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Novel mixed *O,O'*-diaryldithiophosphate complexes of vanadium(III): Synthesis, Characterization and Antimicrobial screening

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ABSTRACT

Novel complexes of vanadium(III) have been synthesized corresponding to the general formula $[\{(ArO)_2PS_2\}_2VL]$ *(Ar =* $2\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, $4\text{-}CH_3C_6H_4$ *and* $4\text{-}Cl\text{-}3\text{-}CH_3C_6H_3$*; L =* $(OCH_2)C(CH_3)_2(CH_2O)PS_2$ *and* $C_6H_5CH_2OCS_2$*) These complexes have been characterized by using various physico-chemical techniques like elemental analysis, IR, heteronuclear NMR (*^1H, ^{13}C *and* ^{31}P*) magnetic, uv and mass spectroscopic studies. Coordination number of six is suggested around the vanadium atom in these complexes, leading to distorted octahedral geometries. The antimicrobial activity depicts that these compounds are active against bacteria Gram–positive: Enterrococcus faecalis and Bacillus cereus and Gram–negative: Eischerichia coli and Klebsiella pneumonia and fungus Fusarium oxysporum.*

Keywords*: *Vanadium, Dithiophosphate, Dithiocarbonate, Sulphur, Antimicrobial

I.INTRODUCTION

Recent major applications of the transition metal complexes include their analyses in medical fields as antibacterial and antitumor agents aiming toward the discovery of effective and safe therapeutic agents for the treatment of bacterial infections and cancers. Research in medicinal inorganic chemistry has prolonged in current years by exploiting a variety of chelating ligands to amend and control the properties of metal ions in biological systems [1–2]. Searching newer and more potent analogs of molecules with already established activities forms a key part of research in the pharmaceutical field. There are several biologically active molecules which contain various heteroatoms such as sulphur and oxygen. Dithiophosphate derivatives are gradually finding their way into the field of pharmacological active agents [3-4]. Literature survey revealed several reports on the mixed ligand complexes of various metal and metalloids [5]. However, no information could be found on the mixed ligand complexes of vanadium(III). It is rather interesting that though several mixed ligand complexes are known but no report available on mixed dithiophosphate-dithiophosphates and

dithiophosphate-dithiocarbonate. So, it was thought interesting to investigate mixed ligand complexes of vanadium(III) in order to create a variety of complexes within dithiophosphate periphery as well as to find some new applications.

II.EXPERIMENTAL

All the experimental manipulations were carried out under moisture free conditions using standard Schlenk techniques. Commercial grade chemicals were used for synthetic purposes. Solvents were dried and distilled before use. The ligands, sodium salts of *O,O'*-di(2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 4-chloro-3-methylphenyl, neopentylene)dithiophosphates and *O*-benzyldithiocarbonate were prepared according to literature report [6]. Vanadium was estimated gravimetrically as Ag_3VO_4 and Chlorine was estimated by Volhard's method [7]. Elemental analyses (C, H, N, S) were measured with the Elemental Analyser Vario EL-III, their results were found to be in good agreement (±0.3%) with the calculated values. Infrared spectra were recorded in the range of 4000– 200 cm^{-1} using pressed KBr pellets on a Perkin Elmer-spectrum RX1 FT-IR spectrophotometer. NMR samples were prepared in deuteriochloroform ($CDCl_3$). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 (300 MHz) and reported relative to an internal reference of TMS. The ^{31}P NMR spectra were recorded using H_3PO_4 (85%) as external reference on a Bruker DRX 300 (300 MHz). The ESI mass spectra were recorded on ESQUIRE3000_00037 spectrophotometer. The electronic spectra of the complexes were recorded in a range of 12500-50000 cm^{-1} on a Shimadzu UV-265FS 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).

2.1. Synthesis of mixed diaryldithiophosphate-alkylenedithiophosphate and diaryldithiophosphate-benzyldithiocarbonate complexes of vanadium(III).

2.1.1. Synthesis of $[\{(2\text{-}CH_3C_6H_4O)_2PS_2\}_2\{(OCH_2)C(CH_3)_2(CH_2O)PS_2\}V]$ (1)

A tetrahydrofuran solution (~15 cm^3) of vanadium trichloride (0.13 g, 0.82 mmol) was added to a tetrahydrofuran solution (~30 cm^3) of sodium *O,O'*-di(2-methylphenyl)dithiophosphate (0.54 g, 1.62 mmol) with constant stirring at room temperature under nitrogen atmosphere. Now, a tetrahydrofuran solution (~10 cm^3) of sodium salt of neopentylene dithiophosphoric acid (0.18 g, 0.82 mmol) was added dropwise with constant stirring. The contents were stirred for two hours followed by refluxing for five hours. There appears formation of white precipitate of sodium chloride. The sodium chloride thus formed was separated by filtration using alkoxy funnel fitted with G-4 disc. Evaporation of tetrahydrofuran in *vacuo* resulted in the formation of the desired complex, $[\{(2\text{-}CH_3C_6H_4O)_2PS_2\}_2\{(OCH_2)C(CH_3)_2(CH_2O)PS_2\}V]$ **(1)** as green solid. Yield: 89 %;

Anal. Calc. for $C_{33}H_{38}O_6P_3S_6V$: C, 45.72; H, 4.42; S, 22.19; V, 5.88, Found: C, 45.69; H, 4.39; S, 22.17; V, 5.86, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1191.1, s [*v*(P)−O−C], 935.8, s [*v*P−O−(C)], 390.7, s [*v*P═S], 547.7, m [*v*P−S], neopentylene dithiophosphate moiety: 998.2, s [*v*(P)−O−C], 779.7, s [*v*P−O−(C)], 623.0, s [*v*P═S], 473.4, m [*v*P−S], 374.2, w [*v*V−S] cm^{-1}. ^1H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.1, s, 12 H (CH_3), 7.0, d, 4 $H_{(3)}$ (J = 8.1); 6.9, t, 4 $H_{(4)}$ (J = 8.2); 7.1, t, 4 $H_{(5)}$ (J = 8.2); 6.7, d, 4 $H_{(6)}$ (J = 8.1), neopentylene dithiophosphate moiety: 1.1, s, 6 H (CH_3); 3.8, s, 4 H (CH_2); ^{31}P NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 98.1, s; neopentylene dithiophosphate moiety: 88.2, s ppm; ^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 20.2 (CH_3), 149.2 (C1), 119.3 (C2), 127.3 (C3), 126.5 (C4), 128.3 (C5), 123.1 (C6); neopentylene dithiophosphate moiety: 22.2 (CH_3), 27.6 (-C-), 70.2 (CH_2) ppm.

2.1.2. Synthesis of [{(3-$CH_3C_6H_4O)_2PS_2$}$_2${$(OCH_2)C(CH_3)_2(CH_2O)PS_2$}V] (2)

The above stated procedure was followed to obtain **2** as green colored solid using sodium *O,O′*-di(3-methylphenyl)dithiophosphate (0.54 g, 1.62 mmol). Yield: 90%; *Anal*. Calc. for $C_{33}H_{38}O_6P_3S_6V$: C, 45.72; H, 4.42; S, 22.19; V, 5.88, Found: C, 45.65; H, 4.33; S, 22.13; V, 5.81, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1204.7, s [*v*(P)−O−C], 961.7, s [*v*P−O−(C)], 687.8, s [*v*P═S], 563.3, m [*v*P−S], neopentylene dithiophosphate moiety: 990.8, s [*v*(P)−O−C], 781.4, s [*v*P−O−(C)], 612.0, s [*v*P═S], 453.1, m [*v*P−S], 377.1, w [*v*V−S] cm^{-1}, ^1H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.2, s, 12 H (CH_3), 6.6, s, 4 $H_{(2)}$; 7.0, t, 4 $H_{(4)}$ (J = 8.1); 7.1, t, 4 $H_{(5)}$ (J = 8.2); 6.8, d, 4 $H_{(6)}$ (J = 8.1), neopentylene dithiophosphate moiety: 1.2, s, 6 H (CH_3); 3.7, s, 4 H (CH_2); ^{31}P NMR ($CDCl_3$): δ = tolyldithiophosphate moiety 97.2, s; neopentylene dithiophosphate moiety, 88.1, s ppm^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 19.9 (CH_3), 156.5 (C1), 117.2 (C2), 123.9 (C3), 122.9 (C4), 127.4 (C5), 131.3 (C6); neopentylene dithiophosphate moiety: 27.1 (CH_3), 32.8 (-C-), 71.4 (CH_2) ppm; [M^+] 866.9 (6) [{(3-$CH_3C_6H_4O)_2PS_2$}$_2${$(OCH_2)C(CH_3)_2(CH_2O)PS_2$}V], [$M^+$] 523.3 (15) [$(OCH_2)C(CH_3)_2(CH_2O)PS_2$}V{$S_2P(OC_6H_4)$}]$^+$, [$M^+$] 425.5 (25) [{$(C_6H_4O)PS_2$}$_2$V] [$M^+$] 357.2 (42) [{(3-$CH_3C_6H_4O)P(O)S_2$}V]$^+$, [$M^+$] 336.1 (32) [{$(OCH_2)C(CH_3)_2(CH_2O)PS_2$}V]$^+$, [$M^+$] 309.3 (86) [(3-$CH_3C_6H_4O)_2PS_2$]$^-$, [$M^+$] 107.2 (98) [3-$CH_3C_6H_4O$]$^-$, [$M^+$] 102.5 (67) [$(OCH_2)_2C(CH_3)_2$]$^-$.

2.1.3. Synthesis of [{(4-$CH_3C_6H_4O)_2PS_2$}$_2${$(OCH_2)C(CH_3)_2(CH_2O)PS_2$}V] (3)

The above stated procedure was followed to obtain **3** as green colored solid using sodium *O,O′*-di(4-methylphenyl)dithiophosphate (1.07 g, 2.64 mmol). Yield: 89%; *Anal*. Calc. for $C_{33}H_{38}O_6P_3S_6V$: C, 45.72; H, 4.42; S, 22.19; V, 5.88, Found: C, 45.68; H, 4.38; S, 22.16; V, 5.85, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1211.1, s [*v*(P)−O−C], 945.9, s [*v*P−O−(C)], 691.1, s [*v*P═S], 552.7, m [*v*P−S], neopentylene dithiophosphate moiety: 998.2, s [*v*(P)−O−C], 775.7, s [*v*P−O−(C)], 608.0, s [*v*P═S], 463.4, m [*v*P−S], 385.3, w [*v*V−S] cm^{-1}; ^1H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.2, s, 12 H (CH_3), 6.6, d, 8 $H_{(2,6)}$ (J = 8.2); 6.9, d, 8 $H_{(3,5)}$ (J = 8.1), neopentylene dithiophosphate moiety: 0.9, s, 6 H (CH_3); 3.9, s, 4 H (CH_2); ^{31}P NMR ($CDCl_3$): δ =

tolyldithiophosphate moiety 97.3, s; neopentylene dithiophosphate moiety, 88.1, s ppm;; ^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 19.9 (CH_3), 154.6 (C1), 114.8 (C2), 129.3 (C3), 127.3 (C4), 129.3 (C5), 114.8 (C6); neopentylene dithiophosphate moiety: 21.7 (CH_3), 25.0 (-C-), 73.7 (CH_2) ppm.

2.1.4. Synthesis of [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}$_2$ {$(\overline{OCH_2})C(CH_3)_2(CH_2O)PS_2$}V] (4)

The above stated procedure was followed to obtain **4** as green colored solid using sodium *O,O′*-di(4-chloro-3-methylphenyl)dithiophosphate (1.07 g, 2.64 mmol). Yield: 91%; *Anal*. Calc. for $C_{33}H_{34}C_{l4}O_6P_3S_6V$: C, 39.45; H, 3.41; Cl, 14.12; S, 19.15; V, 5.07, Found: , 39.42; H, 3.39; Cl, 14.10; S, 19.13; V, 5.03, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1243.1, s [*ν*(P)−O−C], 987.5, s [*ν*P−O−(C)], 682.2, s [*ν*P═S], 532.0, m [*ν*P−S], neopentylene dithiophosphate moiety: 1011.2, s [*ν*(P)−O−C], 781.8, s [*ν*P−O−(C)], 596.0, s [*ν*P═S], 463.5, m [*ν*P−S], 813.3, w [*ν*C−Cl], 372.3, w [*ν*V−S] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.1, s, 12 H (CH_3), 6.4, s, 4 $H_{(2)}$; 6.5, d, 4 $H_{(6}$ (J = 8.1)$_,$; 6.9, d, 4 $H_{(5)}$ (J = 8.1), neopentylene dithiophosphate moiety: 1.1, s, 6 H (CH_3); 3.4, s, 4 H (CH_2); ^{31}P NMR ($CDCl_3$): δ = tolyldithiophosphate moiety 97.5, s; neopentylene dithiophosphate moiety, 88.2, s ppm^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 19.1 (CH_3), 155.1 (C1), 113.2 (C2), 123.3 (C3), 135.7 (C4), 128.6 (C5), 116.8 (C6); neopentylene dithiophosphate moiety: 28.7 (CH_3), 32.1 (-C-), 73.4 (CH_2) ppm **.**

2.1.5. Synthesis of [{(2-$CH_3C_6H_4O)_2PS_2$}$_2${$C_6H_5CH_2OCS_2$}V] (5)

A tetrahydrofuran solution (~15 cm^3) of vanadium trichloride (0.13 g, 0.82 mmol) was added to a tetrahydrofuran solution (~30 cm^3) of sodium *O,O′*-2-ditolyldithiophosphate (0.54 g, 1.62 mmol) with constant stirring at room temperature under nitrogen atmosphere. Now, a tetrahydrofuran solution (~10 cm^3) of sodium salt of benzyldithiocarbonates (0.17 g, 0.82 mmol) was added dropwise with constant stirring. The contents were stirred for two hours followed by refluxing for five hours. There appears formation of white precipitate of sodium chloride. The sodium chloride thus formed was separated by filtration using alkoxy funnel fitted with G-4 disc. Evaporation of tetrahydrofuran in *vacuo* resulted in the formation of the desired complex, [{(2-$CH_3C_6H_4O)_2PS_2$}$_2${$C_6H_5CH_2OCS_2$}V] **(5)**. Yield: 91%; *Anal*. Calc. for $C_{36}H_{35}O_5P_2S_6V$: C, 50.69; H, 4.14; S, 22.56; V, 5.97, Found: C, 50.64; H, 4.14; S, 22.51; V, 5.91; IR (cm^{-1}) = tolyl dithiophosphate moiety: 1198.4, s [*ν*(P)−O−C], 920.1, s [*ν*P−O−(C)], 687.0, s [*ν*P═S], 530.1, m [*ν*P−S], benzyldithiocarbonate moiety: 1165.1, s [*ν*C−O−C], 1017.4, s [*ν*C═S], 923.6, m [*ν*C−S], 382.3, w [*ν*V−S] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.2, s, 12 H (CH_3), 7.1, d, 4 $H_{(3)}$ (J = 8.1); 6.9, t, 4 $H_{(4)}$ (J = 8.2); 7.2, d, 4 $H_{(5)}$ (J = 8.1); 6.6, t, 4 $H_{(6)}$ (J = 8.2), benzyldithiocarbonate moiety: 4.5, s, 8 H (CH_2), 7.1-7.3, m, 5 H (C_6H_5) (J = 8.4) ppm, ^{31}P NMR ($CDCl_3$): δ = 98.4 ppm; ^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 20.5 (CH_3), 148.4 (C1), 120.7 (C2), 128.1 (C3), 125.2 (C4), 129.8 (C5), 121.2 (C6); benzyldithiocarbonate moiety: 68.6 (CH_2), 137.6 (C1), 128.4 (C2), 128.9 (C3), 128.6 (C4), 128.9 (C5), 128.9 (C6), 171.1 (C-S) ppm.

2.1.6. Synthesis of [{(3-$CH_3C_6H_4O)_2PS_2$}$_2${$C_6H_5CH_2OCS_2$}V] (6)

The above stated procedure for complex (**5**) was followed to obtain **6** as green colored solid using sodium *O,O′*-di(3-methylphenyl)dithiophosphate (0.54 g, 1.62 mmol). Yield: 90%; *Anal*. Calc. for $C_{36}H_{35}O_5P_2S_6V$: C, 50.69; H, 4.14; S, 22.56; V, 5.97, Found: C, 50.64; H, 4.10; S, 22.51; V, 5.92 IR (cm^{-1}) = tolyl dithiophosphate moiety: 1210.5, s [*ν*(P)−O−C], 897.6, s [*ν*P−O−(C)], 688.5, s [*ν*P═S], 528.0, m [*ν*P−S], benzyldithiocarbonate moiety: 1163.0, s [*ν*C−O−C], 1017.4, s [*ν*C═S], 923.6, m [*ν*C−S], 382.3, w [*ν*V−S] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.0, s, 12 H (CH_3), 6.6, s, 4 $H_{(2)}$; 6.9, t, 4 $H_{(4)}$ (J = 8.2); 7.1, t, 4 $H_{(5)}$ (J = 8.1); 6.7, d, 4 $H_{(6)}$ (J = 8.2), benzyldithiocarbonate moiety: 4.7, s, 8 H (CH_2), 7.2-7.3, m, 5 H (C_6H_5) (J = 8.3) ppm, ^{31}P NMR ($CDCl_3$): δ = 97.6 ppm; ^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 19.3 (CH_3), 152.2 (C1), 117.7 (C2), 121.5 (C3), 120.7 (C4), 127.3 (C5), 129.5 (C6); benzyldithiocarbonate moiety: 66.2 (CH_2), 137.9 (C1), 125.4 (C2), 128.2 (C3), 127.4 (C4), 128.2 (C5), 125.4 (C6), 168.4 (C-S) ppm.

2.1.7. Synthesis of [{(4-$CH_3C_6H_4O)_2PS_2$}$_2${$C_6H_5CH_2OCS_2$}V] (7)

The above stated procedure for complex (**5**) was followed to obtain **7** as green colored solid using sodium *O,O′*-di(4-methylphenyl)dithiophosphate (0.54 g, 1.62 mmol). Yield: 91%; *Anal*. Calc. for $C_{36}H_{35}O_5P_2S_6V$: C, 50.69; H, 4.14; S, 22.56; V, 5.97, Found: C, 50.62; H, 4.11; S, 22.51; V, 5.92 IR (cm^{-1}) = tolyl dithiophosphate moiety: 1193.0, s [*ν*(P)−O−C], 887.2, s [*ν*P−O−(C)], 701.3, s [*ν*P═S], 530.2, m [*ν*P−S], benzyldithiocarbonate moiety: 1160.6, s [*ν*C−O−C], 1018.8, s [*ν*C═S], 928.1, m [*ν*C−S], 371.9, w [*ν*V−S] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.2, s, 12 H (CH_3), 7.1, d, 4 $H_{(3)}$ (J = 8.1); 6.9, t, 4 $H_{(4)}$ (J = 8.2); 7.2, d, 4 $H_{(5)}$ (J = 8.1); 6.6, t, 4 $H_{(6)}$ (J = 8.2), benzyldithiocarbonate moiety: 4.5, s, 8 H (CH_2), 7.1-7.3, m, 5 H (C_6H_5) (J = 8.4) ppm, ^{31}P NMR ($CDCl_3$): δ = 98.4 ppm; ^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 21.2 (CH_3), 153.4 (C1), 117.7 (C2), 121.5 (C3), 120.7 (C4), 127.3 (C5), 129.5 (C6); benzyldithiocarbonate moiety: 69.2 (CH_2), 138.9 (C1), 125.4 (C2), 127.0 (C3), 126.0 (C4), 127.0 (C5), 125.4 (C6), 170.3 (C-S) ppm; [M^+] 852.9 (4) [{(4-$CH_3C_6H_4O)_2PS_2$}$_2$V($C_6H_5CH_2OCS_2$)], [M^+] 543.5 (7) [{(4-$CH_3C_6H_4O)_2PS_2$}V($C_6H_5CH_2OCS_2$)]$^+$, [M^+] 421.4 (22) [($C_6H_4OPS_2$)V($C_6H_5CH_2OCS_2$)]$^+$, [M^+] 345.3 (27) [(OPS_2)V($C_6H_5CH_2OCS_2$)]$^+$, [M^+] 253.1 (81) [(4-$CH_3C_6H_4OPS_2$)V]$^+$, [M^+] 202.3 (38) [(4-$CH_3C_6H_4O)PS_2$]$^-$, [M^+] 183.3 (52) [$C_6H_5CH_2OCS_2$], [M^+] 107.1 (64) [$CH_3C_6H_4O$]$^-$.

2.1.8. Synthesis of [{(4-Cl-3-$CH_3C_6H_4O)_2PS_2$}$_2${$C_6H_5CH_2OCS_2$}V] (8)

The above stated procedure for complex (**5**) was followed to obtain **8** as green colored solid using sodium *O,O′*-di(4-chloro-3-methylphenyl)dithiophosphate (0.54 g, 1.62 mmol). Yield: 92%; *Anal*. Calc. for $C_{36}H_{31}Cl_4O_5P_2S_6V$: C, 43.64; H, 3.15; Cl, 14.31; S, 19.42; V, 5.14 Found: C, 43.61; H, 3.11; Cl, 14.28; S, 19.34; V, 5.09, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1225.8, s [*ν*(P)−O−C], 967.9, s [*ν*P−O−(C)], 712.8, s [*ν*P═S],

560.1, m [*v*P−S], benzyldithiocarbonate moiety: 1167.4, s [*v*C−O−C], 1012.8, s [*v*C═S], 923.9, m [*v*C−S], 383.0, w [*v*V−S] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 2.2, s, 12 H (CH_3), 6.7, s, 4 $H_{(2)}$; 6.8, d, 4 $H_{(6)}$ (J = 8.1); 7.0, d, 4 $H_{(5)}$ (J = 8.1); benzyldithiocarbonate moiety: 4.6, s, 8 H (CH_2), 7.2-7.3, m, 5 H (C_6H_5) (J = 8.3) ppm, ^{31}P NMR ($CDCl_3$): δ = 97.9 ppm; ^{13}C NMR ($CDCl_3$): δ = tolyldithiophosphate moiety: 19.9 (CH_3), 152.6 (C1), 114.5 (C2), 123.7 (C3), 134.2 (C4), 127.6 (C5), 117.1 (C6); benzyldithiocarbonate moiety: 66.8 (CH_2), 139.7 (C1), 127.4 (C2), 129.1 (C3), 128.6 (C4), 129.1 (C5), 127.4 (C6), 168.5 (C-S) ppm.

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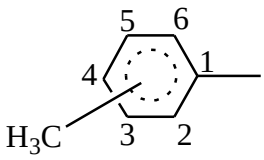

tolyl ring

Fig.1: Ring labeling assignments for predicting ^{1}H and ^{31}C NMR chemical shifts.

2.2. *Antibacterial*

The antibacterial screening was carried out by agar well diffusion technique [8]. Test samples were prepared in different concentrations (100, 200, 400 and 800 ppm) in DMSO. Agar medium (20 mL) was poured into each petri plate and left to solidify. The plates were then swabbed with broth cultures of the respective four bacterial strains Gram–positive: *Enterrococcus faecalis* and *Bacillus cereus* and Gram–negative: *Eischerichia coli* and *Klebsiella pneumoniae* and kept for 15 min for adsorption to take place. Using a punch, ≈ 6 mm diameter, wells were bored in the seeded agar plates and 100 µl of the DMSO solution of each test compound was added into the wells. DMSO was used as the control for all the test compounds as it exhibited no effect on the organism tested and Ciprofloxacin was used as the standard drug. After holding the plates at room temperature for 2 h to allow diffusion of the compounds into the agar, the plates were incubated at 37°C for 24 h. The antibacterial activity was determined by measuring the diameter of the inhibition zone. The entire tests were made in triplicates and the mean of the diameter of zone of inhibition was calculated.

2.3. *Antifungal Activity*

The antifungal screening was carried out by poisoned food technique [9] Potato dextrose medium (PDA) was prepared in a flask and sterilized. 100 µl of each sample was added to the PDA medium and poured into each sterilized Petri plate. Mycelial discs taken from the standard culture (*Fusarium oxysporum*) of fungi were grown

on PDA medium for 7 days. These cultures were used for aseptic inoculation in the sterilized Petri dish. Standard cultures, inoculated at 28 ± 1°C, were used as the control. The efficacy of each sample was determined by measuring the radial fungal growth. The radial growth of the colony was measured in two directions at right angle to each other, and the average of two replicates was recorded in each case. Data were expressed as percent inhibition over the control from the size of the colonies. The percent inhibition was calculated using the formulae: % Inhibition = ((C–T)/C)×100, where C is the diameter of the fungus colony in the control plate after 96 h incubation and T is the diameter of the fungus colony in the tested plate after the same incubation period. Both antibacterial and antifungal activities were tested in the Bio-assay lab, Department of Chemistry, University of Jammu, Jammu.

III.RESULTS AND DISCUSSION

Mixed diaryldithiophosphate-neopentylenedithiophosphate complexes of vanadium were obtained in 89-91% yield as green solid by reaction of sodium *O,O′*-diarylphosphorodithioate, $(ArO)_2PS_2Na$ [Ar = 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, and 4-Cl-3-$CH_3C_6H_3$] sodium *O,O′*-neopentylenephosphorodithioate, $(OCH_2)C(CH_3)_2(CH_2O)PS_2Na$ with vanadium trichloride, VCl_3 in 2:1:1 molar ratio in tetrahydrofuran under anhydrous conditions. The mixed diaryldithiophosphate-benzyldithiocarbonate complexes of vanadium(III) were also obtained as dark green semi-solid by reaction of sodium *O,O′*-diarylphosphorodithioate, sodium benzyldithiocarbonate with vanadium trichloride in 2:1:1 molar ratio in tetrahydrofuran under anhydrous conditions in 90-92% yield **(Scheme 1)**.

$$2\,(ArO)_2PS_2Na + VCl_3 + LNa \xrightarrow[\text{Reflux ~5 h}\\ N_2\text{ atm, -3NaCl}]{\text{THF}} [\{(ArO)_2PS_2\}_2VL]$$

[Ar = 2-$CH_3C_6H_4$ **(1, 5)**, 3-$CH_3C_6H_4$ **(2, 6)**, 4-$CH_3C_6H_4$ **(3, 7)** and 4-Cl-3-$CH_3C_6H_3$ **(4, 8)**

L = $(OCH_2)C(CH_3)_2(CH_2O)PS_2$ **(1-4)**, $C_6H_5CH_2OCS_2$ **(5-8)**

Scheme 1: Synthesis of mixed complexes of vanadium(III).

These are green colored complexes and highly sensitive to air and moisture, however, these can be kept unchanged under anhydrous atmosphere. These complexes and adducts are soluble in common organic solvents (toluene, acetonitrile, methanol, chloroform), however, insoluble in solvents like *n*-hexane and carbon tetrachloride. These complexes are non-volatile even under the reduced pressure. The elemental analyses (C, H, N, S, Cl and V) were found consistent with the molecular formula of these complexes. These complexes were

further characterized by IR, heteronuclear NMR (^{1}H, ^{13}C, ^{31}P), magnetic susceptibility, UV and mass spectroscopic studies**.**

3.1. Infrared Spectral data

IR spectra of these complexes were recorded in KBr pellets in the range of 4000-200 cm^{-1} and the tentative assignments were made on the basis of relevant literature reports [4,6,10]. The comparison of IR spectra of these complexes with starting materials has also shown significant and characteristic changes and shifting of bands. Two strong intensity bands were observed in the region 1243.1-1191.1 cm^{-1} and 987.5-887.2 cm^{-1}, which may be ascribed to the *ν*(P)−O−C and *ν*P−O−(C) vibrations of the diaryldithiophosphate moiety, respectively. Furthermore, two strong intensity bands were observed in the IR spectra of complexes **1-4** in the region 1011.2-988.2 cm^{-1} and 781.4-775.7 cm^{-1}, which may be ascribed to the *ν*(P)−O−C and *ν*P−O−(C) vibration of the neopentylenedithiophosphate moiety, respectively. This is an indicative of presence of two types of dithiophosphate moieties. The bands for *ν*P=S and *ν*P−S were observed in the region 712.8-682.2 cm^{-1} and 563.3-528.0 cm^{-1}, which depicted a shift of 10-30 cm^{-1} toward the lower frequency region compared to the parent diaryldithiophosphate ligand. The bands in the region 623.0-596.0 cm^{-1} and 473.4-453.1 cm^{-1} have been assigned to *ν*P=S and *ν*P−S, respectively, for the neopentylenedithiophosphate moiety. The shift of *ν*P−S vibration is due to bidentate mode of bonding by the dithiophosphate ligands with vanadium. In complexes **4** and **8,** a band for *ν*C–Cl is observed in the region 814.8-813.3 cm^{-1}. Strong intensity bands at 1167.4-1160.6 cm^{-1}, 1023.3-1012.8 and 930.0-923.6 cm^{-1} in the IR spectra of the complexes **5-8** have been ascribed to *ν*C–O–C, *ν*C=S and *ν*C−S of the benzyldithiocarbonate moiety. The presence of a new band for *ν*V−S in the region 385.3-371.9 cm^{-1} in the spectra of these complexes is an indicative of the formation of vanadium-sulfur bond.

3.2. ^{1}H NMR Spectral data

The ^{1}H NMR ($CDCl_3$ and DMSO) spectral data of the complexes **1-8** have been analyzed. It was observed that the chemical shift for methyl ($–CH_3$) protons, attached to aryl, appeared in the region 2.0-2.2 ppm as singlet in the complexes in these complexes. This chemical shift did not show any deviation either to lower or higher field side compared to the parent ligands. There were two resonances for ring protons of *para* complexes **(3, 7),** whereas four resonances were observed for *ortho* **(1, 5)** and *meta* **(2, 4, 6, 8)** derivatives. The chemical shift for the aryl ring protons was observed in the region 6.4-7.2 ppm as multiplet in these complexes. The chemical shift for methyl ($–CH_3$) protons of the neopentylenedithiophosphate moiety appeared in the region 0.9-1.2 ppm while the chemical shift for methylene ($–CH_2$) protons appeared in the region 3.4-3.9 ppm. In the mixed dithiophosphate-dithiocarbonate complexes **(5-8)**, the methylene ($–CH_2$) protons of benzyldithiocarbonate moiety gave resonance in the region 4.5-4.7 ppm as singlet. The chemical shifts for the benzyldithiocarbonate

ring protons were observed in the region 7.1-7.3 ppm. The presence of all characteristic chemical shifts in the ^{1}H NMR spectra favors the formation of these complexes.

3.3. ^{31}P NMR Spectral data

The ^{31}P NMR spectra of these complexes depicted the chemical shift for the phosphorus atom as singlet in the region 97.2-98.4 ppm for the diaryldithiophosphate moiety. In the spectra for the complexes **1-4** chemical shift for the phosphorus atom appeared as singlet in the region 88.1-88.2 ppm for the neopentylenedithiophosphate moiety. Occurrence of two singlets in these complexes **(1-4)** for both the dithiophosphate moieties is suggestive of formation of mixed diaryldithiophosphate-neopentylenedithiophosphate complexes. Furthermore, occurrence of a downfield shift in comparison to the parent dithiophosphate ligands is indicative of the bidentate mode of linkage of both the dithiophosphate ligands with vanadium [4,6,11].The down field shift may also be due to the formation of vanadium-sulfur bond in these complexes.

3.4. ^{13}C NMR Spectral data

The ^{13}C NMR spectra of the complexes (in $CDCl_3$) exhibited the chemical shift for methyl carbon ($-CH_3$) attached to the aryl ring in the region 19.1-21.2 ppm in these complexes. The carbon nuclei of the aryl group resonate in the region 113.2-156.5 ppm. In the complexes **1-4**, the methyl ($-CH_3$) carbon of the neopentylenedithiophosphate moiety resonates at 21.7-28.7 ppm, the methylene ($-CH_2O$) carbon appears at 70.2-73.7 ppm and the quaternary carbon atom (−C−) resonates at 25.0-32.8 ppm. In the complexes **5-8**, the methylene ($-CH_2$) carbon of benzyldithiocarbonate moiety gave resonance in the region 66.2-69.2 ppm and the chemical shifts for dithiocarbonate carbon [$-(O)CS_2$] and benzyldithiocarbonate ring carbon were observed in the region 168.4-171.1 and 125.4-139.7 ppm, respectively.

3.5. Mass Spectral data

The mass spectra of few representative mixed ligand vanadium(III) complexes have shown the molecular ion peak [M^+] at 866.9 (m/z) **(2)**, 852.9 (m/z) **(6)**. 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. The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes.

3.6. UV-Visible Spectral data

The UV-Visible spectra of the complexes were recorded in the range of 12500-50000 cm^{-1}. The intense electronic spectra of these complexes shows absorption in the range of 14814 -15384 cm^{-1} and 18436-20836 cm^{-1}, which may be ascribed to $^{3}T_{1g}$ (F) → $^{3}T_{2g}$ (F) and $^{3}T_{1g}$ (F) → $^{3}T_{1g}$ (P) assigned to *d-d* transition and the shoulder at 25026-31554 cm^{-1} can be tentatively assigned to a $^{3}T_{1g}$ (F) → $^{3}A_{2g}$ (F) transition, which is weaker

and of higher energy compared with the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition [12-13]. The transition in these complexes indicated that the vanadium is d^2 with the ground term ^3F. The tentative assignments of the important bands for the complexes **(1-8)** have been made and summarized in **Table 1**.

Table1: Electronic spectral bands (in cm^{-1}) of the complexes (13-21) with their assignments.

**S. No.	λ_{max} (cm^{-1})	Assignments
1.	15037 18518 28735	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$
2.	15384 18436 25026	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$
3.	15313 20408 25641	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$
4.	14814 19801 31554	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$

5.	15128 19237 29063	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$
6.	14972 18730 28197	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$
7.	15209 20836 27309	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$
8.	14872 19630 29308	$^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$

3.7 Magnetic Susceptibility Measurements

The magnetic moment of a representative mixed complex [{(2-$CH_3C_6H_4O)_2PS_2\}_2\{(OCH_2)C(CH_3)_2(CH_2O)PS_2\}V$] **(1)** was carried out on vibrating sample magnetometer (VSM) at room temperature. The weak field nature of dithiophosphate ligand is revealed by the high effective magnetic moment value (μ_{eff}) (2.81 B.M) [14] of this complex which gives $t_{2g}^{\ 2}$ and $e_g^{\ 0}$ configuration to

vanadium(III) and implies very weak paramagnetic nature of this complex. These magnetic moment value of the complex depicts the octahedral geometry around the vanadium(III) atom, which is also indicating anti-ferromagnetic interaction.

3.8. Antibacterial

The antibacterial screening of these complexes also exhibited significant inhibition of bacterial strains Gram–positive: *Enterrococcus faecalis* and *Bacillus cereus* and Gram–negative: *Eischerichia coli* and *Klebsiella pneumoniae* with increasing concentration of the complexes. The observed zone of inhibition for each concentration of the complexes has been given in the **Table 2** which also shows high antibacterial activity of these complexes against the bacterial strain especially for *E. coli.* The observed enhancement in antibacterial activity of the metal complexes in comparison to simple ligands can be explained on the basis of Overtone's concept and Tweedy's chelation theory [15]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only the lipid-soluble materials makes which liposolubility is an important factor, which controls the antibacterial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of n-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of the proteins that restricts further growth of the organism. The antibacterial screening data has been tabulated in T**able 2** and comparison of antibacterial activity of vanadium(III) complexes and free ligands is described diagrammatically in **Figure 2**.

Table 2: Antibacterial screening data of mixed ligand complexes of vanadium(III).

S. No.	Concentration (in ppm)	Zone of Inhibition
o-ligand	100	-0.2
	200	-0.3
	400	-0.4
	800	-0.4
4	100	0.4
	200	0.5
	400	0.9
	800	1

6	100	0.2
	200	0.5
	400	1.1
	800	1.4

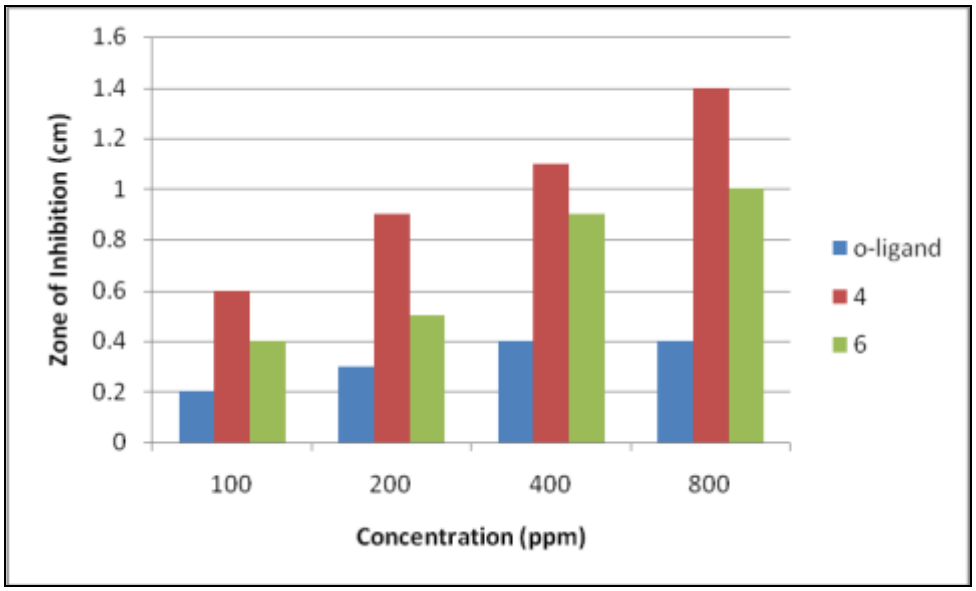

Fig. 2: Graphical comparison of antibacterial screening data

3.9. Antifungal Activity

The antifungal activity of ligands and a few representative metal complexes were evaluated by the poisoned food technique against plant pathogenic strain, *Fusarium oxysporum*. The antifungal screening data are given in **Table 3**, which shows on enhancing the concentration of the complex, the colony diameter of the fungus decreases and hence percent inhibition increases *i.e.* all the complexes inhibited the growth of fungus significantly. This shows a linear relationship between concentration and percent inhibition. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to combined activity effect of the metal and the ligand. The chelation theory accounts for the increased activity of the metal complexes. The results of fungi-toxicity analysis have been illustrated in the **Figure 3**. Both antibacterial and antifungal activities were tested in the Bio-assay lab, Department of Chemistry, University of Jammu, Jammu.

Table 3: Antifungal screening data of mixed ligand complexes of vanadium(III)

S. No.	100 ppm		200 ppm		400 ppm		800 ppm	
	Colony diameter, (cm)	Inhibition over control (%)	Colony diameter, (cm)	Inhibition over control (%)	Colony diameter, (cm)	Inhibition over control (%)	Colony diameter, (cm)	Inhibition over control (%)
o-ligand	3.6	10	2.4	40	1.9	52.5	1.5	62.5
16	0.9	77.5	0.6	85	0.6	85	0.6	85
19	1	75	0.8	80	0.6	85	0.6	85
Control	4	0	4	0	4	0	4	0

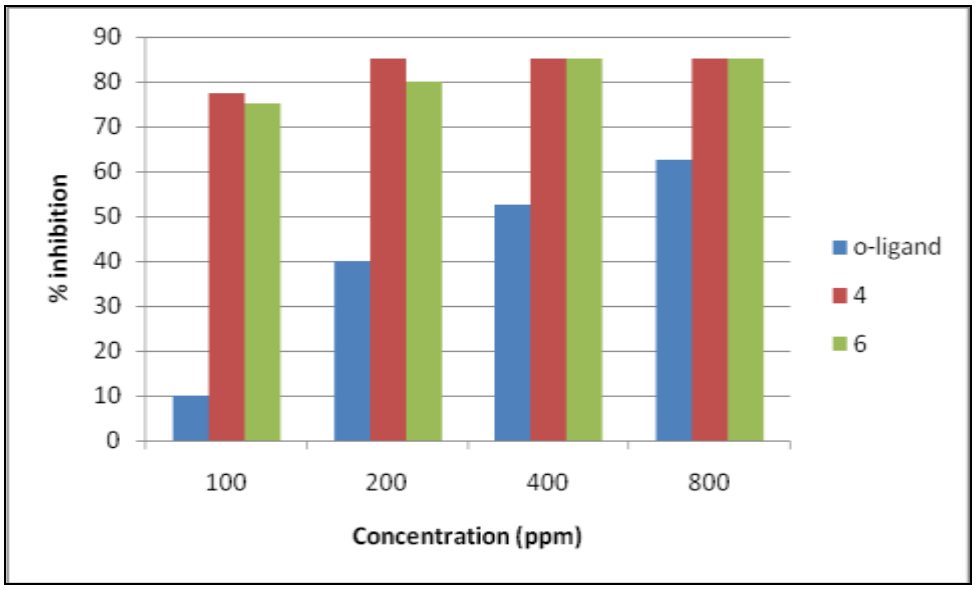

Fig. 3: Graphical comparison of antifungal screening data.

IV.CONCLUSION

On the basis of literature reports and various physico-chemical studies like elemental analysis, magnetic studies, mass, UV, IR, NMR (^{1}H, ^{13}C, ^{31}P and ^{51} V) six-folded geometries may tentatively be proposed for the mixed diaryldithiophosphate-neopentylenedithiophosphates and diaryldithiophosphate-benzyldithiocarbonates of vanadium(III) complexes. The $\Delta\nu$ in the ν(P)−O−C, νP−O−(C), νP=S and νP−S bands for dithiophosphate moiety in comparison to the parent dithiophosphate ligands indicates the formation of these complexes **(1-10)**. It is interesting to note that appearance of new bands was observed in the IR spectra of these complexes in

comparison to the parent dithiophosphate ligands. A new band ascribed to *v*V−S is indicative of formation of vanadium-sulfur bond in these complexes. The Δ*v* in for *v*P=S and *v*P−S bands for both the dithio moieties in comparison to the parent dithiophosphate ligands also indicate the formation of these complexes. A downfield singlet for the phosphorus atom of the dithiophosphato moiety indicates the bidentate mode of chelation by dithiophosphate ligand in addition to the equivalent nature of the phosphorus atom in these complexes. Two singlets observed for the phosphorus atom of the ditolyldithiophosphate moiety and the neopentylenedithiophosphate moiety indicates the presence of both the phosphorus atoms of different ligands in these complexes. Therefore, distorted octahedral geometry may be proposed around the vanadium(III) atom in the complexes **(Figure 4 a-b)**.

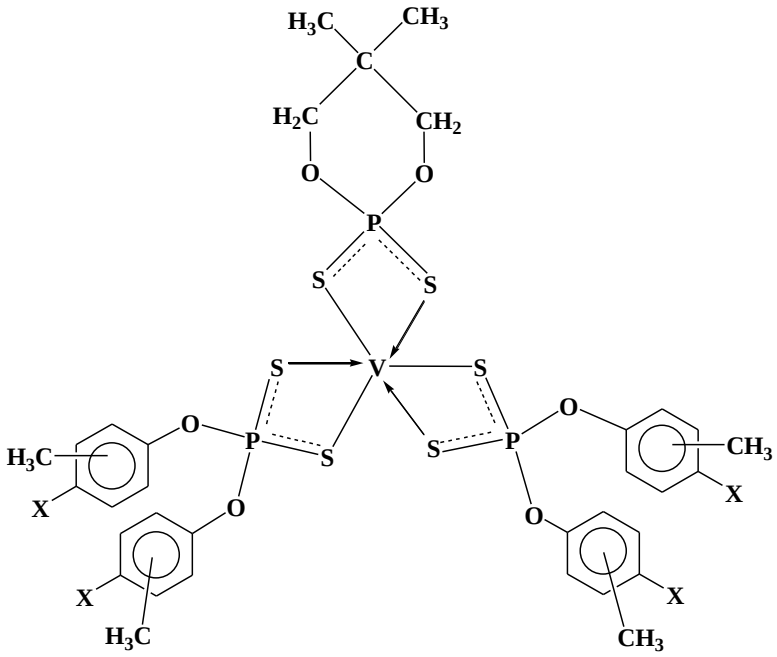

Fig. 4 (a): Proposed distorted octahedral geometry of diaryldithiophosphate-neopentylenedithiophosphates of vanadium(III) (1-4); X = H (1, 2), CH_3 (3) or Cl (4).

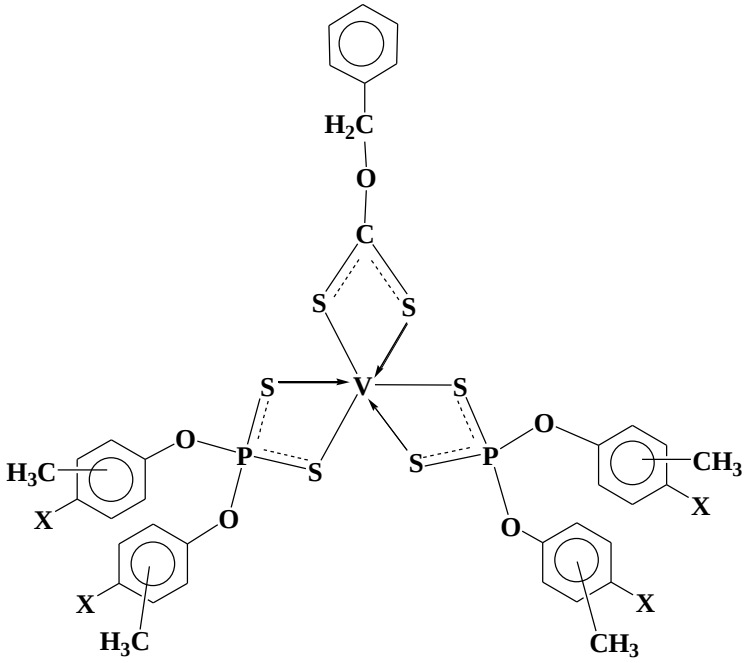

Fig. 4 (b): Proposed octahedral geometry of mixed diaryldithiophosphate-dithiocarbonate of vanadium(III) (5-8); X = H (5, 6), CH_3 (7) or Cl (8).

V.ACKNOWLEGDEMENT

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