Scientific paper

Synthesis, Spectral and Antifungal Analysis of Diaryldithiophosphates of Mono- and Dibutyltin(IV): X-ray Structure of $[\{(3,5\text{-}CH_3)_2C_6H_3O)_2PS_2\}_2Sn(^nBu)_2]$

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Abstract

Diaryldithiophosphate complexes of mono- and dibutyltin(IV) corresponding to $[\{(ArO)_2PS_2\}_nSn(^nBu)_xCl_{4-x-n}]$ (Ar = *o*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, 4-Cl-3-$CH_3C_6H_3$, (3,5-$CH_3)_2C_6H_3$; n = 1, 2 for x = 1 and n = 2 for x = 2) were successfully isolated and characterized by elemental analyses, IR, multinuclear NMR (^1H, ^{13}C, ^{31}P and ^{119}Sn) spectroscopy and X-ray analysis. The thermal properties of the complex $[\{(3,5\text{-}CH_3)_2C_6H_3O\}_2PS_2]_2Sn(^nBu)_2$ **(12)** have been examined by combined DTA/ DTG thermal analyses. Single crystal X-ray analysis of $[\{(3,5\text{-}CH_3)_2C_6H_3O\}_2PS_2]_2Sn(^nBu)_2$ **(12)** revealed that two diaryldithiophosphate ions are coordinated to tin atom in an anisobidentate fashion through the sulfur atoms of each dithiophosphate moiety leading to distorted *skew-trapezoidal bipyramidal* geometry. The antifungal activity depicts that these complexes are active against fungus *Penicillium chrysogenium*.

Keywords: Diaryldithiophosphate, Tin compounds, Phosphorus compounds, Spectroscopy, X-ray structure determination

1. Introduction

Organotin compounds have the widest range of uses of all main-group organometallic compounds. The increase in the industrial use is due to the diverse technical applications,[1–2] toxicological[3] and environment[4–5] properties. The majority of organotin compounds comprises of six major commercial applications like PVC,[6] heat stabilizers,[7] biocides,[8–9] catalysts,[10] agrochemicals[11] and glass coatings.[12] R_3SnX (R = Me, Et, ^{i}Pr, ^{n}Bu; X = Cl, Br) compounds are mainly used in biological application as pesticides, insecticides, fungicides and acaricides.[8] Tributyltin oxide is used to preserve cellulose, wood and stonework to prevent fungal attack.[13] Recent work has raised the possibility that certain dialkyltin compounds may have a role to play in cancer chemotheraphy.[14–17] Particularly, the organotin complexes with sulfur donor ligands show interesting cytostatic activity.[18] Non-biocide uses of organotin compounds are mainly found in R_2SnX_2 and $RSnX_3$. Mono- and dialkyltin compounds are mainly used as stabilizers in PVC against thermal and photochemical degradation.[6] Dimethyltin dichloride is used as a precursor for forming thin surface films of SnO_2 on glass[1] at the temperature of 500–600 °C. Dibutyltin compounds are used as homogenous catalysts in the manufacture of polyurethane foam.[10] Certain monobutyltin compounds are also used as catalyst in the trans-esterification of oil.[19]

Among the variety of the ligands, organotin complexes of dithiophosphates have been extensively studied because of their interesting structural features and biological activities.[20–23] The biological aspect of dithiophosphates has been well established in the rapidly growing field of phosphorus-sulfur chemistry.[24–25] The dithiophosphates have received much attention for their extensive applications as biocides,[26] analytical reagents,[27] antiwear and antioxidant additives in motor oils.[28] A literature survey showed scarce reports on diaryldithiophosphate complexes of mono- and dibutyltin(IV) compared to dialkyl- and alkylenedithiophosphates.[21–22] So, we herein report for the first time the synthesis, characterization and *in vitro* biolo-

gical activity of diaryldithiophosphate complexes of tin(IV) including the single crystal structure of [{(3,5-$CH_3)_2C_6H_3O\}_2PS_2]_2Sn(^nBu)_2$.

2. Experimental

2. 1. Materials and Measurements

All the experimental manipulations were carried out under moisture free conditions using standard Schlenk techniques. Solvents were dried and distilled before use. The ligands, sodium salts of *O,O'*-di(*o*-, *m*-, *p*-methyl, 4-chloro-3-methyl and 3,5-dimethylphenyl)dithiophosphates, were prepared according to literature report.[29] Tin was estimated gravimetrically as SnO_2 and chlorine was estimated by Volhard's method.[30] 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 $CDCl_3$. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 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 Avance III 400 MHz. The ^{119}Sn NMR spectra were recorded on a Bruker 400 Avance II spectrometer using tetramethyltin as an external standard. The thermogram was analyzed by using Perkin Elmer, diamond TG/DTA instrument. Recrystallized alumina sample holder was used and the heating rate of 20 °C min^{-1}. The thermogram was recorded in the temperature range from 30 °C to 1000 °C. The experiment was carried out under a flow rate of 50 mL min^{-1} of nitrogen atmosphere.

2. 2. Synthesis of [{(*o*-$CH_3C_6H_4O)_2PS_2$} $Sn(^nBu)Cl_2$] (1)

A toluene solution (10 mL) of *n*-butyltin(IV) trichloride, $^nBuSnCl_3$, (0.85 g, 3.01 mM) was added dropwise to a suspension (20 mL) of sodium *O,O'*-*o*-ditolyldithiophosphate, (*o*-$CH_3C_6H_4O)_2PS_2Na$, (1.00 g, 3.01 mM) in toluene with constant stirring. The contents were stirred for 24 h at room temperature. The precipitated sodium chloride was removed by filtration in *vacuo*. The removal of volatiles from the filtrate in *vacuo* yielded the desired product as pale yellow solid. Yield: 1.51 g (90%); m.p. 70–71 °C (dec.); IR (KBr, cm^{-1}): 1127.4 s [ν(P)-O-C], 957.5 s [νP-O-(C)], 855.5 s [νP=S], 533.58 m [νP-S], 481.2 w [νSn-S], 337.4 w [νSn-Cl] cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.9 (t, 3H, CH_3), 1.3–1.7 (m, 6H, $Sn(CH_2)_3$), 2.4 (s, 6 H, CH_3), 6.8 (d, 2 H, *ortho*), 7.1 (t, 2 H, *para*), 7.2 (d, 2 H, *meta*), 7.3 (t, 2 H, *meta'*), ppm; ^{13}C NMR ($CDCl_3$): δ = 13.3, 24.4, 30.8, 36.1, ($CH_3CH_2CH_2CH_2Sn$), 19.5 (CH_3), 118.2 (C_{ortho}), 129.7 (C_{para}), 131.4 (C–CH_3), 132.3 (C_{meta}), 133.8 ($C_{meta'}$), 149.5 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 86.5, s ppm; ^{119}Sn NMR ($CDCl_3$): δ = –174.4, s ppm.

2. 3. Synthesis of [{(*m*-$CH_3C_6H_4O)_2PS_2$} $Sn(^nBu)Cl_2$] (2)

Complex **2** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, $^nBuSnCl_3$, (0.85 g, 3.01 mM) and sodium *O,O'*-*m*-ditolyldithiophosphate, (*m*-$CH_3C_6H_4O)_2PS_2Na$, (1.00 g, 3.01 mM). Yield: 1.48 g (87%); m.p. 71–72 °C (dec.); IR (KBr, cm^{-1}): 1149.9 s [ν(P)-O-C], 967.3 s [νP-O-(C)], 871.6 s [νP=S], 534.2 m [νP-S], 470.8 w [νSn-S], 341.8 w [νSn-Cl] cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.8 (t, 3H, CH_3), 1.4–1.8 (m, 6H, $Sn(CH_2)_3$), 2.3 (s, 6 H, CH_3), 6.6 (d, 2 H, *ortho*), 6.7 (s, 2 H, *ortho'*), 6.8 (d, 2 H, *para*), 7.1 (t, 2 H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.5, 25.7, 30.4, 35.9, ($CH_3CH_2CH_2CH_2Sn$), 19.2 (CH_3), 111.3(C_{ortho}), 119.7 ($C_{ortho'}$), 126.3 (C_{para}), 127.9 (C_{meta}), 131.1 (C–CH_3), 153.5 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 91.5, s ppm.

2. 4. Synthesis of [{(*p*-$CH_3C_6H_4O)_2PS_2$} $Sn(^nBu)Cl_2$] (3)

Complex **3** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, $^nBuSnCl_3$, (0.85 g, 3.01 mM) and sodium *O,O'*-*p*-ditolyldithiophosphate, (*p*-$CH_3C_6H_4O)_2PS_2Na$, (1.00 g, 3.01 mM). Yield: 1.39 g (83%); m.p. 77–78 °C (dec.); IR (KBr, cm^{-1}): 1157.6 s [ν(P)-O-C], 956.8 s [νP-O-(C)], 865.4 s [νP=S], 532.2 m [νP-S], 475.9 w [νSn-S], 349.6 w [νSn-Cl] cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.7 (t, 3H, CH_3), 1.3–1.8 (m, 6H, $Sn(CH_2)_3$), 2.4 (s, 6 H, CH_3), 6.9 (d, 4 H, *ortho*), 7.2 (d, 4 H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.9, 23.4, 31.0, 36.6, ($CH_3CH_2CH_2CH_2Sn$), 21.4 (CH_3), 114.2 (C_{ortho}), 122.3 (C–CH_3), 139.3 (C_{meta}), 155.7 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 87.9, s ppm.

2. 5. Synthesis of [{(4-Cl-3-$CH_3C_6H_3O)_2PS_2$} $Sn(^nBu)Cl_2$] (4)

Complex **4** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, $^nBuSnCl_3$, (0.70 g, 2.48 mM) and sodium *O,O'*-di(4-chloro-3-methylphenyl)dithiophosphate, (4-Cl-3-$CH_3C_6H_3O)_2PS_2Na$, (1.00 g, 2.49 mM). Yield: 1.39 g (89%); m.p. 73–74 °C (dec.); IR (KBr, cm^{-1}): 1147.2, s [ν(P)-O-C], 968.2 s [νP-O-(C)], 861.2 s [νP=S], 541.1 m [νP-S], 479.6 w [νSn-S], 340.4 w [νSn-Cl] cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.6 (t, 3H, CH_3), 1.4–1.7 (m, 6H, $Sn(CH_2)_3$), 2.4 (s, 6 H, CH_3), 6.7s–6.9 (m, 4 H, *ortho*), 7.2 (d, 2 H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.7, 23.9, 30.4, 36.1, ($CH_3CH_2CH_2CH_2Sn$), 18.1 (CH_3), 119.2(C_{ortho}), 120.2 ($C_{ortho'}$), 127.7 (C_{para}), 128.9 (C_{meta}), 130.4 (C–CH_3), 152.5 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 85.8, s ppm.

2. 6. Synthesis of [{(3,5-$(CH_3)_2C_6H_3O)_2PS_2$} Sn(^{n}Bu)Cl_2] (5)

Complex **5** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, ^{n}BuSnCl_3, (0.78 g, 2.76 mM) and sodium *O,O'*-di(3,5-dimethylphenyl)dithiophosphate, (3,5-$(CH_3)_2C_6H_3O)_2PS_2Na$, (1.00 g, 2.78 mM). Yield: 1.38 g (85%); m.p. 75–76 °C (dec.); IR (KBr, cm^{-1}): 1178.1 s [*ν*(P)-O-C], 973.9 s [*ν*P-O-(C)], 872.3 s [*ν*P=S], 539.7 m [*ν*P-S], 471.2 w [*ν*Sn-S], 342.9 w [*ν*Sn-Cl] cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.7 (t, 3H, CH_3), 1.4–1.9 (m, 6H, Sn(CH_2)$_3$), 2.3 (s, 12 H, CH_3), 6.7 (s, 4 H, *ortho*), 7.0 (s, 2 H, *para*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.9, 25.2, 30.1, 36.8, ($CH_3CH_2CH_2CH_2$Sn), 21.2 (CH_3), 119.3 (C_{ortho}), 126.5 (C_{para}), 138.9 (C–CH_3), 151.6 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 89.4, s ppm.

2. 7. Synthesis of [{(*o*-$CH_3C_6H_4O)_2PS_2$}$_2$ Sn(^{n}Bu)Cl] (6)

Complex **6** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, ^{n}BuSnCl_3, (0.42 g, 1.49 mM) and sodium *O,O'*-*o*-ditolyldithiophosphate, (*o*-$CH_3C_6H_4O)_2PS_2Na$, (1.00 g, 3.01 mM). Yield: 1.05 g (84%); m.p. 66–67 °C (dec.); IR (KBr, cm^{-1}): 1162.5 s [*ν*(P)-O-C], 979.1 s [*ν*P-O-(C)], 860.1 s [*ν*P=S], 536.9 m [*ν*P-S], 479.1 w [*ν*Sn-S], 338.5 w [*ν*Sn-Cl] cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.7 (t, 3H, CH_3), 1.4–1.7 (m, 6H, Sn(CH_2)$_3$), 2.4 (s, 12H, CH_3), 6.7 (d, 4 H, *ortho*), 6.9 (t, 4 H, *para*), 7.0 (d, 4 H, *meta*), 7.2 (t, 4 H, *meta'*), ppm; ^{13}C NMR ($CDCl_3$): δ = 13.9, 25.1, 30.2, 35.4, ($CH_3CH_2CH_2CH_2$Sn), 20.5 (CH_3), 115.0 (C_{ortho}), 129.9 (C_{para}), 134.9 (C–CH_3), 135.0 (C_{meta}), 135.5 ($C_{meta'}$), 148.0 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 87.6, s ppm.

2. 8. Synthesis of [{(*m*-$CH_3C_6H_4O)_2PS_2$}$_2$ Sn(^{n}Bu)Cl] (7)

Complex **7** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, ^{n}BuSnCl_3, (0.42 g, 1.49 mM) and sodium *O,O'*-*m*-ditolyldithiophosphate, (*m*-$CH_3C_6H_4O)_2PS_2Na$, (1.00 g, 3.01 mM). Yield: 1.01 g (81%); m.p. 68–69 °C (dec.); IR (KBr, cm^{-1}): 1159.2 s [*ν*(P)-O-C], 960.1 s [*ν*P-O-(C)], 867.2 s [*ν*P=S], 542.1 m [*ν*P-S], 470.1 w [*ν*Sn-S], 344.3 w [*ν*Sn-Cl] cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.8 (t, 3H, CH_3), 1.3–1.7 (m, 6H, Sn(CH_2)$_3$), 2.4 (s, 12 H, CH_3), 6.6 (d, 4 H, *ortho*), 6.8 (s, 4 H, *ortho'*), 6.9 (d, 4 H, *para*), 7.1 (t, 4 H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.8, 25.7, 29.1, 35.9, ($CH_3CH_2CH_2CH_2$Sn), 19.5 (CH_3), 115.1(C_{ortho}), 118.5 ($C_{ortho'}$), 125.6 (C_{para}), 128.9 (C_{meta}), 132.3 (C–CH_3), 152.7 (C–O) ppm; ^{1}P NMR ($CDCl_3$): δ = 87.3, s ppm.

2. 9. Synthesis of [{(*p*-$CH_3C_6H_4O)_2PS_2$}$_2$ Sn(^{n}Bu)Cl] (8)

Complex **8** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, ^{n}BuSnCl_3, (0.42 g, 1.49 mM) and sodium *O,O'*-*p*-ditolyldithiophosphate, (*p*-$CH_3C_6H_4O)_2PS_2Na$, (1.00 g, 3.01 mM). Yield: 1.04 g (81%); m.p. 72–73 °C (dec.); IR (KBr, cm^{-1}): 1153.5 s [*ν*(P)-O-C], 972.7 s [*ν*P-O-(C)], 865.4 s [*ν*P=S], 538.7 m [*ν*P-S], 476.1 w [*ν*Sn-S], 345.9 w [*ν*Sn-Cl] cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.8 (t, 3H, CH_3), 1.3–1.5 (m, 6H, Sn(CH_2)$_3$), 2.3 (s, 12 H, CH_3), 6.7 (d, 8 H, *ortho*), 7.3 (d, 8 H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.8, 24.9, 28.6, 36.6, ($CH_3CH_2CH_2CH_2$Sn), 18.1 (CH_3), 128.8 (C_{ortho}), 128.2 (C–CH_3), 131.6 (C_{meta}), 152.9 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 88.9, s; ^{119}Sn NMR ($CDCl_3$): δ = –185.3, s ppm.

2. 10. Synthesis of [{(4-Cl-3-$CH_3C_6H_3O)_2$ PS_2}$_2$Sn(^{n}Bu)Cl] (9)

Complex **9** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, ^{n}BuSnCl_3, (0.35 g, 1.24 mM) and sodium *O,O'*-di(4-chloro-3-methylphenyl)dithiophosphate, (4-Cl-3-$CH_3C_6H_3O)_2PS_2Na$, (1.00 g, 2.49 mM). Yield: 1.02 g (84%); m.p. 69–70 °C (dec.); IR (KBr, cm^{-1}): 1138.7 s [*ν*(P)-O-C], 961.4 s [*ν*P-O-(C)], 870.3 s [*ν*P=S], 539.9 m [*ν*P-S], 478.6 w [*ν*Sn-S], 339.1 w [*ν*Sn-Cl] cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.7 (t, 3H, CH_3), 1.3–1.6 (m, 6H, Sn(CH_2)$_3$), 2.4 (s, 12 H, CH_3), 6.8–7.0 (m, 8 H, *ortho*), 7.2 (d, 4 H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.7, 25.7, 28.4, 36.7, ($CH_3CH_2CH_2CH_2$Sn), 17.0 (CH_3), 119.7 (C_{ortho}), 121.0 ($C_{ortho'}$), 127.0 (C_{para}), 130.9 (C_{meta}), 131.2 (C–CH_3), 154.8 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 87.9, s ppm.

2. 11. Synthesis of [{(3,5-$(CH_3)_2C_6H_3O)_2$ PS_2}$_2$Sn(^{n}Bu)Cl] (10)

Complex **10** was synthesized as described for **1** from *n*-butyltin(IV) trichloride, ^{n}BuSnCl_3, (0.39 g, 1.38 mM) and sodium *O,O'*-di(3,5-dimethylphenyl)dithiophosphate, (3,5-$(CH_3)_2C_6H_3O)_2PS_2Na$, (1.00 g, 2.76 mM). Yield: 1.02 g (83%); m.p. 77–78 °C (dec.); IR (KBr, cm^{-1}): 1173.4 s [*ν*(P)-O-C], 959.9 s [*ν*P-O-(C)], 869.2 s [*ν*P=S], 541.7 m [*ν*P-S], 471.6 w [*ν*Sn-S], 337.9 w [*ν*Sn-Cl] cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.6 (t, 3H, CH_3), 1.4–1.8 (m, 6H, Sn(CH_2)$_3$), 2.3 (s, 24 H, CH_3), 6.9 (s, 8 H, *ortho*), 7.2 (s, 4 H, *para*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.8, 24.8, 30.1, 36.8, ($CH_3CH_2CH_2CH_2$Sn), 21.2 (CH_3), 119.3 (C_{ortho}), 126.5 (C_{para}), 138.9 (C–CH_3), 151.6 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 92.3, s ppm.

2. 12. Synthesis of [{(4-Cl-3-$CH_3C_6H_3O)_2$ PS_2}$_2$Sn(^{n}Bu)$_2$] (11)

Complex **11** was synthesized as described for **1** from di-*n*-butyltin(IV) dichloride, ^{n}Bu$_2$SnCl_2, (0.38 g, 1.25 mM) and sodium *O,O'*-di(4-chloro-3-methylphenyl)dithiophosphate, (4-Cl-3-$CH_3C_6H_3O)_2PS_2Na$, (1.00 g, 2.49 mM). Yield: 1.12 g (91%); m.p. 78–79 °C (dec.); IR (KBr, cm^{-1}): 1139.6 s [*ν*(P)-O-C], 973.8 s [*ν*P-O-(C)], 869.4 s [*ν*P=S], 538.8 m [*ν*P-S], 473.0 w [*ν*Sn-S] cm^{-1}; ^{1}H NMR ($CDCl_3$):

δ = 0.7 (t, 6H, CH_3), 1.3–1.7 (m, 12H, $Sn(CH_2)_3$), 2.4 (s, 12 H, CH_3), 6.8–7.1 (m, 8 H, *ortho*), 7.3 (d, 4 H, *meta*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.6, 25.3, 28.3, 35.6, ($CH_3CH_2CH_2CH_2Sn$), 17.9 (CH_3), 119.5(C_{ortho}), 121.9 ($C_{ortho'}$), 128.8 (C_{para}), 129.1 (C_{meta}), 130.8 (C–CH_3), 151.5 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 91.2, s ppm.

2. 13. Synthesis of [{(3,5-$(CH_3)_2C_6H_3O)_2PS_2$}$_2$Sn(^{n}Bu)$_2$] (12)

Complex **12** was synthesized as described for **1** from di-*n*-butyltin(IV) dichloride, ^{n}Bu$_2$SnCl$_2$, (0.42 g, 1.38 m-M) and sodium *O,O'*-di(3,5-dimethylphenyl)dithiophosphate, (3,5-$(CH_3)_2C_6H_3O)_2PS_2Na$, (1.00 g, 2.76 mM). Yield: 1.18 g (94%); m.p. 81–82 °C (dec.); IR (KBr, cm^{-1}): 1128.9 s [ν(P)-O-C], 954.8 s [νP-O-(C)], 861.1 s [νP=S], 535.3 m [νP-S], 471.3 w [νSn-S] cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.8 (t, 6H, CH_3), 1.2–1.9 (m, 12H, $Sn(CH_2)_3$), 2.3 (s, 24 H, CH_3), 7.0 (s, 8 H, *ortho*), 7.3 (s, 4 H, *para*) ppm; ^{13}C NMR ($CDCl_3$): δ = 13.4, 25.9, 27.9, 35.7, ($CH_3CH_2CH_2CH_2Sn$), 21.3 (CH_3), 119.5 (C_{ortho}), 127.3 (C_{para}), 139.2 (C–CH_3), 150.5 (C–O) ppm; ^{31}P NMR ($CDCl_3$): δ = 93.5, s ppm; ^{119}Sn NMR ($CDCl_3$): δ = –200.3, s ppm.

Table 1. Crystal data and structure refinements for complex **12**.

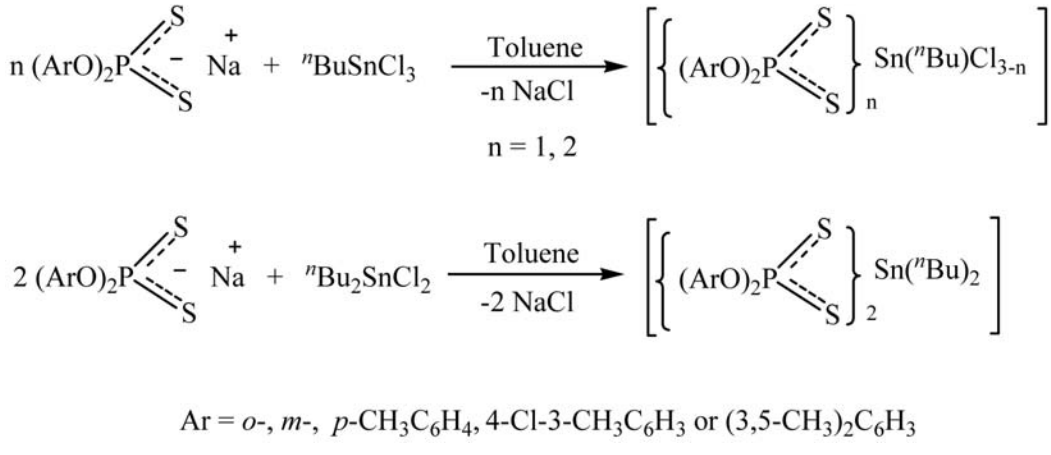
Complex	12
Crystal system	*triclinic*
Space group	*P*-1
Temperature, K	296(2)
Empirical formula	C_{40} H_{54} O_4 P_2 S_4 Sn
Z	2
Formula weight	907.76
a (Å)	12.3211(16)
b (Å)	14.0300(16)
c (Å)	15.1473(19)
α (°)	70.485(6)
β (°)	79.212(6)
γ (°)	68.642(6)
V (Å^3)	2292.1(5)
D_{calc} (g/cm^3)	1.315
F(000)	940
θ range for data collection (°)	1.43-27.92
No. of collected reflections	39997
Independent reflections	10817 [R(int) = 0.0313]
No. of data/restraints/parameters	10818 /6/470
R1, wR2 [$I - 2\sigma(I)$]	0.0330, 0.0839
R1, wR2 (all data)	0.0496, 0.0973
Goodness-of-fit on F^2	0.986
Largest difference in peak/hole, (e Å^{-3})	0.434/–0.465

2. 14. X-ray Crystallographic Study

Crystallization of complex **12** achieved by dissolving the sample in toluene-*n*-hexane solution for 2–3 days in the refrigerator. The data were measured on a Bruker Apex-II CCD diffractometer using Mo Kα (λ = 0.71069 Å). The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS using software supplied by Bruker-AXS. The structure was solved by direct methods, using SIR-92 [31] and refined by full-matrix least squares refinement methods based on F^2, using SHELX-97.[32] All non-hydrogen atoms were refined anisotropically. All calculations were performed using WINGX package.[33] Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

2. 15. Antifungal Activity

Antifungal activity assay was carried out by agar well diffusion method.[34] A few representative complexes (**2, 6, 10, 12**) were screened for antifungal activity. With sterile cork borer of size 6 mm. 48 hours old cultures grown on potato dextrose agar (PDA) were used for preparing spore suspension for inoculation. 0.1 mL of test



Scheme 1: Synthesis of diaryldithiophosphate derivatives of tin(IV)

fungal spore suspension was spread on sterile agar plates. Appropriate wells were made on agar plate by using cork borer and 50 μL of complex of different concentrations were loaded. Plates were kept for pre-incubation for 30 min in refrigerator and then were incubated for 48 hours at 27 °C. The antifungal activity was evaluated by measuring zone of inhibition of fungal growth surrounding the well with complex solution in DMSO. The experiment was carried out in triplicate.

3. Results and Discussion

n-Butyltin(IV) trichloride and di-*n*-butyltin(IV) dichloride were reacted with sodium salts of *O*,*O'*-di(*o*-, *m*-, *p*-methyl, 4-chloro-3-methyl and 3,5-dimethylphenyl)dithiophosphoric acid in dry toluene in molar ratios of 1 : 1 and 1 : 2 to afford the diaryldithiophosphates, *i.e.* $[\{(ArO)_2PS_2\}_nSn(^nBu)Cl_{3-n}]$ and $[\{(ArO)_2PS_2\}_2Sn(^nBu)_2]$ (Ar = *o*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, 4-Cl-3-$CH_3C_6H_3$, (3,5-CH_3)$_2C_6H_3$; n = 1, 2) (Scheme 1).

3. 1. Spectroscopic Studies

The IR spectra of the complexes **1–12** were interpreted on the comparison basis with relevant literature reports.[20–22,35] Only slight shifting of bands in the IR spectra was observed compared to free ligands. The diagnostic vibrational frequencies are the two strong intensity bands for *ν*(P)-O-C (1178.1–1127.4 cm^{-1}) and *ν*P-O-(C) (979.1 –954.8 cm^{-1}) alongwith the two medium intensity bands for *ν*P=S (872.3–855.5 cm^{-1}) and *ν*P-S (547.6–532.2 cm^{-1}). The Δ*ν* value (~ 300 cm^{-1}) for *ν*P=S and *ν*P-S bands signifies anisobidentate binding mode. Furthermore, the presence of a band for *ν*Sn-S in the region 481.2–471.3 cm^{-1} is indicative of the formation of tin-sulfur bond. The weak band in the region 349.6–337.4 cm^{-1} is attributed to *ν*Sn-Cl.

The ^{1}H NMR spectra ($CDCl_3$) of these complexes show negligible shifting of the proton resonances of aryl protons in comparison to the parent ligands. The protons associated with the butyl moiety show a complex pattern. The terminal CH_3 protons resonated as a triplet (0.6–0.9 ppm), while α, β and γCH_2 protons gave their chemical shift as a multiplet in the region 1.2–1.9 ppm. The chemical shift for the methyl protons of the aryl ring was observed in the region 2.3–2.4 ppm as singlet. The chemical shifts for the aryl ring protons were observed in the region 6.5–7.3 ppm as multiplet. Four resonances were observed for the *ortho* and *meta* derivatives while two resonances were observed for the *para* and 3,5-dimethylphenyl derivatives. The 4-chloro-3-methylphenyldithiophosphato derivatives exhibited three resonances for aryl protons.

The phosphorus atom of the dithiophosphate moiety appears as a singlet in the region 85.8–93.5 ppm in the ^{31}P NMR spectra, indicating its equivalent nature. This range observed for ^{31}P nucleus in these complexes may be correlated with anisobidentate behavior of dithiophosphate moiety.[36]

The ^{13}C NMR spectra of the complexes did not show any shift compared to corresponding carbons in the uncoordinated ligand and metal salt. The carbon nuclei of the butyl moiety resonated in the region 13.4–36.6 ppm. The chemical shift for the methyl carbon, attached to aryl ring, was found in the region 17.0–21.4 ppm. The carbon nuclei of the aryl ring have displayed their resonance in the region 113.3–155.7 ppm.

The ^{119}Sn NMR spectra (in $CDCl_3$) of few representative complexes $[\{(o\text{-}CH_3C_6H_4O)_2PS_2\}Sn(^nBu)Cl_2]$ (**1**), $[\{(p\text{-}CH_3C_6H_4O)_2PS_2\}_2Sn(^nBu)Cl]$ (**8**) and $[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Sn(^nBu)_2]$ (**12**) show the chemical shift toward lower frequency region of –174.4, –185.3 and –200.3 ppm, respectively. The signal for the complex **1** is observed downfield in comparison to that for the complex **8**. This may be attributed to the presence of chlorine atom. With the displacement of electronegative chlorine atom from parent metal salt by the ligand, a shielding effect is produced that is resulting in an upfield shift. Moreover, ^{119}Sn chemical shift is also influenced by the coordination number around the tin atom and the observed resonance for complex **1** corresponds to a five coordinate tin center. The upfield chemical shift for complexes **8** and **12** indicate displacement of chlorine atoms and the asymmetric chelation *i.e.* switch over between five and six coordinate tin center. In conjunction with the literature reports[20–22,37] and observed ^{119}Sn NMR spectral data, an anisobidentate chelation is supported through the sulfur atoms of the dithiophosphate ligand. Hence, the complexes **1**–**5** might have five fold coordinated tin atom and achieving *trigonal bipyramidal* geometry while the complexes **6**–**12** have six fold coordination around the tin atom. The single crystal X-ray analysis of complex **12** revealed the same and *skew trapezoidal bipyramidal* geometry is observed.

3. 2. Thermal Behavior

The thermogravimetric analysis of the complex**,** $[\{(3,5\text{-}(CH_3)_2C_6H_3O)_2PS_2\}_2Sn(^nBu)_2]$ (**12**) displayed a thermolysis step that covers a temperature range from 0 to 900 °C. The diagnostic weight loss of initial weight occurs in the steeply descending segment of the TGA curve (Figure 1). The weight loss *i.e.* 56.98% at 300.6 °C is due to the formation of the dithiophosphate corresponding to $[Sn(O_2PS_2)]$, (the calculated weight loss is 58.92%) as an intermediate product, which agrees with thermogravimetric data for dithiophosphates. The weight loss leading to the formation of the final residue is 79.89% of the initial weight of the sample corresponds to SnS_2; contaminated with other thermolysis products (the calculated weight loss is 79.86%) at 885.6 °C.

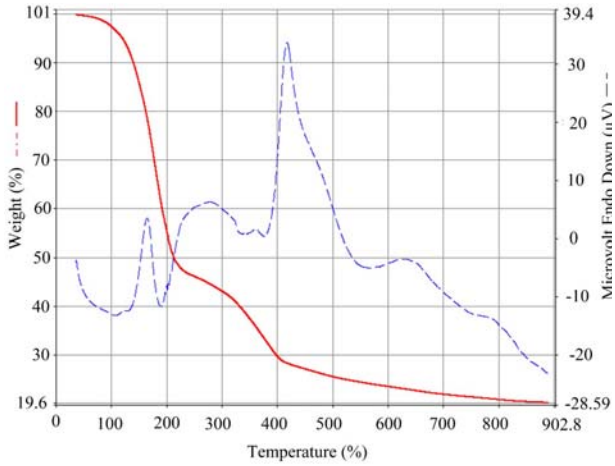


Fig. 1: TGA curve of [{(3,5-$(CH_3)_2C_6H_3O)_2PS_2$}$_2$Sn(^{n}Bu)$_2$]

3. 3. Crystal and Molecular Structures

The X-ray diffraction analysis of complex [{(3,5-$(CH_3)_2C_6H_3O)_2PS_2$}$_2$Sn(^{n}Bu)$_2$] (**12**) reveals a monomeric trigonal geometry around the tin centre (Figure 2). The tin atom is coordinated by sulfur atoms from two acyclic dithiophosphato ligands and by two α-carbon atoms from two butyl ligands. Values of selected bonds lengths and angles for the complex are given in Table 2. The Sn(1)–S(1) (2.5080(7)Å) and Sn(1)–S(3) (2.5092(8) (8) Å) bond distances are found to be consistent with the tin sulfur single bond.[38] The Sn(1)–S(2) (3.209(12) Å) and Sn(1)–S(4) (3.189(6) Å) bond distances are considerably farther from the tin atom but still well within the sum of the Van der Waals radii of 4.0 Å.[39] Hence, the two dithiophosphato ligands are coordinated to tin atom in anisobidentate fashion. Asymmetric coordination by two sulfur atoms from ligand indicates the chelating and resonating behaviour of dithiophosphato ligand in the complex.[20] The P(1)–S(1) and P(2)–S(3) bond length are 2.0198(10) Å and 2.0249(10)Å while P(1)–S(2) and P(2)–S(4) bond lengths are 1.9284(10) Å and 1.9288(11) Å. The P(1)–S(2) and P(2)–S(4) bond are shorter in length compared to P(1)–S(1) and P(2)–S(3) bond, perhaps due to somewhat asymmetric nature of ligand and π bonding in P(1)–S(2) and P(2)–S(4) bonds. Moreover, P–S bond lengths in complex **12** al-

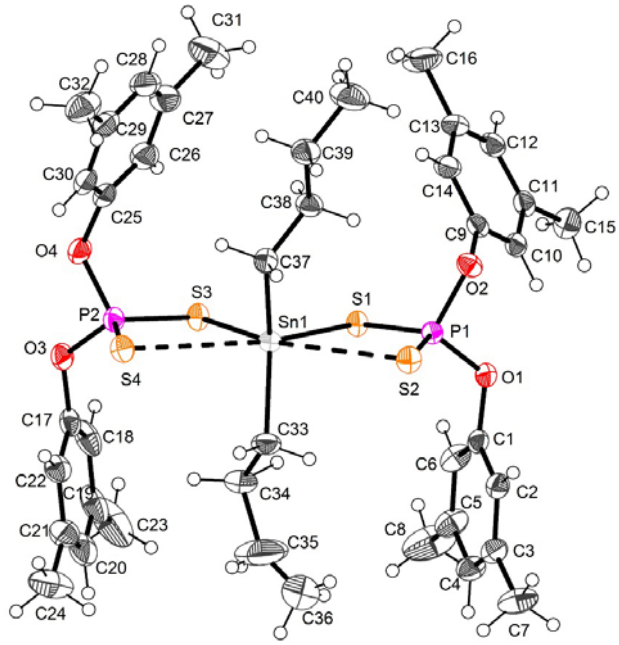


Fig. 2: ORTEP view of [{(3,5-$CH_3)_2C_6H_3O\}_2PS_2]_2$Sn(^{n}Bu)$_2$

Table 2. Selected bond lengths[Å] and angles [°] for complex **12**.

Bond Distances			
O(1)-P(1)	1.5958(19)	P(2)-S(4)	1.9288(11)
O(2)-P(1)	1.5952(19)	P(2)-S(3)	2.0249(10)
O(3)-P(2)	1.591(2)	S(1)-Sn(1)	2.5080(7)
O(4)-P(2)	1.598(2)	S(2)-Sn(1)	3.209(12)
P(1)-S(2)	1.9284(10)	S(3)-Sn(1)	2.5092(8)
P(1)-S(1)	2.0198(10)	S(4)-Sn(1)	3.189(6)
Bond Angles			
O(2)-P(1)-O(1)	98.94(11)	S(4)-P(2)-S(3)	114.10(5)
O(2)-P(1)-S(2)	110.92(8)	P(1)-S(1)-Sn(1)	96.60(3)
O(1)-P(1)- S(2)	115.63(8)	P(2)-S(3)-Sn(1)	96.38(3)
O(2)-P(1)- S(1)	107.82(8)	C(33)-Sn(1)-C(37)	134.43(13)
O(1)-P(1)-S(1)	107.54(8)	C(33)-Sn(1)-S(1)	104.81(10)
S(2)-P(1)-S(1)	114.66(4)	C(37)-Sn(1)-S(1)	109.35(8)
O(3)-P(2)-O(4)	94.08(11)	C(33)-Sn(1)-S(3)	105.91(10)
O(3)-P(2)-S(4)	116.01(9)	C(37)-Sn(1)-S(3)	107.52(8)
O(4)-P(2)-S(4)	115.33(10)	S(1)-Sn(1)-S(3)	82.68(2)
O(3)-P(2)-O(3)	107.79(9)	S(4)-Sn(1)-S(3)	70.06(2)
O(4)-P(2)-O(3)	107.55(9)	S(1)-Sn(1)-S(2)	69.86(2)
S(2)-Sn(1)-S(4)	137.40(3)	S(3)-Sn(1)-S(2)	152.54(2)

most falls in similar range as observed in [{*o*-$CH_3C_6H_4O$}$_2PS_2$]$_2$Sn(^{n}Bu)$_2$ (1.9339(8) Å, 1.9440(8) Å, 2.0242(8) Å and 2.0283(7) Å).[20] The bond lengths for the bonds O(1)–P(1), O(2)–P(1), O(3)–P(2) and O(4)–P(2) are 1.5958(19) Å, 1.5952(19) Å, 1.591(2)) Å and 1.598(2) Å, respectively.

The observed C–Sn–C bond angles further emphasize the existence of the *skew trapezoidal bipyramidal* geometry rather than the octahedral geometry. The angle C(37)–Sn(1)–C(33) [134.43(13)°] is closer to [{*o*-$CH_3C_6H_4O$}$_2PS_2$]$_2$Sn(^{n}Bu)$_2$ 136.3(1)°.[20] The *trapezoid* plane is de?ned by the four sulfur atoms derived from the two asymmetrically coordinating dithiophophate ligands. The sum of the four angles S(1)–Sn(1)–S(3), S(3)–Sn(1)–S(4), S(2)–Sn(1)–S(4) and S(1)–Sn(1)–S(2) of 360° emphasizes on the formation of a plane by one tin and the four sulfur atoms which is as good as the corresponding angles in [{*o*$CH_3C_6H_4O$}$_2PS_2$]$_2$Sn(^{n}Bu)$_2$.[20]

3. 4. Antifungal Activity

The antifungal activity of ligands and a few representative metal complexes was studied against *Penicillium chrysogenum*. The antifungal screening data (Table 3) established a linear relationship between concentration and percent inhibition. On enhancing the concentration of the complex, the inhibition zone increases *i.e.* all the complexes inhibited the growth of fungus significantly. 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.[40] The chlorine atom in the complex also seems to enhance the inhibitory effect and therefore, demonstrates its secondary role. As shown in mammalia, organotin compounds are inhibitors of oxidizing phosphorylation in mitochondria.[41] The same mechanism is believed to act in mold, whereas the thio groups also participate in this process. The illustrated comparative results of antifungal analysis are given graphically in figure 3.

Table 3. Comparative results of antifungal actvity.

Complex	Concentration (ppm)	Zone of Inhibition (in cm)
(*o*-$CH_3C_6H_4O)_2PS_2Na$	100	0.0
	500	0.0
	1000	0.0
(4-Cl-3-$CH_3C_6H_3O)_2PS_2Na$	100	0.5
	500	0.7
	1000	1.0
[(*m*-$CH_3C_6H_4O)_2PS_2$}Sn(^{n}Bu)Cl_2] (2)	100	0.6
	500	0.7
	1000	0.9
[(*o*-$CH_3C_6H_4O)_2PS_2$}$_2$Sn(^{n}Bu)Cl] (6)	100	0.5
	500	0.8
	1000	1.0
[(4-Cl-3-$CH_3C_6H_3O)_2PS_2$}$_2$Sn(^{n}Bu)Cl](10)	100	0.8
	500	0.9
	1000	1.2
[{(3,5-$(CH_3)_2C_6H_3O$}$_2PS_2$]$_2$Sn(^{n}Bu)$_2$](12)	100	0.4
	500	0.5
	1000	0.7

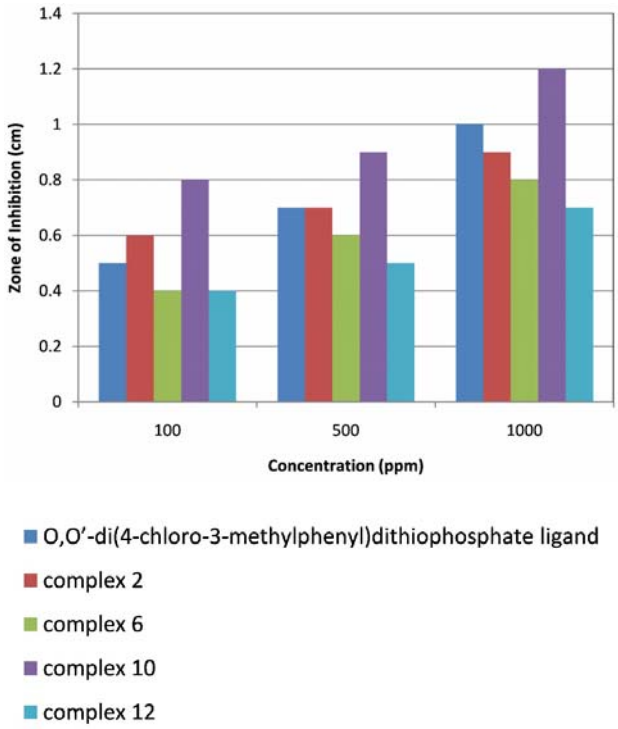


Fig. 3: Comparative results of antifungal screening data of complexes

4. Conclusion

The present study describes a series of twelve dithiophosphato complexes of organotin(IV) that have been characterized by elemental analysis, IR, NMR (^{1}H, ^{13}C, ^{31}P and ^{119}Sn) spectroscopy and thermogravimetric analysis. The complexes **1**–**5** have five coordinated tin atom (tbp) as a consequence of anisobidentate mode of chelation. The structure of complex **12**, [{((3,5-$(CH_3)_2C_6H_3O)_2$ PS_2}$_2$Sn(^{n}Bu)$_2$], in solid has been confirmed by single crystal X-ray diffraction analysis. In this complex, tin is coordinated by four sulfur atoms of two dithiophosphate moieties and α-carbon atoms of two butyl ligands leading to *skew trapezoidal bipyramidal* geometry. The thermogram exhibited the decline curve characteristic for dithiophosphate complexes. The antifungal screening depicted that the dithiophosphate ligands augmented the toxic effect of organotin compounds.

5. Supplementary Information

CCDC 990938 contains the supplementary crystallographic data for compounds (**12**). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

6. Acknowledgements

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Povzetek

Diarilditiofosfatni kompleksi mono- in dibutilkositra(IV) s formula [{$(ArO)_2PS_2$}$_n$Sn(^{n}Bu)Cl_{3-n}] in [{$(ArO)_2PS_2$}$_2$Sn(^{n}Bu)$_2$] (Ar = *o*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, 4-Cl-3-$CH_3C_6H_3$, (3,5-$CH_3)_2C_6H_3$; n = 1, 2) so bili izolirani in okarakterizirani z elementno analizo, IR in NMR (^{1}H, ^{13}C, ^{31}P and ^{119}Sn) spektroskopijo ter rentgensko strukturno analizo. Termične lastnosti spojine [{(3,5-$CH_3)_2C_6H_3O$}$_2PS_2$]$_2$Sn(^{n}Bu)$_2$ (**12**) so bile testirane z DTA/DTG termično analizo. Rentgenska monokristalna analiza [{(3,5-$CH_3)_2C_6H_3O$}$_2PS_2$]$_2$Sn(^{n}Bu)$_2$ (**12**) je razkrila, da sta dva diarilditiofosfatna iona koordinirana na kositrov atom v anizobidentatni obliki preko žveplovih atomov posamezne ditiofosfatne skupine, kar vodi do nastanka popačene trapezoidne bipiramidalne geometrije. Protiglivična aktivnost kaže, da so ti kompleksi aktivni proti glivi *Penicillium chrysogenium*.