{C}_6\text{H}_4-$)

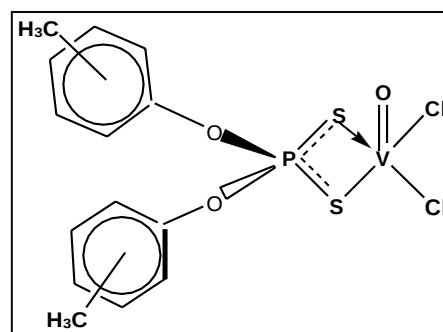


Figure 3: Proposed square bipyramidal structure of the complexes of the type $[\{(\text{CreO})_2 \text{PS}_2 \} \text{VOCl}_2]$ (**1-3**); ($\text{Cre} = o-, m- \text{ or } p\text{-CH}_3\text{C}_6\text{H}_4-$)

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Table 5. Mass spectral data of Vanadium(V) (*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates).

S. No.	M. W.	m/z, relative intensities of the ions and assignment
1	447.2	$[M^+]$ 447.2 (10) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{VOCl}_2\}^+$, $[M^+]$ 417.3 (28) [$(\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\text{VOCl}_2\}^+$, $[M^+]$ 269.2 (31) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{P}(\text{O})\text{S}_2\}\text{VOCl}_2\}^+$, $[M^+]$ 233.7 (45) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{P}(\text{O})\text{S}_2\}\text{VOCl}\}^+$, $[M^+]$ 198.2 (48) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{P}(\text{O})\text{S}_2\}\text{VO}\}^+$, $[M^+]$ 202.3 (66) [$(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}^-$, $[M^+]$ 107.1 (91) [$\text{CH}_3\text{C}_6\text{H}_4\text{O}\}^-$
4	756.7	$[M^+]$ 756.7 (11), 758.7 (3) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}\}^+$, $[M^+]$ 661 (20), 663 (7) [$\{(\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}\}^+$, $[M^+]$ 625.5 (26) [$\{(\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VO}\}^+$, $[M^+]$ 279.3 (48) [$(\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}^-$, $[M^+]$ 285.2 (31) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{P}(\text{O})\text{S}_2\}\text{VO}\}^+$, $[M^+]$ 202.3 (56) [$(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}^-$, $[M^+]$ 107.1 (91) [$\text{CH}_3\text{C}_6\text{H}_4\text{O}\}^-$
7	1030.0	$[M^+]$ 1030.0 (10) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}\}^+$, $[M^+]$ 721.2 (21) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VO}\}^+$, $[M^+]$ 625.5 (28) [$\{(\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VO}\}^+$, $[M^+]$ 279.3 (48) [$(\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}^-$, $[M^+]$ 285.2 (31) [$\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{P}(\text{O})\text{S}_2\}\text{VO}\}^+$, $[M^+]$ 202.3 (56) [$(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}^-$, $[M^+]$ 107.1 (91) [$\text{CH}_3\text{C}_6\text{H}_4\text{O}\}^-$
10	447.2	$[M^+]$ 447.2 (15) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}\text{VOCl}_2\}^+$, $[M^+]$ 269.2 (28) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{P}(\text{O})\text{S}_2\}\text{VOCl}_2\}^+$, $[M^+]$ 233.7 (45) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{P}(\text{O})\text{S}_2\}\text{VOCl}\}^+$, $[M^+]$ 198.2 (48) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{P}(\text{O})\text{S}_2\}\text{VO}\}^+$, $[M^+]$ 202.3 (66) [$(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}^-$, $[M^+]$ 156.3 (88) [$(\text{C}_6\text{H}_5)_2\}^-$, $[M^+]$ 107.1 (91) [$\text{C}_6\text{H}_5\text{CH}_2\text{O}\}^-$
11	756.7	$[M^+]$ 756.7 (11), 758.7 (3) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_2\text{VOCl}\}^+$, $[M^+]$ 482.7 (20), 484.7 (7) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}\text{VOCl}\}^+$, $[M^+]$ 285.2 (31) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{P}(\text{O})\text{S}_2\}\text{VO}\}^+$, $[M^+]$ 202.3 (56) [$(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}^-$, $[M^+]$ 156.3 (88) [$(\text{C}_6\text{H}_5)_2\}^-$, $[M^+]$ 107.1 (91) [$\text{C}_6\text{H}_5\text{CH}_2\text{O}\}^-$
12	1030.0	$[M^+]$ 1030.0 (10) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_3\text{VO}\}^+$, $[M^+]$ 721.2 (21) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_2\text{VO}\}^+$, $[M^+]$ 285.2 (31) [$\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{P}(\text{O})\text{S}_2\}\text{VO}\}^+$, $[M^+]$ 202.3 (56) [$(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}^-$, $[M^+]$ 156.3 (88) [$(\text{C}_6\text{H}_5)_2\}^-$, $[M^+]$ 107.1 (91) [$\text{C}_6\text{H}_5\text{CH}_2\text{O}\}^-$



Table 1. Synthesis and physical properties of Vanadium(V) (*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates).

S.No	Reactants	VOCl ₃ (mmol)	Molar ratio	Compounds	Yield %	Analyses		calculated(found)	
	Ligand, g (mmol)			Physical state		V	S	C	Cl
(1)	(<i>o</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 1.01(3.001)	0.529(3.001)	1:1	{(<i>o</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ }VOCl ₂ yellowish sticky-solid	86	11.29 (11.39)	14.27 (14.31)	18.75 (18.78)	15.80 (15.87)
(2)	(<i>m</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 1.01(3.001)	0.529(3.001)	1:1	{(<i>m</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ }VOCl ₂ yellowish sticky-solid	85	11.34 (11.39)	14.29 (14.31)	18.70 (18.78)	15.85 (15.87)
(3)	(<i>p</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 1.01(3.001)	0.529(3.001)	1:1	{(<i>p</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ }VOCl ₂ yellowish sticky-solid	87	11.37 (11.39)	14.25 (14.31)	18.76 (18.78)	15.82 (15.87)
(4)	(<i>o</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 2.01(6.001)	0.529(3.001)	1:2	{(<i>o</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ } ₂ VOCl Light yellow viscous solid	83	6.99 (7.07)	17.67 (17.75)	23.27 (23.30)	4.87 (4.92)
(5)	(<i>m</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 1.01(3.001)	0.285(1.016)	1:2	{(<i>m</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ } ₂ VOCl Light yellow viscous solid	83	7.01 (7.07)	17.71 (17.75)	23.29 (23.30)	4.78 (4.92)
(6)	(<i>p</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 1.01(3.001)	0.285(1.016)	1:2	{(<i>p</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ } ₂ VOCl Light yellow viscous solid	84	7.03 (7.07)	17.73 (17.75)	23.24 (23.30)	4.90 (4.92)
(7)	(<i>o</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 2.01(6.001)	0.345(2.001)	1:3	{(<i>o</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ } ₃ VO Light yellow viscous solid	86	5.01 (5.12)	19.20 (19.30)	25.30 (25.33)	-----
(8)	(<i>m</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 2.01(6.001)	0.345(2.001)	1:3	{(<i>m</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ } ₃ VO Light yellow viscous solid	87	5.10 (5.12)	19.25 (19.30)	25.27 (25.33)	-----
(9)	(<i>p</i> -MeC ₆ H ₄ O) ₂ PS ₂ Na 2.01(6.001)	0.345(2.001)	1:3	{(<i>p</i> -CH ₃ C ₆ H ₄ O) ₂ PS ₂ } ₃ VO Light yellow viscous solid	83	5.00 (5.12)	19.27 (19.30)	25.31 (25.33)	-----
(10)	(C ₆ H ₅ CH ₂ O)PS ₂ Na 0.529(3.001)	0.529(3.001)	1:1	[{(C ₆ H ₅ CH ₂ O) ₂ PS ₂ }VOCl ₂] Light yellow viscous liquid	83	11.28 (11.39)	14.27 (14.31)	18.76 (18.78)	15.83 (15.87)
(11)	(C ₆ H ₅ CH ₂ O)PS ₂ Na 0.529(3.001)	0.529(3.001)	1:2	[{(C ₆ H ₅ CH ₂ O) ₂ PS ₂ } ₂]VOCl Light yellow viscous liquid	84	7.02 (7.07)	17.71 (17.75)	23.25 (23.30)	4.89 (4.92)
(12)	(C ₆ H ₅ CH ₂ O)PS ₂ Na 0.345(2.001)	0.345(2.001)	1:3	[{(C ₆ H ₅ CH ₂ O) ₂ PS ₂ } ₃ VO] Light yellow viscous liquid	85	5.11 (5.12)	19.24 (19.30)	25.32 (25.33)	

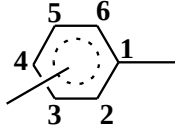


Table 2: IR spectral data of Vanadium(V)(*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates (cm^{-1}).

S. No.	Compounds	$\nu(\text{P})\text{-O-C}$	$\nu\text{P-O-(C)}$	Aromatic Ar-H	$\nu(\text{P-S})_{(asym)}$	$\nu(\text{P-S})_{(sym)}$	$\nu(\text{V-Cl})$	$\nu(\text{V-S})$	$\nu(\text{V=O})$
1	$(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\text{VOCl}_2$	1155,s	941,s	2928,b	661,s	553,s	546,m	446,m	940,s
2	$(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\text{VOCl}_2$	1150,s	946,s	2929,b	659,s	552,s	545,m	445,m	937,s
3	$(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\text{VOCl}_2$	1161,s	944,s	2927,b	657,s	556,s	546,m	439,m	940,s
4	$[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}]$	1104,s	940,s	2930,b	651,s	526,s	535,m	446,m	927,s
5	$[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}]$	1140,s	932,s	2927,b	661,s	527,s	532,m	448,m	937,s
6	$[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}]$	1158,s	935,s	2930,b	659,s	529,s	530,m	446,m	939,s
7	$[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}]$	1134,s	936,s	2928,b	657,s	566,s	--	444,m	920,s
8	$[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}]$	1132,s	934,s	2929,b	658,s	554,s	--	467,m	924,s
9	$[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}]$	1134,s	937,s	2930,b	660,s	567,s	--	448,m	925,s
10	$(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\text{VOCl}_2$	990,s	820,m	2920,b	660,s	555,m	546,m	440,m	941,s
11	$[\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_2\text{VOCl}_2]$	985,s	825,m	2929,b	660,s	530,s	535,m	448,m	940,s
12	$[\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_3\text{VO}]$	990,s	835,s	2930,b	661,s	568,s	--	445,m	925,s

m = medium, s = sharp, b = broad.

Table 3. ^1H and ^{31}P NMR spectral data of Vanadium(V) (*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates in ppm.

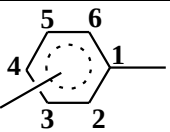
S. No	Compound	^1H NMR		^{31}P NMR
		CH ₃		
1	$[(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]\text{VOCl}_2$	1.9, s, 6H, -CH ₃	6.9, d, 2 H ₍₃₎ ($J = 7.6$ Hz); 6.6, t, 2 H ₍₄₎ ($J = 8.4$ Hz); 7.0, t, 2 H ₍₅₎ ($J = 7.4$ Hz); 6.7, d, 2 H ₍₆₎ ($J = 8.4$ Hz)	71.2
2	$[(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]\text{VOCl}_2$	2.1, s, 6H, -CH ₃	6.6, s, 2 H ₍₂₎ ; 6.9, d, 2 H ₍₄₎ ($J = 8.4$ Hz); 7.0, t, 2 H ₍₅₎ ($J = 7.4$ Hz); 6.7, d, 2 H ₍₆₎ ($J = 8.4$ Hz)	73.2
3	$[(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]\text{VOCl}_2$	2.3, s, 6H, -CH ₃	6.9, d, 4 H _(2,6) ($J = 8.4$ Hz); 6.6, d, 4 H _(3,5) ($J = 8.2$ Hz)	73.5
4	$[(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_2\text{VOCl}$	1.9, s, 12H, -CH ₃	6.9, d, 4 H ₍₃₎ ($J = 7.6$ Hz); 6.6, t, 4 H ₍₄₎ ($J = 8.4$ Hz); 7.0, t, 4 H ₍₅₎ ($J = 7.4$ Hz); 6.7, d, 4 H ₍₆₎ ($J = 8.4$ Hz)	75.3
5	$[(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_2\text{VOCl}$	2.1, s, 12H, -CH ₃	6.6, s, 4 H ₍₂₎ ; 6.9, d, 4 H ₍₄₎ ($J = 8.4$ Hz); 7.0, t, 4 H ₍₅₎ ($J = 7.4$ Hz); 6.7, d, 4 H ₍₆₎ ($J = 8.4$ Hz)	76.1
6	$[(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_2\text{VOCl}$	2.3, s, 12H, -CH ₃	6.9, d, 8 H _(2,6) ($J = 8.4$ Hz); 6.6, d, 8 H _(3,5) ($J = 8.2$ Hz)	75.2
7	$[(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_3\text{VO}$	1.9, s, 18H, -CH ₃	6.9, d, 6 H ₍₃₎ ($J = 7.6$ Hz); 6.6, t, 6 H ₍₄₎ ($J = 8.4$ Hz); 7.0, t, 6 H ₍₅₎ ($J = 7.4$ Hz); 6.7, d, 6 H ₍₆₎ ($J = 8.4$ Hz)	80.1
8	$[(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_3\text{VO}$	2.1, s, 18H, -CH ₃	6.6, s, 6 H ₍₂₎ ; 6.9, d, 6 H ₍₄₎ ($J = 8.4$ Hz); 7.0, t, 6 H ₍₅₎ ($J = 7.4$ Hz); 6.7, d, 6 H ₍₆₎ ($J = 8.4$ Hz)	79.5
9	$[(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]_3\text{VO}$	2.3, s, 18H, -CH ₃	6.9, d, 12 H _(2,6) ($J = 8.4$ Hz); 6.6, d, 12 H _(3,5) ($J = 8.2$ Hz).	79.5
10	$\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\text{VOCl}_2$	5.2, s, 4H, -CH ₂ -	6.7, d, 4H _(2,6) ($J = 8.2$), 7.0, d, 4H _(3,5) ($J = 8.0$), 7.5, t, 2H ₍₄₎ ($J = 7.8$ Hz).	70.5
11	$[(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2]_2\text{VOCl}$	5.2, s, 8H, -CH ₂ -	6.7, d, 8H _(2,6) ($J = 8.2$), 7.0, d, 8H _(3,5) ($J = 8.0$), 7.5, t, 4H ₍₄₎ ($J = 7.8$ Hz).	73.5
12	$[(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2]_3\text{VO}$	5.2, s, 12H, -CH ₂ -	6.7, d, 12H _(2,6) ($J = 8.2$), 7.0, d, 12H _(3,5) ($J = 8.0$), 7.5, t, 6H ₍₄₎ ($J = 7.8$ Hz).	80.5

s = singlet, d= doublet, m = multiple



Table 4: ^{13}C NMR spectral data of Vanadium(V)(*o*-, *m*- or *p*-ditolyl)/dibenzylthiophosphates in ppm.

s = singlet, m = multiplet; a = chemical shift value of $-\text{CH}_3$ moiety attached to tolyl ring and b = chemical shift value of hydrogen bonded oxygen

									
S. No	Compound	$-\text{CH}_3^a$	C- CH_2	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
1	$[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{VOCl}_2]$	20.7	--	144.0	115.6*	120.7	130.2	121.5	129.7
2	$[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{VOCl}_2]$	20.8	--	149.0	116.3	120.2*	130.3	131.5	134.6
3	$[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{VOCl}_2]$	20.6	--	150.6	115.3	120.9	130.8*	120.9	115.3
4	$[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}]$	20.9	--	144.9	115.6*	121.7	131.1	125.5	132.5
5	$[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}]$	21.2	--	149.7	118.1	120.2*	131.2	131.7	133.6
6	$[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{VOCl}]$	21.0	--	150.4	117.8	121.9	130.8*	121.9	117.8
7	$[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}]$	20.8	--	145.0	115.6*	125.1	134.1	121.5	129.7
8	$[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}]$	20.9	--	149.3	115.4	120.2*	134.9	131.5	134.6
9	$[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{VO}]$	21.0	--	151.0	115.8	124.3	130.8*	124.3	115.8
10	$[\{\text{C}_6\text{H}_5\text{CH}_2\text{O}\}_2\text{PS}_2\}\text{VOCl}_2]$	--	77.6	149.5	115	121.3	131.4	121.3	115
11	$[\{\{\text{C}_6\text{H}_5\text{CH}_2\text{O}\}_2\text{PS}_2\}_2\text{VOCl}_2]$	--	77.7	150	116	123.2	132.2	123.2	116
12	$[\{\{\text{C}_6\text{H}_5\text{CH}_2\text{O}\}_2\text{PS}_2\}_3\text{VO}]$	--	77.8	150	114	125.1	134.5	125.1	114