

Bis and Mono Halide Bismuth(III) *O,O'*-Ditolyl Dithiophosphates

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Abstract

Bis and mono halide bismuth(III) *O,O'*-ditolyl dithiophosphate complexes of the type $[\text{Bi}\{\text{S}_2\text{P}(\text{OR})_2\}_n\text{Cl}_{3-n}]$ (where R = *o*-, *m*-, *p*-C₆H₄Me; n = 1-2) were synthesized by the reactions of Bismuth(III) chloride with ammonium ditolyldithiophosphates in 1:2 and 1:1 stoichiometric ratio. These novel complexes were characterized by elemental analysis, IR, ¹H NMR and ³¹P NMR spectroscopy. On the basis of comparison with the earlier reported literature distorted trigonal bipyramidal geometry (tbp) may be proposed for the complexes corresponds to [(*o*-, *m*- or *p*-MeC₆H₄O)₂PS₂BiCl₂] while an octahedral geometry for the complexes [(*o*-, *m*- or *p*-MeC₆H₄O)₂PS₂]₂BiCl].

Keywords: Bis and mono halide, Bismuth Complexes, Dithiophosphates

Introduction

Group 15 metal halides function as weak Lewis acids towards thio ethers¹ and show strong affinity for anionic dithiolato ligands²⁻¹⁷. These complexes exhibit remarkable diversity in their bonding patterns towards metals because these complexes exhibit interesting structural behaviour owing to the presence of lone pair of electrons on the metal, tiny ligand bites and molecular associations. The dithiolato ligands exhibit versatile modes of coordination such as monodentate⁹⁻¹⁰, bidentate⁸⁻¹² and bridging¹³. The bidentate and bridging coordination patterns are comparatively more stable than monodentate coordination pattern possibly due to inorganic ring formation. A number of Bismuth(III) complexes with dithiophosphate ligands have been described and $[\text{Bi}\{\text{S}_2\text{P}(\text{OMe})_2\}_3]$ ¹⁵, $[\text{Bi}\{\text{S}_2\text{P}(\text{OEt})_2\}_3]$ ¹⁶, $[\text{Bi}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}_3]$ ¹⁰, $[\text{Bi}\{\text{S}_2\text{P}(\text{OCH}(\text{Me})\text{CH}(\text{Me})\text{O})_3\}]$ ¹⁷, $[\text{Bi}\{\text{S}_2\text{P}(\text{OCH}_2\text{CEt}_2\text{CH}_2\text{O})_3\}]$ ¹⁷, $[\text{Bi}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4\text{Me-}m)_2\}_3]$ ¹¹, $[\text{Bi}(\text{C}_{12}\text{H}_{22}\text{O}_2\text{PS}_2)_3] \cdot 2\text{CHCl}_3$ ¹⁸ etc. have also been characterized by single crystal X-ray structural analysis.

$[\text{Bi}\{\text{S}_2\text{P}(\text{OEt})_2\}_3]$ ¹⁶ was explored in lubrication engineering as decontaminant agents in the catalytic cracking of petroleum. Organobismuth(III) thiolate compounds were mentioned as potent anticancer agents in Ehrlich ascites tumor in mice.¹⁹ Organobismuth(III) compounds were reported as extreme pressure additives for rolling bearing applications with extended service life²⁰. Trindade and co-workers reported one of the first example of the chemical vapour deposition (CVD) of Bi₂S₃ from the air-stable $[\text{Bi}(\text{S}_2\text{CNET}_2)_3]$ using LP-MOCVD²¹. Ditolyldithiophosphate ligands have been used as rubber vulcanizers, aerofloats, polymerization catalysts, oil additives, insecticides, herbicides and acaricides²².

Owing to interesting facets and persistence of our previous work with arsenic, antimony and bismuth dithiophosphate complexes^{3,4,11} we present herein the synthesis and characterization of some new

complexes of Bismuth(III) with *O,O'*-ditolyl dithiophosphate ligands by using 1:2 and 1:1 molar stoichiometric ratio of Bismuth trichloride and ditolyldithiophosphate ligands.

Experimental

Keeping in mind enormously hydrolysable nature of the starting materials as well as the newly synthesized compounds, rigorous precautions were taken to eliminate atmospheric moisture throughout all the experimental procedures. P_2S_5 and $BiCl_3$ were purchased from Sigma Aldrich and used as received without further purification. *o*-, *m*-, *p*- cresols, benzene and *n*-hexane were distilled before use. *O,O'*-ditolyl dithiophosphoric acids were prepared by Literature methods¹⁸⁻²⁰. Ammonium salts of the dithiophosphoric acids were prepared by reaction with an equimolar amount of ammonia in benzene.

Messenger's method was used for the estimation of Sulphur as barium sulphate²³ and Bismuth(III) was estimated by titration against standard EDTA solution using xylenol-orange as indicator²³. Perkin-Elmer 577 spectrophotometer was used to record IR spectra in the range $350-4000\text{ cm}^{-1}$. Bruker DRX-300 spectrometer was used to record 1H NMR and ^{31}P NMR spectra in $CDCl_3$ solutions using TMS and H_3PO_4 as an internal and external standard respectively.

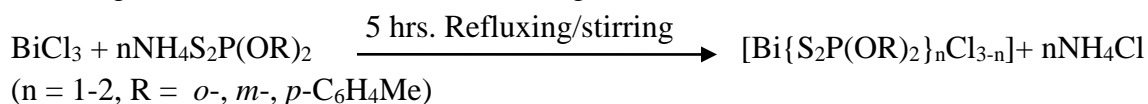
Synthesis of $[Bi\{S_2P(O-C_6H_4Me-o)_2\}_2Cl]$

The benzene solution of (10 ml) Bismuth(III) chloride (0.22gm, 0.69 mmol) was added drop wise with regular stirring to benzene suspension of ammonium salt of di-(*m*-tolyl)dithiophosphoric acid (0.45gm, 1.38 mmol). The reaction mixture was turned to yellow which was then refluxed for ~5 hrs. Ammonium chloride was removed by filtration under anhydrous environment and afterward an excess of solvent was evaporated under reduced pressure. Final drying of the product in vacuo for three to four hours resulted in the formation of pale yellow viscous oily liquid.

Yield: 0.45g, 75%; *Anal.* Calc. for $C_{28}H_{28}O_4S_4P_2ClBi$: Bi, 24.20; S, 14.80. Found: Bi, 22.70; S, 15.30 %. Other complexes of Bismuth(III) trichloride with ammonium ditolyl dithiophosphates in 1:2 and 1:1 stoichiometric ratio were prepared by the same method. (Table 1)

Results and discussion

Bis and mono halide bismuth(III) *O,O'*-ditolyl dithiophosphate complexes of the type $[Bi\{S_2P(OR)_2\}_nCl_{3-n}]$ ($n = 1-2$, $R = o-, m-, p-C_6H_4Me$) were synthesized by the reactions of Bismuth(III) chloride with ammonium ditolyldithiophosphates in 1:2 and 1:1 stoichiometric ratio by refluxing in benzene with continuous stirring.



These novel complexes were yellow viscous liquids which were soluble in common organic solvents such as acetone, benzene, chloroform, dichloromethane, toluene etc and insoluble in the non polar organic solvents as carbon tetrachloride and hexane. Various attempts were made to obtain the crystals either by cooling or by slow evaporation of the solution of these complex but they were found unsuccessful. The products were analysed by elemental analysis, IR, 1H and $^{31}P\{^1H\}$ NMR spectroscopy. The elemental analyses were found in support to the molecular formula of the complexes.

IR Spectra

The IR spectra of Bismuth(III) (*O,O'*-ditolyl dithiophosphate) complexes (Table 2) was recorded in the

range 4000-350 cm^{-1} and all the bands were assigned by comparing spectra of salts derived from *O,O'*-di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acids ^[24-26] and similar Bismuth(III) *O,O'*-dialkyl/ditoyl dithiophosphates^{11,14} complexes. Two energy bands are present in the region 1172-1113 and 826-788 cm^{-1} , corresponding to $\nu[(\text{P})\text{-O}\text{-C}]$ and $\nu[\text{P}\text{-O}\text{-}(\text{C})]$ stretching vibrations in complexes **1-6**. The medium intensity bands are located in the regions 679-639 and 555-523 cm^{-1} attributed to $\nu(\text{P}=\text{S})$ and $\nu(\text{P}\text{-S})$ respectively. Due to the binding of sulphur of $\text{P}=\text{S}$ to bismuth, these bands are notably shifted to lower frequency as compared to their free ligands.

¹H NMR Spectra

The ¹H NMR spectra for the complexes **1-6** were recorded in CDCl_3 at room temperature. The spectral data of Bismuth(III) (*O,O'*-ditoyl dithiophosphate) complexes (Table 3) is similar to that of corresponding salts of dithiophosphoric acids, this may be due to the large separation between Bismuth and the hydrogen atoms. The methyl proton of the tolyl group manifested as a distinct singlet within the 2.16-2.31 ppm range, displaying a subtle shift when compared with the salts derived from *O,O'*-di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acids. The phenyl protons were detected within the anticipated range of 6.87-7.25 ppm in these complexes, exhibiting a marginal shift in comparison to the free ligand. This suggests the coordination of the ligand to the metal center. The integration of these shifts further indicates the formation of 1:2 and 1:1 complexes of $[\text{Bi}\{\text{S}_2\text{P}(\text{OR})_2\}_n\text{Cl}_{3-n}]$ ($n = 1-2$, $\text{R} = o\text{-}, m\text{-}, p\text{-C}_6\text{H}_4\text{Me}$).

³¹P{¹H} NMR Spectra

The ³¹P{¹H}NMR spectra of complexes 1-6 were recorded in CDCl_3 (refer to Table 3). A comparison of the ³¹P{¹H}NMR chemical shifts with those of various metal dialkyldithiophosphates, as studied by Glidewell²⁷, revealed that complexes featuring bidentate ligands exhibited signals within the range of 82-101 ppm, while those with signals below 82 ppm typically involved monodentate ligands. The presence of a sharp singlet within the region of 93.49-95.27 ppm suggests the anisobidentate coordination of the dithiophosphate group to the metal center in these complexes. The occurrence of a single signal implies a uniform nature of phosphorus nuclei and indicates both the molecular homogeneity and purity of the compound. Furthermore, the observed ³¹P{¹H}NMR chemical shifts for complexes 1-6, shifted by 17-20 ppm lower in frequency compared to those of the ligands, substantiate the coordination of the sulfur of $\text{P}=\text{S}$ to bismuth.

Conclusions

Based on the spectroscopic investigations and a thorough comparison of relevant data with existing literature, a plausible geometry is proposed for these complexes, involving an anisobidentate coordination of the ligands to the bismuth atom. It is noteworthy that our research team has previously established the anisobidentate coordination pattern of *O,O'*-di(*o*-, *m*- or *p*-tolyl) dithiophosphoric acid ligands with the bismuth atom in a 1:3 molar ratio through single crystal X-ray diffraction studies^{4,11}. The spectroscopic findings presented here strongly suggest a distorted trigonal bipyramidal geometry for $[(o\text{-}, m\text{-}, \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\text{BiCl}_2]$ (Figure 1), featuring a four coordinated bismuth atom and demonstrating the anisobidentate nature of the ditoyldithiophosphate moieties. The corresponding complex $[(o\text{-}, m\text{-} \text{ or } p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2]_2\text{BiCl}$ (Figure 2) similarly exhibit an octahedral geometry,

featuring a five coordinated bismuth atom. In both structures, bismuth maintains a stereochemically active lone pair of electrons at the axial position.

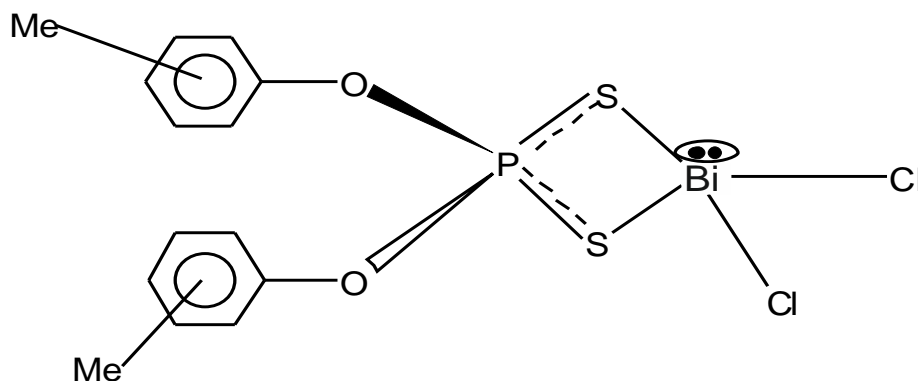


Figure 1 Proposed trigonal bipyramidal geometry of the complexes $[(o-, m-, p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\text{BiCl}_2]$

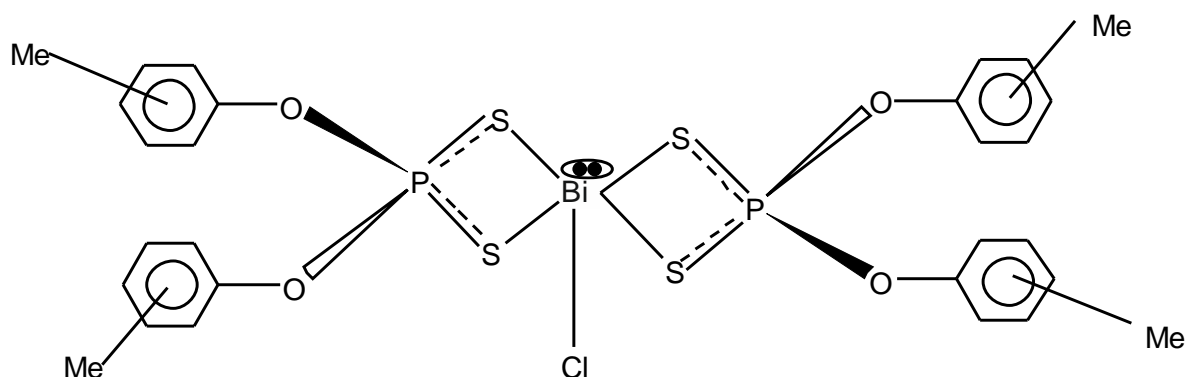


Figure 2 Proposed octahedral geometry of the complexes $[\{(o-, m-, p\text{-MeC}_6\text{H}_4\text{O})_2\text{PS}_2\}_2\text{BiCl}]$

Acknowledgments

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Table 1: Synthetic and Analytical data of Bismuth(III) (*O,O'*-ditolyl dithiophosphate) Complexes

| Reactants gm (mmol) | | Molar Ratio | Product (gm) | Yield (%) | Elemental Analysis (%) | |
|---------------------------------|---|-------------|--|-----------|------------------------|------------|
| BiCl ₃ | Ligand | | | | Calcd | Found |
| BiCl ₃ 0.22(0.69) | NH ₄ S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ 0.45(1.38) | 1:2 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ } ₂ Cl] | 75 | 24.2 (22.7) | 14.8(15.3) |
| BiCl ₃ 0.35(1.10) | NH ₄ S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ 0.35(1.10) | 1:1 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ }Cl ₂] | 92 | 35.4 (34.5) | 10.8(10.5) |
| BiCl ₃ 0.30(0.95) | NH ₄ S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ 0.62(1.90) | 1:2 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ } ₂ Cl] (0.67) | 81 | 24.2(24.7) | 14.8(14.4) |
| BiCl ₃ 0.32(1.01) | NH ₄ S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ 0.33(1.01) | 1:1 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ }Cl ₂] | 93 | 35.4(34.2) | 10.8(10.6) |
| BiCl ₃ 0.25(0.79) | NH ₄ S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ 0.51(1.58) | 1:2 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ } ₂ Cl] | 88 | 24.2(23.4) | 14.8(13.8) |

| | | | | | | |
|---------------------------------|--|-----|---|----|------------|------------|
| BiCl ₃ 0.30(0.95) | NH ₄ S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ 0.31(0.95) | 1:1 | Bi{S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ }Cl ₂ (0.15) | 81 | 35.4(33.0) | 10.8 (9.5) |
|---------------------------------|--|-----|---|----|------------|------------|

Table 2: Selected IR Spectroscopic Data (cm⁻¹) for the Bismuth(III) (*O,O'*-ditolyl dithiophosphate) Complexes in KBr pellets in the range (4000-350) cm⁻¹

| S.No | Compound | □ [(P)-O-C] | □ [P-O- (C)] | □ (P=S) | □ (P-S) |
|------|--|-------------|-----------------|---------|---------|
| 1 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ } ₂ Cl] | 1172s | 799s | 679m | 546m |
| 2 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ }Cl ₂] | 1113s | 809s | 646m | 543m |
| 3 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ } ₂ Cl] | 1143m | 790s | 649m | 555m |
| 4 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ }Cl ₂] | 1142s | 788s | 646m | 553s |
| 5 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ } ₂ Cl] | 1168s | 824m | 639s | 525s |
| 6 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ }Cl ₂] | 1169s | 826s | 640s | 523s |

Key: s = strong, m = medium

Table 3: Selected ¹H NMR and ³¹P{¹H} NMR Spectroscopic Data for Bismuth(III) (*O,O'*-ditolyl dithiophosphate) Complexes

| S. No | Compound | ¹ H NMR (δ ppm)* | ³¹ P{ ¹ H} NMR |
|-------|--|---|--------------------------------------|
| 1 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ } ₂ Cl] | 2.17(s,[12H],Me),6.99-7.24(m,[16H],OC ₆ H ₄) | 94.23 |
| 2 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>o</i>) ₂ }Cl ₂] | 2.17(s, [6H],Me), 6.96-7.25 (m, [8H],OC ₆ H ₄) | 95.27 |
| 3 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ } ₂ Cl] | 2.31(s,[12H],Me),6.98-7.23(m,[16H],OC ₆ H ₄) | 94.08 |
| 4 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>m</i>) ₂ }Cl ₂] | 2.30 (s, [6H],Me), 6.98-7.23(m, [8H],OC ₆ H ₄) | 93.49 |
| 5 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ } ₂ Cl] | 2.16(s,[12H],Me),6.98-7.20(m,[16H],OC ₆ H ₄) | 95.15 |
| 6 | [Bi{S ₂ P(OC ₆ H ₄ Me- <i>p</i>) ₂ }Cl ₂] | 2.16 (s, [6H],Me), 6.87-7.21(m, [8H],OC ₆ H ₄) | 95.23 |

Keys: s = singlet, m= multiplet

*¹H NMR and ³¹P{¹H}NMR spectra using tetramethylsilane as an internal standard and 85% H₃PO₄ as an external standard respectively were recorded on a Bruker DRX-300(300MHz) spectrometer in CDCl₃ solutions.