ISSN: 0976-3031

Available Online at http://www.recentscientific.com

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 9, Issue, 4(A), pp. 25584-25587, April, 2018

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF O-ALKYL/ O-ARYL TRITHIOPHOSPHATE DERIVATIVES OF VANADIUM (III)

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DOI: http://dx.doi.org/10.24327/ijrsr.2018.0904.1887

ARTICLE INFO

Article History:

Received 11th January, 2018
Received in revised form 5th February, 2018
Accepted 24th March, 2018
Published online 28th April, 2018

Key Words:

Vanadium (III) chloride, O-alkyl /O-aryl trithiophosphate, octahedral geometry, antibacterial activity, gram positive and gram negative bacteria.

ABSTRACT

O-alkyl/O-aryl trithiophosphates of Vanadium (III) of general formula $V[SSH(S)POR]_3$ where (R= Me, Et, Pr^i, Bu^i, Ph, CH_3Ph) have been synthesized by the reaction of Vanadium trichloride and O-alkyl/O-aryl trithiophosphoric acid in 1:3 molar ratio, respectively and refluxed in methanol. The newly synthesized derivatives are dark green sticky solids which convert into needle liked crystals, insoluble in common organic solvent but soluble in co-ordinating solvents like DMSO, DMF etc. These derivatives have been characterized by elemental analysis (C,H,S), molecular weight measurement and spectral studies such as IR and NMR(^1H, ^{13}C, ^{31}P). On the basis of above chemical parameters and spectral studies, bidentate behaviour of trithiophosphate ligand and octahedral geometry have been proposed for these monomeric derivatives.

The newly synthesized derivatives show effectiveness for antibacterial activities against gram positive and gram negative bacteria. Comparative study of antibacterial effect has also been made with standard drugs. Paper disc method was used for antibacterial activities.

INTRODUCTION

The chemistry of organic derivatives of transistion and non transistion metals with sulphur and phosphorus containing ligand has been one of the most active area of metallo-organic chemistry during last 3-4 decades[1-5]. It is partly due to their wide industrial and biological applications as well as interesting structural features and partly due to unusual bonding modes (monodentate, bidentate, chelating and bridging) of many complexes with sulphur containing ligands. These compounds are widely used as pesticides[6], insecticides[7-8], bacteriocides[9] etc. So it was interested to extend the investigation to trithiophosphate ligand. Synthesizing and screening the antibacterial activity of various metal derivatives of trithiophosphates ligand have been done in recent years[10-14]. Many O-alkyl/O-aryl trithiophosphate derivatives of the tin[15-16], arsenic[17], boron[18] aluminium[19], iron[20], chromium[21], zinc[22], manganese[23] and acetyl, benzyl and benzoyl chloride[24] have been prepared and studied in our laboratory. O-alkyl and O-alkylene dithiophosphate of Vanadium[25] have been prepared but synthesis, characterization and antibacterial study have not been carried out on O-alkyl/O-aryl trithiophosphate derivatives of Vanadium(III). Vanadium trichloride acts as a reducing agent. It is used as catalyst in organic reactions. The most important use of Vanadium is an additive for steel. It is used as rust resistant. It is also added to steel to stabilize carbides. Due to its low fission neutron cross section Vanadium is also used in nuclear applicatons.

In the view of this it was considered worthwhile to synthesize O-alkyl/O-aryl trithiophosphate derivatives of Vanadium (III) and study their chemical bonding modes, antibacterial activity and to compare their antibacterial activities with standard drugs like Imipenem and Linezolid.

Expeimental

Stringent precautions were taken to exclude moisture from experimental setup. Solvents (benzene, methanol, DMSO) were dried by standard methods. Alcohols were purified before use. VCl_3 was procured from Sigma Aldrich and was used as received. Carbon and hydrogen were estimated by coleman C, H and N analyser. Messenger's method[26] was used for estimation of sulphur. Molecular weight were determined by Knauer vapour pressure osmometer in $CHCl_3$. IR spectra were

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recorded as KBr pallets on Perkin Elmer spectrum version 10.4.00 spectrophotometer. NMR spectra(^{1}H, ^{13}C, ^{31}P) were recorded in deuteriated DMSO using DELTA 2_NMR spectrophotometer.

Synthesis of $[C_6H_5OP(S)SSH]_3V$

To weighed amount of Vanadium trichloride (0.2363g, 1.5019mmol) in methanol (approx. 25mL), $H_2S_3POC_6H_5$ (1.0010g, 4.5059mmol) was added in 1:3 molar ratio. Immediately the colour of reaction mixture changed from dark brown to dark green. The mixture was refluxed for 8-10 hours until the liberation of hydrochloride gas ceased. Solvent was removed under pressure. Product obtained as dark green sticky solids converts into needle like crystals. They have been washed with aqueous ethanol and recrystalized.

All other derivatives were synthesized by similar method. The relevant synthetic and analytic data are given in table-1.

IR Spectra

IR spectra of new derivatives have been measured in the range 4000-200cm^{-1}. Following characteristic band were obtained in IR spectra of these derivatives:

1. The strong intensity bands present in the region 1149.75-1218.85 cm^{-1} and 995.50-1055.28cm^{-1} have been assigned to (P)-O-C and P-O-(C) vibrations, respectively.
2. A sharp band present in the region 756.08-816.97 cm^{-1} were observed for P=S vibrations. These bands shows shifting of 20-30cm^{-1} towards lower frequency with respect to its position in free ligand. The shifting is probably due to co-ordination of sulphur of P=S group to the metal atom.
3. Medium intensity band in the region 555.90-693.37cm^{-1} was attributed to P-S vibrations.

Table 1 Synthetic and Analytic Data of $V[SSH(S)POR]_3$

S. No.	Reactant .....g....(mmol)		Product ....g… ...%..	Analysis % found (calcd.)				Molecular Weight found (calcd.)
	VCl_3	$ROPS_3H_2$ R = ……..		C	H	S	V	
1.	0.3279 [2.0844]	CH_3 1.0015 [6.2535]	$V[CH_3OP(S)SSH]_3$ 1.0070 91.4	6.45 (6.81)	2.13 (2.27)	53.45 (54.60)	8.93 (9.64)	497.95 (528.39)
2.	0.3035 [1.9293]	C_2H_5 1.0080 [5.7881]	$V[C_2H_5OP(S)SSH]_3$ 1.0200 92.7	11.89 (12.62)	3.04 (3.15)	49.78 (50.58)	8.35 (8.93)	
3.	0.2802 [1.7814]	$^{i}C_3H_7$ 1.0055 [5.3441]	$V[^{i}C_3H_7OP(S)SSH]_3$ 0.9978 90.8	16.86 (17.63)	3.62 (3.92)	46.94 (47.12)	7.87 (8.32)	583.97 (612.39)
4.	0.2596 [1.6504]	$^{i}C_4H_9$ 1.0009 [4.9513]	$V[^{i}C_4H_9OP(S)SSH]_3$ 0.9612 89.0	20.93 (22.01)	4.31 (4.58)	43.67 (44.09)	6.89 (7.78)	
5.	0.2363 [1.5019]	C_6H_5 1.0010 [4.5059]	$V[C_6H_5OP(S)SSH]_3$ 1.0089 94.0	29.48 (30.23)	2.27 (2.52)	39.98 (40.38)	6.76 (7.13)	684.25 (714.39)
6.	0.2230 [1.4179]	o-$CH_3C_6H_4$ 1.0045 [4.2536]	$V[o\text{-}CH_3C_6H_4OP(S)SSH]_3$ 1.0026 93.5	32.19 (33.32)	2.97 (3.17)	37.75 (38.15)	5.93 (6.73)	730.07 (756.39)
7.	0.2226 [1.4150]	m-$CH_3C_6H_4$ 1.0025 [4.2451]	$V[m\text{-}CH_3C_6H_4OP(S)SSH]_3$ 0.9745 91.0	32.56 (33.32)	3.01 (3.17)	37.67 (38.15)	5.79 (6.73)	
8.	0.2221 [1.4124]	p-$CH_3C_6H_4$ 1.0006 [4.2371]	$V[p\text{-}CH_3C_6H_4OP(S)SSH]_3$ 1.0006 96.0	32.70 (33.32)	2.99 (3.17)	37.83 (38.15)	5.49 (6.73)	

RESULTS AND DISCUSSION

O-alkyl / O-aryl trithiophosphoric acid have been synthesized by dropwise addition of mixture of triethylamine and appropriate alcohol in 1:3 molar ratio to a suspension of phosphorus pentasulphide in benzene. Two layers were obtained. Layers were separated. Lower layer was dried from solvent and was used for further reaction with VCl_3.

$$P_2S_5 + 3ROH + 3Et_3N \longrightarrow H_2S_3POR$$

(where R = Me, Et, Pr^{i}, Bu^{i}, Ph, CH_3-Ph)

The metal derivatives of type $V[SSH(S)POR]_3$ were obtained by reaction of Vanadium trichloride with O-alkyl/O-aryl trithiophosphoric acid in 1:3 molar ratio, respectively in methanol. Reaction mixture have been refluxed for 8-10 hours.

$$VCl_3 + 3H_2S_3POR \longrightarrow V[SSH(S)POR]_3 + 3HCl$$

(where R = Me, Et, Pr^{i}, Bu^{i}, Ph, CH_3-Ph)

Newly synthesized derivatives are dark green coloured sticky solids converts into needle like crystals. They have been washed with aqueous ethanol and recrystallized. They were found to be non-volatile and monomeric in nature.

4. Appearance of new, medium and weak intensity absorbtion band in region 502.10-537.32cm^{-1} indicates the formation of V-S bond.
5. Expected S-H vibrations in region 2459.94-2510.43cm^{-1} were observed in IR spectra of newly synthesized derivatives.

NMR spectra

^{1}H NMR spectra:- The ^{1}H NMR spectra of these derivatives were recorded in deutriated DMSO in 0-10 ppm region. Charateristics signals of these derivatives are listed in Table -3. These derivatives show characteristics resonance signals due to OCH_3, OC_2H_5, OC_3H_7, OC_6H_5, $OC_6H_4CH_3$ protons which are present in expected region[27]. The peak due to SH proton (present in the region3.00- 3.25ppm) indicates the presence of SH group in new derivatives.

^{31}P NMR spectra:- ^{31}P NMR spectra of newly synthesized derivatives have been scanned in deutirated DMSO and spectral data are summarized in Table-3. Only one peak for each derivative was obtained in the range 94.47-116.48ppm indicating only one type of phosphorus nucleus in the molecule. Deshielding of phosphorus atom to the extent of about 20-30ppm from parent trithiophosphoric acid ligand, indicates the bidentate mode of bonding of ligand in these derivatives.

Antibacterial activity

All newly synthesized derivatives also show antibacterial activity against gram positive and gram negative bacteria. Paper disc method was used for antibacterial activity and inhibition zone is measured in mm. The compounds are tested at 100 µg/mL concentration in DMSO solvent. Imipenem and linezolid were used as standard drugs for comparative studies.

Table 2 IR spectra data of $V[SSH(S)POR]_3$

S.No.	COMPOUND	υ(P)-O-C	υP-O-(C)	υP=S	υP-S	υV-S	υS-H
1.	$V[CH_3OP(S)SSH]_3$	1185.74 Vs	1035.25 Vs	794.87 Vs	587.56 s	502.10 w	2491.00 w
2.	$V[C_2H_5OP(S)SSH]_3$	1173.28 Vs	1020.09 s	785.05 w	575.70 s	509.95 w	2480.45 s
3.	$V[^iC_3H_7OP(S)SSH]_3$	1160.30 s	1007.85 s	773.89 s	566.04w	514.30 w	2473.65 w
4.	$V[^iC_4H_9OP(S)SSH]_3$	1149.75 Vs	995.50 s	760.20 s	555.90 w	521.17 s	2459.94 w
5.	$V[C_6H_5OP(S)SSH]_3$	1218.85 Vs	1032.16 Vs	756.08 Vs	693.37 w	537.32 w	2490.52 w
6.	$V[o\text{-}CH_3C_6H_4OP(S)SSH]_3$	1203.29 s	1055.28 Vs	799.20 s	597.40 s	520.80 s	2510.43 s
7.	$V[m\text{-}CH_3C_6H_4OP(S)SSH]_3$	1198.65 s	1049.75 Vs	780.38 Vs	590.26 w	516.37 s	2508.87 s
8.	$V[p\text{-}CH_3C_6H_4OP(S)SSH]_3$	1206.36 Vs	1038.10vs	816.97 Vs	582.71 s	508.63 w	2507.00 w

Vs = very strong, s = strong, w = weak

Table 3 ^1H NMR spectra and ^{31}P NMR spectra of $V[SSH(S)POR]_3$

S. No.	Compound	^1H chemical shift (ppm)	^{31}P Chemical shift (ppm)
1.	$V[CH_3OP(S)SSH]_3$	2.52, s, 3H (OCH_3) 3.10, s, 1H(SH)	112.49
2.	$V[C_2H_5OP(S)SSH]_3$	1.79, t, 3H (CH_3) 3.18, q, 2H (OCH_2) 3.15, s, 1H(SH)	108.97
3.	$V[^iC_3H_7OP(S)SSH]_3$	1.19, d, 6H (CH_3) 2.98-3.31, m (OCH) 3.19, s, 1H(SH)	103.86
4.	$V[^iC_4H_9OP(S)SSH]_3$	1.27, d, 6H (CH_3) 2.38-2.41, m, 1H (CH) 3.38, d, 2H (OCH_2) 3.25, s, 1H(SH)	98.55
5.	$V[C_6H_5OP(S)SSH]_3$	6.51-6.75, m, 5H (OC_6H_5)3.21, s, 1H(SH)	116.48
6.	$V[o\text{-}CH_3C_6H_4OP(S)SSH]_3$	6.93-7.09, m, 12H (C_6H_4) 2.59, s, 3H (CH_3) 3.18, s, 1H(SH)	99.19
7.	$V[m\text{-}CH_3C_6H_4OP(S)SSH]_3$	6.75-6.99, m, 12H (C_6H_4) 2.37, s, 3H (CH_3) 3.10, s, 1H(SH)	96.85
8.	$V[p\text{-}CH_3C_6H_4OP(S)SSH]_3$	6.59-6.90, m, 12H (C_6H_4) 2.15, s, 3H (CH_3) 3.00, s, 1H(SH)	94.47

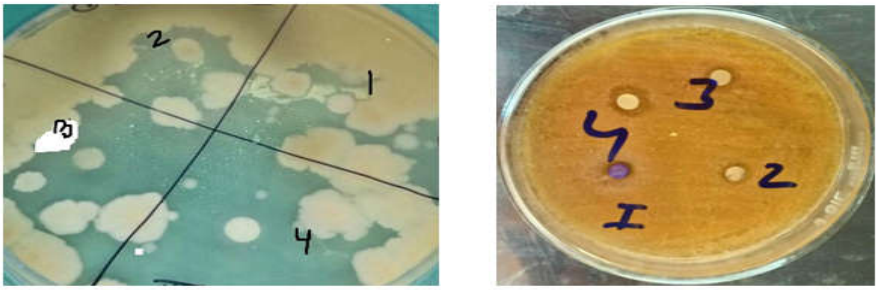
The observations show that compounds 10, 11, 12, 13 are more effective against gram positive bacteria and compounds 14, 15, 16, 17 are more effective against gram negative bacteria.

Effect of V $[p\text{-}CH_3C_6H_4OP(S)SSH]_3$ on gram positive and gram negative bacteria

Effect on gram positive bacteria Effect on gram negative bacteria

I, V -V $[p\text{-}CH_3C_6H_4OP(S)SSH]_3$ **II**- Ligand **III**- Solvent **IV**- VCl_3

Effect of $V[^iC_3H\text{-}OP(S)SSH]_3$ on gram positive and gram negative bacteria



Effect on gram positive bacteria Effect on gram negative bacteria

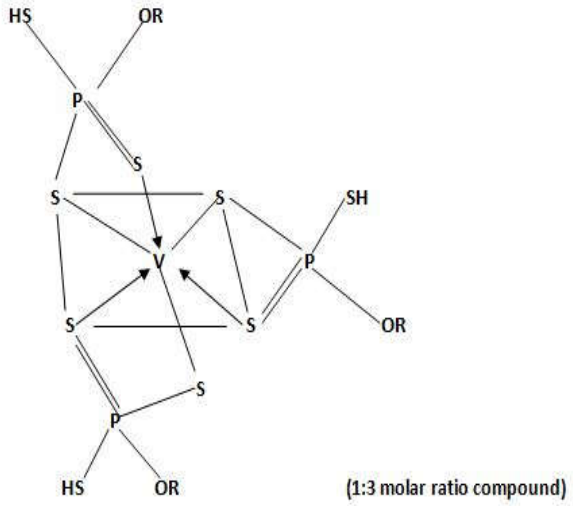
1- Solvent **2**-VCl_3 **3**- Ligand **4**- $V[^iC_3H\text{-}OP(S)SSH]_3$

Table 4 Antibacterial activity of Vanadium (III) derivatives of the type $V[SSH(S)POR]_3$

Sr. No.	Compund	Gram positive bacteria zone of inhibition in mm	Gram negative bacteria zone of inhibition in mm
1.	Solvent	0	0
2.	$CH_3OPS(S)(SH)_2$	9	6
3.	$C_2H_5OPS(S)(SH)_2$	7	5
4.	$^{i}PrOP(S)(SH)_2$	10	4
5.	$^{i}BuOP(S)(SH)_2$	6	8
6.	$PhOP(S)(SH)_2$	10	12
7.	o-CH_3 $PhOP(S)(SH)_2$	12	14
8.	m-CH_3 $PhOP(S)(SH)_2$	11	13
9.	p-CH_3 $PhOP(S)(SH)_2$	9	10
10.	$V[CH_3OP(S)SSH]_3$	31	20
11.	$V[C_2H_5OP(S)SSH]_3$	25	18
12.	$V[^{i}C_3H_7OP(S)SSH]_3$	35	22
13.	$V[^{i}C_4H_9OP(S)SSH]_3$	29	19
14.	$V[C_6H_5OP(S)SSH]_3$	26	35
15.	$V[o\text{-}CH_3C_6H_4OP(S)SSH]_3$	28	39
16.	$V[m\text{-}CH_3C_6H_4OP(S)SSH]_3$	23	36
17.	$V[p\text{-}CH_3C_6H_4OP(S)SSH]_3$	25	37
18.	Imipenem	12	30
19.	Linezolid	8	10

CONCLUSION

On the basis of above IR and NMR (^{1}H, ^{13}C, ^{31}P) studies following structure may be proposed for the newly synthesized derivatives. In these derivatives trithiophosphate moiety behaves as bidentate ligand. Octahedral geometry has been assigned to the complexes having d^2sp^3 hybridisation.



(1:3 molar ratio compound)

Acknowledgement

One of the authors (Suman Bhatti) is thankful to M.N.I.T Jaipur for spectral analysis.

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How to cite this article:

Suman Bhatti and Alok Chaturvedi.2018, Synthesis, Characterization and Antibacterial activity of o-alkyl/ O-aryl trithiophosphate derivatives of vanadium (iii). *Int J Recent Sci Res.* 9(4), pp. 25584-25587.
DOI: http://dx.doi.org/10.24327/ijrsr.2018.0904.1887