



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

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**Abstract-** Reaction of Vanadiumoxytrichloride,  $\text{VOCl}_3$  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*- $\text{MeC}_6\text{H}_4\text{O}$ ) $_2\text{PS}_2\text{VOCl}_2$ ], [ $\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}_2\text{VOCl}_2$ ], [ $\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})\text{PS}_2\}_2\text{VOCl}$ ], [ $\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_2\text{VOCl}$ ], [ $\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_3\text{VO}$ ] and [ $\{(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\}_3\text{VO}$ ]. 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  $^{31}\text{P}$  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: Gramepositive, *Enterococcus faecalis* and Gramenegative, *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<sup>1-2</sup>, industrial<sup>3</sup> and catalytical<sup>4</sup> processes. Vanadate acts as inhibitors<sup>5-6</sup> 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<sup>3,7</sup>. Uses of  $\text{V}^{\text{IV}}\text{O}$  and  $\text{V}^{\text{VO}}$  complexes as catalyst for conversion of sulfide to sulfoxide are known<sup>8</sup>. Dialkylphosphonates, dialkyldithiophosphonates, *O*,*O'*-dialkyldithiophosphates and *O*,*O'*-alkylenedithiophosphates are well known due to their versatile utility as active pesticides<sup>9-10</sup> and also for providing various aspects of bonding with several metals and metalloids<sup>11-14</sup>. These derivatives find

extensive application in agriculture<sup>15-16</sup>, industries<sup>17-18</sup> and analytical studies<sup>19-20</sup>. Usually these ligands predominantly exhibited bidentate mode of bonding<sup>21-27</sup>. Moreover the less common monodentate linkages have also been observed in the case of nickel and tin<sup>28-29</sup>. Recently, the synthesis and characterization of ditolyldithiophosphates added a new development in the area of dithiophosphate chemistry<sup>30-31</sup>. Some metal complexes with the ditolyl/dibenzyl dithiophosphate ligands have also been reported<sup>23, 32-39</sup>. Some interesting application of ditolyl and benzyl dithiophosphates has also been reported such as rubber vulcanizers<sup>40</sup>, aerofloats<sup>37</sup>, polymerization catalyst<sup>42</sup>, oil additives<sup>39</sup> and acaricides<sup>43</sup>. 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<sup>32-33</sup>.  $\text{VOCl}_3$  was prepared<sup>25</sup> by the reaction of  $\text{V}_2\text{O}_3$  with  $\text{SOCl}_2$ . Sulfur was estimated as  $\text{BaSO}_4$



(Messenger's method) and vanadium was estimated as  $\text{AgVO}_4$ . 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  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a brucker DRX 500 MHz spectrometer using TMS as the internal reference for  $^1\text{H}$  NMR and 85%  $\text{H}_3\text{PO}_4$  as an internal reference for  $^{31}\text{P}$  NMR at University of Panjab, Chandigarh.

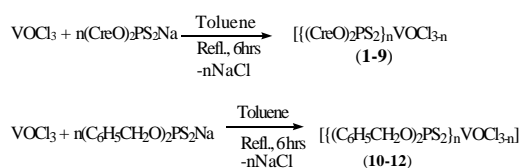
**Synthesis of**  $[(o-, m- \text{ and } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]_n\text{VOCl}_{3-n}$ , (where  $n=0,1,2$ ).

To a toluene solution ( $\sim 25$ ) of vanadyloxychloride,  $\text{VOCl}_3$ , (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  $\sim 6$  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  $\text{VOCl}_3$  with sodium salt of ditolyl and benzyl dithiophosphonate, (*o*-, *m*- and *p*- $\text{MeC}_6\text{H}_4\text{O}$ ) $_2\text{PS}_2\text{Na}$ , ( $\text{C}_6\text{H}_5\text{CH}_2\text{O}$ ) $_2\text{PS}_2\text{Na}$ , 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  $[(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\text{VOCl}_2]$ ,  $[(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2\text{VOCl}_2]$ ,  $[(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]_2\text{VOCl}$ ,  $[(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2]_2\text{VOCl}$ ,  $[(o-, m- \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]_3\text{VO}$  and  $[(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{PS}_2]_3\text{VO}$  (scheme 1).



**Scheme 1.** Reaction of  $\text{VOCl}_3$  with  $\{(\text{CreO})_2\text{PS}_2\text{Na}\}$ ; (where Cre = *o*-, *m*- or *p*- $\text{MeC}_6\text{H}_4$ - 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 appear 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 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 spectra<sup>34-37</sup> of these complexes have shown characteristic 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 characteristic 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>

### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectra<sup>34-37</sup> of these complexes (in  $\text{CDCl}_3$ ) 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**.

### $^{31}\text{P}$ NMR spectra

The  $^{31}\text{P}$  NMR spectra<sup>34-37</sup> (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  $^{31}\text{P}$  NMR spectral data are given in the **Table 3**.

<Insert Table 3>

#### $^{13}\text{C}$ NMR spectra

The  $^{13}\text{C}$  NMR spectral<sup>34-37</sup> data of few representative compounds have been recorded in  $\text{CDCl}_3$ , 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-( $\text{CH}_3$ ) carbon was observed at 115.6 ppm, 120.2 ppm and 130.8 ppm respectively. The  $^{13}\text{C}$  NMR spectral data are given in the **Table 4**.

<Insert table 4>

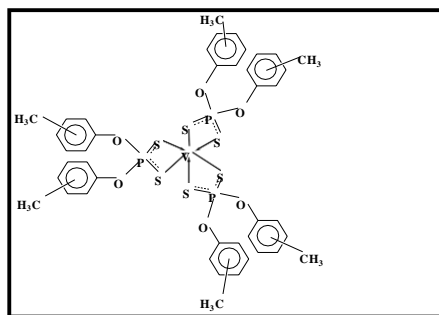
#### MASS SPECTRA

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**.

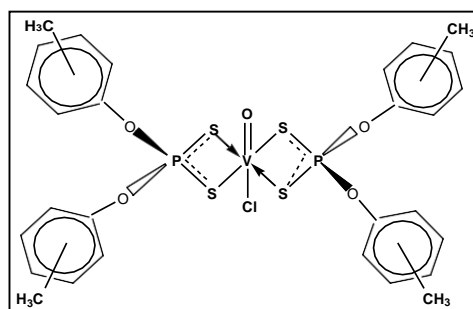
<Insert table 5>

#### Structural features

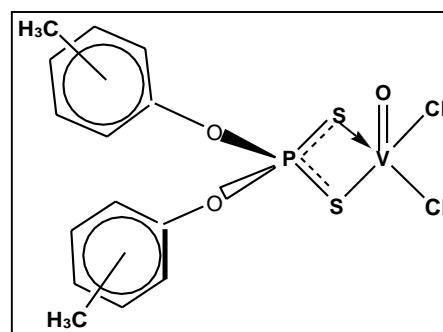
*O, O'*-Alkylenedithiophosphate and *O, O'*-ditolydithiophosphate ligands mostly binds with the transition metal center in bidentate mode as illustrated by the literature survey<sup>34-37</sup>. Since the efforts to get the suitable crystals were not successful, so it would not be appropriate to predict 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 ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ ) and mass spectra, a pentagonal bipyramidal ( $\text{tbp-spd}^3$ ) geometry akin to  $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_2(\text{L-L}')]^n$ <sup>40</sup> 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  $\text{exo}[\text{VO}_2\{\text{N}-(2\text{-oxidonaphthal)-His}\}]$ <sup>41</sup>, 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  $[\{(CreO)_2PS_2\}_3VO]$  (**7-9**); (Cre = *o*-, *m*- or *p*- $\text{CH}_3\text{C}_6\text{H}_4$ -)



**Figure 2:** Proposed square bipyramidal structure of the complexes of the type  $[\{(CreO)_2PS_2\}_2VOCl]$  (**4-6**); (Cre = *o*-, *m*- or *p*- $\text{CH}_3\text{C}_6\text{H}_4$ -)



**Figure 3:** Proposed square bipyramidal structure of the complexes of the type  $[\{(CreO)_2PS_2\}VOCl_2]$  (**1-3**); (Cre = *o*-, *m*- or *p*- $\text{CH}_3\text{C}_6\text{H}_4$ -)

#### REFERENCES

- [1]. Chasteen N. D., *Kulwer Academic Publishers, Dordrecht, The Netherland, (1990)*.
- [2]. Rehder D., *Angew. Chem., Int. Ed. Engl.*, **30**, 148, (1991).
- [3]. Roxel J. and Brec r., *Ann. Rev. Master. Sci.*, **16**, 137 (1986).
- [4]. Thompson K. H., McNeil J. H. and Orvig., *Chem. Rev.*, **99**, 2561 (1999).



- [5]. Nielson F. H., Marcel Dekker, *New York*, **31**, 543 (1995).
- [6]. Rehder D., Wolfgang p. and Oeynhausen V, *Angewandte Chemie, International Edition in English* **28**, 1221-1222 (1989).
- [7]. Reynold J. F., Biggs W. R and Fetzer J. C., *Liq. Fuel. Technol.*, **3**, 423 (1985).
- [8]. Nakajima K., Kojima M., Fujita J., Tortumi K and Saito K., *Bull. Chem. Soc. Jpn.*, **62**, 760 (1989).
- [9]. Fest. C and Schmidt. K. J., *The Chemistry of Organophosphorous Pesticides (2nd Ed.)* Springer Verlag, NewYork (1982).
- [10]. Umemura M., Konishi M., Fukushima A., Hisano J and Okamoto T., *EVR Pat. EP*. **205**, 165; *Chem. Abstr.*, **106**, 87468n (1987).
- [11]. Wasson J. R., Waltermann G. M. and Stocklosa H. J., *Top. Curr. Chem.*, **35**, 65 (1973).
- [12]. Chauhan B. P. S., Srivastava G. and Mehrotra R. C., *Coord. Chem. Rev.*, **55**, 207 (1984).
- [13]. Chauhan H. P. S., *Coord. Chem.Rev.*, **173** (1), 1-30 (1998).
- [14]. Haiduc I., *Rev. Inorg. Chem.*, **3**, 353 (1981).
- [15]. Mihailovski, US Pat. No 4071545 (1978), Mihailovski, *Chem. Abstr.*, **88**, 170295j (1978).
- [16]. Kanazawa J., Kubo H. and Sato R., *Agric. Biol. Chem.*, **29**, 43 (1965).
- [17]. Farmer H. H., Malone B. W. and Tompkins H. F., *S. African Pat.*, **68**, 02, 189 (1968), *Chem. Abstr.*, **71**, 23626f (1969).
- [18]. Stewart C. L., (Ominitec Inc., USA), US Pat **200**, 106, 04 (2002), *Chem. Abstr.*, **138**, 41800 (2002).
- [19]. Hayashi K., Sasaki Y., Tagashira S., Soma Y. and Kato S., *Anal. Sci.*, **105**, 237529d (1986).
- [20]. Shishkov A. and Atanasova D., Nauchi. Tr. Plovdivski Univ., 19, 265 (1982), *Chem. Abstr.*, 98, 190813 (1983).
- [21]. Pandey S. K., Srivastava G. and Mehrotra R. C., *Synth. React. Inorg. Met-Org. Chem.*, **19**, 795 (1989).
- [22]. S. K. Pandey, G. Srivastava and R. C. Mehrotra, *J. Ind. Chem. Soc.*, 1989, **66**, 558.
- [23]. Chander R., Kalsotra B. L and Pandey S. K., *Ind. L. Chem.*, 43A, 1134 (2004).
- [24]. Lefferts J. L., Molloy, K. C , Zuckerman J. J., Hauduc, I., Curtui M., Gutal G. and Ruse d., *Inorg. Chem.*, **19**, 2861 (1980).
- [25]. Tripathi U. N., Bipin P. P., Mirza. And Chaturvedi A., *Pol. J. Chem.*, **73**, 1751 (1999).
- [26]. R. Chander, B. L. Kalsotra and S. K. Pandey, *Trans. Met. Chem.*, 2003, **28**, 405.
- [27]. Tripathi U. N., *Phosph-sulfur. Silicon and the Related Elements*, **159** (1), 47 (2000).
- [28]. Shetty P. S. and Fernando Q., *J. Am. Chem. Soc.*, 92, 3964 (1970).
- [29]. Molloy K. C., Hussain M. B., Helm D.V., Zuckerman J. J. and Hauduc I., *Inorg. Chem.*, **18** (12), 3507 (1979).
- [30]. A. Kumar, K. R. Sharma and S. K. Pandey, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2007, 182, 1023.
- [31]. J. E. Drake, C. L. B. McDonald, A. Kumar, S. K. Pandey and R. Ratnani, *J. Chem. Crystallgr.*, 2005, **35**, 447.
- [32]. B. Gupta, S. Magotra and S. K. Pandey, *Monatsh. Chem.*, 2008, 139, 747.
- [33]. B. Gupta, K. Kumar and S. K. Pandey, *Synth. React. Inorg. Met-Org. Nano Met. Chem.*, 2009, **39**, 559.
- [34]. D. Kumar, B. Gupta and S. K. Pandey, *Int. J. Chem.*, 2012, **1**, 247.
- [35]. S. Kour, B. Gupta, R. Chander and S. K. Pandey, *Main Group Met. Chem.*, 2009, **32**, 195.
- [36]. S. Sharma, S. Magotra and S. K. Pandey, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2009, **184**, 2140.
- [37]. A. Kumar, D. Kumar and S. K. Pandey, *Synth. React. Inorg. Met-Org. Nano Met. Chem.*, 2007, **37**, 697.
- [38]. K. R. Sharma, D. Kumar and S. K. Pandey, *J. Coord. Chem*, 2008, **61**, 1811.
- [39]. A. Kumar, K. Kumar and S. K. Pandey, *Pol. J. Chem.*, 2009, **83**, 2097.
- [40]. Drake J. E., Gurnani C., Hursthouse M. B., Light M. E., Nirwan M. and Ratnani R., *App. Org.-Met. Chem.*, **21** (7), 539 (2007).
- [41]. A.Kumar,; D.Kumar,; S.K.Pandey., *Synth. And React. Inorg. Met-Org. Nano Met. Chem.*, **37**, 697 (2007).
- [42]. Mc cleverty J. A., Kowalaski R. S. Z., Bailey N. A., Mulvaney R. and Cleirigh O., *J. Chem. Soc. Dalton Trans*, **4**, 627 (1983).
- [43]. N. N. Glebova, O. K. Sharaev, E. I. Tinyakova and B. A. Dolgoplosk, *Petrochem. Synth.*, 1995, **37**, 1145 (*Chem. Abstr.* 1996, **125**, 143371g).
- [44]. F. Yuan, Y. Haung and Q. Xie, *App. Orgomet. Chem.*, 2002, **16**, 660.





**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 <sup>+</sup> ] 447.2 (10) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> }VOCl <sub>2</sub> ] <sup>+</sup> ,<br>[M <sup>+</sup> ] 417.3 (28) [(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> VOCl <sub>2</sub> ] <sup>+</sup> ,<br>[M <sup>+</sup> ] 269.2 (31) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)P(O)S <sub>2</sub> }VOCl <sub>2</sub> ] <sup>+</sup> ,<br>[M <sup>+</sup> ] 233.7 (45) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)P(O)S <sub>2</sub> }VOCl] <sup>+</sup> ,<br>[M <sup>+</sup> ] 198.2 (48) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)P(O)S <sub>2</sub> }VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 202.3 (66) [(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 107.1 (91) [CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O] <sup>-</sup> |
| 4      | 756.7  | [M <sup>+</sup> ] 756.7 (11), 758.7 (3) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>2</sub> VOCl] <sup>+</sup> ,<br>[M <sup>+</sup> ] 661 (20), 663 (7) [ {(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>2</sub> VOCl] <sup>+</sup> ,<br>[M <sup>+</sup> ] 625.5 (26) [ {(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>2</sub> VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 279.3 (48) [(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 285.2 (31) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)P(O)S <sub>2</sub> }VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 202.3 (56) [(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 107.1 (91) [CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O] <sup>-</sup>   |
| 7      | 1030.0 | [M <sup>+</sup> ] 1030.0 (10) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>3</sub> VO],<br>[M <sup>+</sup> ] 721.2 (21) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>2</sub> VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 625.5 (28) [ {(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>2</sub> VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 279.3 (48) [(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 285.2 (31) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)P(O)S <sub>2</sub> }VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 202.3 (56) [(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 107.1 (91) [CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O] <sup>-</sup>                    |
| 10     | 447.2  | [M <sup>+</sup> ] 447.2 (15) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O) <sub>2</sub> PS <sub>2</sub> }VOCl <sub>2</sub> ] <sup>+</sup> ,<br>[M <sup>+</sup> ] 269.2 (28) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)P(O)S <sub>2</sub> }VOCl <sub>2</sub> ] <sup>+</sup> ,<br>[M <sup>+</sup> ] 233.7 (45) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)P(O)S <sub>2</sub> }VOCl] <sup>+</sup> ,<br>[M <sup>+</sup> ] 198.2 (48) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)P(O)S <sub>2</sub> }VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 202.3 (66) [(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 156.3 (88) [(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 107.1 (91) [C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O] <sup>-</sup>  |
| 11     | 756.7  | [M <sup>+</sup> ] 756.7 (11), 758.7 (3) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>2</sub> VOCl] <sup>+</sup> ,<br>[M <sup>+</sup> ] 482.7 (20), 484.7 (7) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O) <sub>2</sub> PS <sub>2</sub> }VOCl] <sup>+</sup> ,<br>[M <sup>+</sup> ] 285.2 (31) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)P(O)S <sub>2</sub> }VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 202.3 (56) [(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 156.3 (88) [(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 107.1 (91) [C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O] <sup>-</sup>  |
| 12     | 1030.0 | [M <sup>+</sup> ] 1030.0 (10) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>3</sub> VO],<br>[M <sup>+</sup> ] 721.2 (21) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sub>2</sub> VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 285.2 (31) [ {(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)P(O)S <sub>2</sub> }VO] <sup>+</sup> ,<br>[M <sup>+</sup> ] 202.3 (56) [(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O)PS <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 156.3 (88) [(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup> ,<br>[M <sup>+</sup> ] 107.1 (91) [C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O] <sup>-</sup>   |

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

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

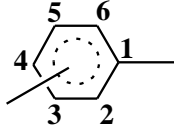


Table 2: IR spectral data of Vanadium(V)(*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates ( $\text{cm}^{-1}$ ).

| S. No. | Compounds   | $\nu(\text{P})\text{-O-C}$ | $\nu\text{P-O-(C)}$ | Aromatic<br>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.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectral data of Vanadium(V) (*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates in ppm.

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

s = singlet, d= doublet, m = multiple





Table 4:  $^{13}\text{C}$  NMR spectral data of Vanadium(V)(*o*-, *m*- or *p*-ditolyl)/dibenzylidithiophosphates 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- $\text{CH}_2$ | 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   |