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Synthesis and Spectral Characterization of Bismuth Dithiolate Derivatives of Disubstituted Diphenyldithiophosphates

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ABSTRACT

The present work deals with the synthesis of four complexes with general formula $[{(ArO)_2PS_2}Bi(SCH_2CH_2S)]$ (1-4), where $Ar = 2,4-(CH_3)_2C_6H_3$, 2,5-(CH_3)_2C_6H_3, 3,4-(CH_3)_2C_6H_3, and 3,5-(CH_3)_2C_6H_3, respectively. The reaction of $[(ArO)_2PS_2Na]$, HSCH₂CH₂SH with Bi(NO₃)₃.5H₂O in toluene in 1:1:1 molar stoichiometry afforded the complexes these complexes. These newly synthesized complexes have been characterized by elemental analysis, Fourier-transform infrared, and multinuclear nuclear magnetic resonance (NMR) (¹H, ¹³C and ³¹P) NMR. The bismuth(III) atom is proposed to be surrounded by four sulfur atoms - two of dithiolate moiety and two from dithiophosphate moiety resulting in trigonal bipyramidal geometry with the fifth position being occupied by the lone pair of electrons.

Key words: Bismuth, Dithiophosphate, Dithiolate, Phosphorus.

1. INTRODUCTION

Extensive applicability of Bi-S compounds as compared to Bi-O compounds in medicine and biology has been established [1,2]. This has been ascertained on the basis of low lability [3] and greater thermodynamic stability [4,5] of Bi-S compounds in comparison to Bi-O compounds. These Bi-S compounds have fascinated many researchers due to their diverse structural features ranging from discrete monomer to polymeric supramolecular assemblies [1-10]. In recent years, the prospective of bismuth-sulfur chemistry in material science [11-15], as X-ray imaging agents [16], and as catalysts [17] has been significant. While the avenues of Bi-S compounds in medicine are essentially related to the treatment of gastrointestinal disorders, tumors, and against microbial infection [18-20]. Moreover, bismuth being the more environmentally acceptable heavy metal, its compounds has increased tremendously in the past decade. Substantial literature is available on the complexes of bismuth with sulfur donor dithiophosphate ligands [21,22]. In the present paper, the syntheses of a mixed ligand new bismuth (III) complexes containing the disubstituted diphenyl dithiophosphate ligands along with ethylene dithiolate moiety as ligand to bismuth atom have been synthesized and characterized.

2. EXPERIMENTAL 2.1. Materials and Methods

Exclusion of moisture is mandatory due to moisture sensitive nature of reactants and products throughout the experimental manipulation using standard Schlenk's technique. Dried solvents were used. Elemental analyses (C, H, S) were conducted using the Elemental Analyzer Vario EL-III (Indian Institute of Integrative Medicine, Jammu). Bismuth was estimated as BiOI [23]. The ligands were prepared by literature method [24]. Infrared (IR) spectra were recorded using KBr pellet in the range of 4000-200 cm⁻¹ on a Perkin Elmer Spectrum 400-I Fourier-transform IR (FT-IR) spectrophotometer. The¹H, ¹³C, and ³¹P nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ on Bruker Avance II and III 400 (400 MHz) spectrometer using TMS as internal reference for ¹H and ${}^{13}C$ NMR and H₃PO₄ (85%) as external reference for ³¹P NMR.

2.2. Synthesis of the Complexes

2.2.1. Synthesis of $[{(2,4-(CH_3)_2C_6H_3O)_2PS_2}Bi (SCH_2CH_2S)]$

A 10 ml toluene solution of $Bi(NO_3)_3$. $5H_2O$ (1.35 g/2.78 mmol) was added dropwise to toluene solution (10 ml) of ethane-1,2-dithiol (0.26 g/2.76 mmol) in a 100 ml round-bottom flask with

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constant stirring for 2 h followed by addition of toluene suspension (30 ml) of $(2,4-(CH_3)_2C_6H_3O)_2PS_2Na$ (1.00 g/2.77 mmol). The reaction contents were further stirred for four hours till the color changed from white to yellow indicating the completion of reaction. The yellow solution showed white turbidity due to precipitation of sodium nitrate and confirmed the formation of the desired complex. The precipitated sodium chloride was filtered off through funnel fitted with G-4 sintered glass disc. The excess solvent was removed from the filtrate under reduced pressure and the product was dried finally in vacuo when the compound isolated as vellow sticky solid in 90% vield. The synthesis of complexes (2-4) was carried out following the same procedure. Analytical calculation for C₁₈H₂₂O₂PS₄Bi: C, 33.86; H, 3.47; S, 20.09; Bi, 32.73, Found: C, 33.76; H, 3.37; S, 20.01; Bi, 32.62; IR (KBr): v= 1149, s [v(P)-O-C], 967, s [vP-O-(C)], 671, s [vP=S], 612, m [vP-S], 444, w [vBi-S], 2925, w [vC-H] cm⁻¹; ¹H NMR (CDCl₃, ppm): = 2.07(s, 6H, 2-CH₃), 2.19 (s, 6H, 4-CH₃), 6.70 (d, J = 8 Hz, 2H, H₅), 7.54 (s, 2H, H₃), 7.27 (d, J = 8 Hz, 2H, H₆), 3.05 (t, J = 7 Hz, 4H, CH₂); ¹³C NMR (CDCl₃, ppm): 15.95 (2-CH₃), 17.45 (4-CH₃), 114.99 (C₆), 121.72 (C₂-CH₃), 124.75 (C₅), 126.93 (C₄-CH₃), 130.87 (C₃), 151.29 (C₁-O), 36.21 (CH₂); ³¹P NMR (CDCl₃, ppm): 94.1 (s).

2.2.2. Synthesis of $[{(2,5-(CH_3)_2C_6H_3O)_2PS_2} Bi(SCH_2CH_2S)]$

The complex 2 was prepared by the same procedure as 1 and isolated as yellow solid. Yield: 89%; analytical calculation for $C_{18}H_{22}O_2PS_4Bi$: C, 33.86; H, 3.47; S, 20.09; Bi, 32.73, found: C, 33.75; H, 3.41; S, 20.02; Bi, 32.65; IR (KBr): v= 1143, s [v(P)–O–C], 961, s [vP–O–(C)], 677, s [v P=S], 619, m [vP–S], 442, w [vBi–S], 2947, w [vC–H] cm⁻¹, ¹H NMR (CDCl₃, ppm): 2.21 (s, 6H, 2-CH₃), 2.18 (s, 6H, 5-CH₃), 6.72 (d, J = 7.6 Hz, 2H, H₃), 7.21 (d, J = 7.6 Hz, 2H, H₄), 7.37 (s, 2H, H₆) 3.12 (t, J = 7 Hz, 4H, CH₂); ¹³C NMR (CDCl₃, ppm): 17.32 (2-CH₃), 19.32 (5-CH₃), 124.52 (C₆), 128.63 (C₄), 129.47 (C₂–CH₃), 132.62 (C₃), 138.42 (C₅–CH₃), 151.52 (C₁–O) 36.26 (CH₂); ³¹P NMR (CDCl₃, ppm): 96.3 (s).

2.2.3. Synthesis of $[{(3,4-(CH_3)_2C_6H_3O)_2PS_2}]$ Bi(SCH₂CH₂S)]

The complex 3 was prepared by the same procedure as 1 and isolated as yellow solid. Yield: 87%; analytical calculation for $C_{18}H_{22}O_2PS_4Bi$: C, 33.86; H, 3.47; S, 20.09; Bi, 32.73, found: C, 33.79; H, 3.39; S, 20.02; Bi, 32.68; IR (KBr): v = 1141, s [v(P)-O-C], 963, s [vP-O-(C]], 672, s [vP=S], 617, m [vP-S], 439, w [vBi-S], 2944, w [vC-H] cm⁻¹;¹H NMR (CDCl₃, ppm): 2.11 (s, 6H, 4-CH₃), 2.12 (s, 6H, 3-CH₃), 6.87 (d, J = 7.61 Hz, 2H, H₆), 7.02 (s, 2H, H₂), 7.26 (d, J = 8 Hz, 2H, H₅) 3.04 (t, J = 7 Hz, 4H, CH₂); ¹³C NMR (CDCl₃, ppm): 19.34 (4-CH₃), 21.01 (3-CH₃), 116.34 (C₆), 118.13 (C₂), 121.96 (C₄-CH₃), 128.84

(C₅), 137.62 (C₃–CH₃), 151.53 (C₁–O) 36.29 (CH₂); ³¹P NMR (CDCl₃, ppm): 96.5(s).

2.2.4. Synthesis of $[{(3,5-(CH_3)_2C_6H_3O)_2PS_2}]$ Bi $(SCH_2CH_2S)]$

The complex 4 was prepared by the same procedure as 1. Yield: 88%; analytical calculation for $C_{18}H_{22}O_2PS_4Bi$: C, 33.86; H, 3.47; S, 20.09; Bi, 32.73, found: C, 33.81; H, 3.41; S, 20.01; Bi, 32.67; IR (KBr): v = 1145, s [v(P)-O-C], 965, s [vP-O-(C)], 633, s [vP=S], 612, m [vP-S], 432, w [vBi-S], 2938, w [vC-H] cm⁻¹,¹H NMR (CDCl₃, ppm): 1.99 (s, 12H, 3,5-(CH₃)₂), 6.55 (s, 4H, H₂), 6.78 (s, 2H, H₄) 3.10 (t, J = 7 Hz, 4H, CH₂); ¹³C NMR (CDCl₃, ppm): 22.12 (3,5-(CH₃)₂), 123.56 (C_{2.6}), 129.64 (C₄), 146.33 (C_{3.5}-CH₃), 155.53 (C₁-O) 36.23 (CH₂); ³¹P NMR (CDCl₃, ppm): 95.6(s).

3. RESULTS AND DISCUSSION

The reaction of bismuth (III) nitrate pentahydrate, ethane-1,2dithiol, and sodium salt of diaryldithiophosphate in 1:1:1 molar ratio in toluene yielded these complexes in 87-90% yield (Scheme 1).

These complexes were obtained after separation from NaNO₃. These complexes are soluble in tetrahydrofuran, chloroform, DMSO, and insoluble in solvents such as n-hexane and carbon tetrachloride. These complexes are slightly moisture sensitive.

3.1. Infrared Spectral Data

The regions of IR spectra for P–S are of particular interest. Bands for $v[P-S]_{asym}$ and $v[P-S]_{sym}$ of diphenyldithiophosphate in these complexes were observed at 677-671 cm⁻¹ and 619-612 cm⁻¹, respectively. This slight shift in comparison to the parent ligands and appearance of closely spaced bands arising from $v(PS_2)$ vibrations are quite diagnostic to propose bidentate bonding of dithiomoiety with bismuth. Appearance of new bands of vBi–S at 444-432 cm⁻¹ indicates formation of bismuth–sulfur bonds [21,22]. The vC–H vibrations were observed in the region 2947-2925 cm⁻¹.



Scheme 1: Ring labeling for nuclear magnetic resonance spectroscopic assignments of complexes 1–4.

Scheme 2: Synthesis of mixed ligand complexes of bismuth(III).

3.2. ¹H NMR Spectral Data

¹H NMR spectra of these complexes exhibited phenyl proton signals with the expected peak multiplicities. The chemical shifts of the methyl protons of the phenyl rings were observed at 1.99-2.21 ppm as a very sharp singlet. The aromatic protons of the phenyl groups were observed at 6.55-7.37 ppm with their characteristic splitting patterns. In addition to these chemical shifts, the chemical shifts for -SCH₂CH₂S- protons in the region 3.04-3.12 ppm in the spectra of these complexes were also observed.

3.3. ¹³C NMR Spectral Data

The¹³C NMR spectral data show the chemical shifts expected for the carbons present in the molecule. The spectra exhibit the chemical shifts of carbons of phenyl rings with a marginal shift in their values compared to the parent ligands. The chemical shift for the methyl (–CH₃) carbon was found at 16.00-22.12 ppm. The aryl group carbon nuclei resonate in the region 116.34-156.97 ppm. The chemical shifts for C–O carbons were observed at 151.52-156.97 ppm. The resonance due to -CH₂ carbon nuclei of the dithiolate moiety in the complexes was observed in the region 36.21-36.29 ppm.

3.4.³¹ PNMR Spectral Data

³¹P NMR spectra (proton-decoupled) displayed a single resonance for each complex. The singlet was observed in the upfield region of 94.1-96.5 ppm compared to the uncoordinated ligands. This shift may be attributed to bidentate dithiophosphate [25]. This behavior confirms the equivalent nature of phosphorus nuclei in the molecule and coordination to bismuth (III).

4. CONCLUSION

In this research, disubstituted new diphenyldithiophosphates complexes of bismuth (III) complexes have been synthesized and characterized by elemental analysis, IR, and heteronuclear NMR (¹H, ¹³C and ³¹P). The appearance of new bands in the IR spectra of these complexes in comparison to the free ligand indicates that the vBi-S bond has been formed. Furthermore, the resonances in the heteronuclear NMR spectra clearly indicate the probable structural geometry of these complxes. Each complex probably forms a four-membered distorted chelate ring as a [BiS₄] unit. A trigonal bipyramidal geometry is proposed with bismuth atom coordinated to two sulfur atoms of ethane-1,2-dithiolate moiety, two sulfur atoms of dithiophosphate moiety, and a lone pair occupying the fifth position of the see-saw structure Figure 1.



Figure 1: Proposed structure of mixed ligand bismuth(III) complexes (Ar = 2,4-(CH3)2C6H3, 2,5-(CH3)2C6H3, 3,4-(CH3)2C6H3 and 3,5-(CH3)2C6H3).

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