

Synthesis and spectral characterization of antimony dithiolate derivatives of disubstituted diphenyldithiophosphates

Atiya Syed

Department of Chemistry, University of Jammu, Baba Saheb Ambedkar Road, Jammu (J & K), (India)

ABSTRACT

The present work deals with the synthesis of four complexes with general formula $[(ArO)_2PS_2]Sb(SCH_2CH_2S)]$ (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. Reaction of $[(ArO)_2PS_2Na]$, $HSCH_2CH_2SH$ with $SbCl_3$ in toluene in 1:1:1 molar stoichiometry afforded the complexes these complexes. These newly synthesized complexes have been characterized by elemental analysis, FT-IR and multinuclear NMR (1H , ^{13}C and ^{31}P) NMR. The antimony(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.

Keywords: Antimony, Dithiophosphate, Dithiolate, Phosphorus.

I. INTRODUCTION

Antimony compounds have been recorded in history for their active medicinal role inspite of regular warnings of its toxicity [1]. Due to serious health issues, its applications have been confined to mainly the industry. In recent years, the prospective of antimony-sulfur chemistry in material science [2], in metallurgy as an additive element [3], an alloying constituent to impart hardness and stiffness [4] and to improve the corrosion resistance [5]. Antimony sulfide is used in vulcanization of rubber [6]. High purity antimony is used in semiconductor technology. Important III-V compounds such as $AlSb$, $InSb$ and $GaSb$ are made from high purity antimony. These compounds may be used as infrared detectors, diodes and Hall effect devices [7-8]. Substantial literature is available on the complexes of antimony with sulfur donor ligands [9-12]. In the present paper, the syntheses of a mixed ligand new antimony(III) complexes containing the disubstituted diphenyl dithiophosphate ligands along with ethylene dithiolate moiety as ligand to antimony atom have been synthesized and characterized.

II. EXPERIMENTAL

Materials and Methods

Removal of moisture is necessary due to moisture sensitive nature of reactants and products throughout the experimental manipulation by implementing standard Schlenk's technique. Dried solvents were used. Elemental analyses (C, H, S) were conducted using the Elemental Analyser Vario EL-III (Indian Institute of Integrative Medicine, Jammu). Antimony was estimated iodometrically [13]. The ligands were prepared by literature method [14]. IR spectra were recorded using KBr pellet in the range of $4000-200\text{ cm}^{-1}$ on a Perkin Elmer Spectrum 400-I FTIR spectrophotometer. The 1H , ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker

Avance II and III 400 (400 MHz) spectrometer using TMS as internal reference for ^1H and ^{13}C NMR and H_3PO_4 (85%) as external reference for ^{31}P NMR.

Synthesis of the Complexes

Synthesis of $[(2,4-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{O})_2\text{PS}_2]\text{Sb}(\text{SCH}_2\text{CH}_2\text{S})$

A 10 ml toluene solution of SbCl_3 (0.63 g/2.76 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 constant stirring for two hours followed by addition of toluene suspension (30 ml) of $(2,4-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\text{Na}$ (1.00 g/ 2.77 mmol). The reaction contents were further stirred for four hours till the colour of changed from white to yellow indicating the completion of reaction. The yellow solution showed white turbidity due to precipitation of sodium chloride 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 yellow sticky solid in 90% yield. The synthesis of complexes (2-4) was carried out following same procedure. *Anal. Calc.* for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{PS}_4\text{Sb}$: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08, Found: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08; IR (KBr): $\nu = 1149$, s $[\nu(\text{P})-\text{O}-\text{C}]$, 967, s $[\nu(\text{P})-\text{O}-(\text{C})]$, 671, s $[\nu\text{P}=\text{S}]$, 612, m $[\nu\text{P}-\text{S}]$, 444, w $[\nu\text{Sb}-\text{S}]$, 2925, w $[\nu\text{C}-\text{H}] \text{ cm}^{-1}$; ^1H NMR (CDCl_3 , ppm): = 2.07 (s, 6H, 2- CH_3), 2.19 (s, 6H, 4- CH_3), 6.70 (d, $J = 8$ Hz, 2H, H_5), 7.54 (s, 2H, H_3), 7.27 (d, $J = 8$ Hz, 2H, H_6), 3.05 (t, $J = 7$ Hz, 4H, CH_2); ^{13}C NMR (CDCl_3 , ppm): 15.95 (2- CH_3), 17.45 (4- CH_3), 114.99 (C_6), 121.72 (C_2-CH_3), 124.75 (C_5), 126.93 (C_4-CH_3), 130.87 (C_3), 151.29 (C_1-O), 36.21 (CH_2); ^{31}P NMR (CDCl_3 , ppm): 94.1 (s).

Synthesis of $[(2,5-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{O})_2\text{PS}_2]\text{Sb}(\text{SCH}_2\text{CH}_2\text{S})$

The complex 2 was prepared by the same procedure as 1 and isolated as yellow solid. Yield: 89%; *Anal. Calc.* for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{PS}_4\text{Sb}$: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08, Found: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08; IR (KBr): $\nu = 1143$, s $[\nu(\text{P})-\text{O}-\text{C}]$, 961, s $[\nu(\text{P})-\text{O}-(\text{C})]$, 677, s $[\nu\text{P}=\text{S}]$, 619, m $[\nu\text{P}-\text{S}]$, 442, w $[\nu\text{Sb}-\text{S}]$, 2947, w $[\nu\text{C}-\text{H}] \text{ cm}^{-1}$; ^1H NMR (CDCl_3 , ppm): 2.21 (s, 6H, 2- CH_3), 2.18 (s, 6H, 5- CH_3), 6.72 (d, $J = 7.6$ Hz, 2H, H_3), 7.21 (d, $J = 7.6$ Hz, 2H, H_4), 7.37 (s, 2H, H_6) 3.12 (t, $J = 7$ Hz, 4H, CH_2); ^{13}C NMR (CDCl_3 , ppm): 17.32 (2- CH_3), 19.32 (5- CH_3), 124.52 (C_6), 128.63 (C_4), 129.47 (C_2-CH_3), 132.62 (C_3), 138.42 (C_5-CH_3), 151.52 (C_1-O) 36.26 (CH_2); ^{31}P NMR (CDCl_3 , ppm): 96.3 (s)

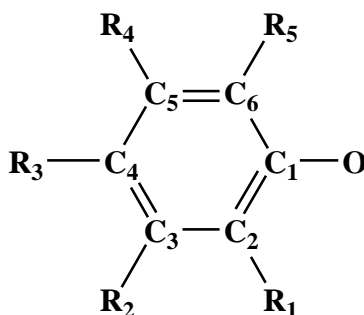
Synthesis of $[(3,4-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{O})_2\text{PS}_2]\text{Sb}(\text{SCH}_2\text{CH}_2\text{S})$

The complex 3 was prepared by the same procedure as 1 and isolated as yellow solid. Yield: 87%; *Anal. Calc.* for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{PS}_4\text{Sb}$: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08, Found: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08; IR (KBr): $\nu = 1141$, s $[\nu(\text{P})-\text{O}-\text{C}]$, 963, s $[\nu(\text{P})-\text{O}-(\text{C})]$, 672, s $[\nu\text{P}=\text{S}]$, 617, m $[\nu\text{P}-\text{S}]$, 439, w $[\nu\text{Sb}-\text{S}]$, 2944, w $[\nu\text{C}-\text{H}] \text{ cm}^{-1}$; ^1H NMR (CDCl_3 , ppm): 2.11 (s, 6H, 4- CH_3), 2.12 (s, 6H, 3- CH_3), 6.87 (d, $J = 7.61$ Hz, 2H, H_6), 7.02 (s, 2H, H_2), 7.26 (d, $J = 8$ Hz, 2H, H_5) 3.04 (t, $J = 7$ Hz, 4H, CH_2); ^{13}C NMR (CDCl_3 , ppm): 19.34 (4- CH_3), 21.01 (3- CH_3), 116.34 (C_6), 118.13 (C_2), 121.96 (C_4-CH_3), 128.84 (C_5), 137.62 (C_3-CH_3), 151.53 (C_1-O) 36.29 (CH_2); ^{31}P NMR (CDCl_3 , ppm): 96.5(s)

Synthesis of $[(3,5-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{O})_2\text{PS}_2]\text{Sb}(\text{SCH}_2\text{CH}_2\text{S})$

The complex 4 was prepared by the same procedure as 1. Yield: 88%; *Anal. Calc.* for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{PS}_4\text{Sb}$: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08, Found: C, 39.21; H, 4.02; S, 23.26; Sb, 22.08; IR (KBr): $\nu = 1145$, s $[\nu(\text{P})-\text{O}-\text{C}]$, 965, s $[\nu(\text{P})-\text{O}-(\text{C})]$, 633, s $[\nu\text{P}=\text{S}]$, 612, m $[\nu\text{P}-\text{S}]$, 432, w $[\nu\text{Sb}-\text{S}]$, 2938, w $[\nu\text{C}-\text{H}] \text{ cm}^{-1}$; ^1H NMR (CDCl_3 ,

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)

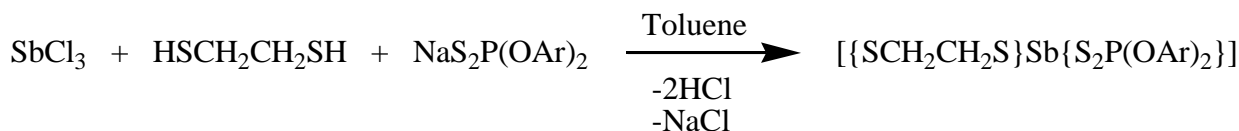


1. R₁ = CH₃, R₂ = H₃, R₃ = CH₃, R₄ = H₅, R₅ = H₆
2. R₁ = CH₃, R₂ = H₃, R₃ = H₄, R₄ = CH₃, R₅ = H₆
3. R₁ = H₂, R₂ = CH₃, R₃ = CH₃, R₄ = H₅, R₅ = H₆
4. R₁ = H₂, R₂ = CH₃, R₃ = H₄, R₄ = CH₃, R₅ = H₆

Scheme 1: Ring labelling for NMR spectroscopic assignments of complexes 1–4.

III. RESULTS AND DISCUSSION

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



Scheme 2: Synthesis of mixed ligand complexes of antimony(III)

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

Infrared Spectral data

The regions of IR spectra for P–S are of particular interest. Bands for $\nu[\text{P-S}]_{\text{asym}}$ and $\nu[\text{P-S}]_{\text{sym}}$ 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 $\nu(\text{PS}_2)$ vibrations are quite diagnostic to propose bidentate bonding of dithiomoiety with antimony. Appearance of new bands of $\nu\text{Sb-S}$ at 444-432 cm⁻¹ indicates formation of antimony–sulfur bonds [9-12]. The $\nu\text{C-H}$ vibrations were observed in the region 2947-2925 cm⁻¹.

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.

The ¹³C NMR spectral data show the chemical shifts expected for the carbons present in the molecule. The spectra of 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 were observed in the region 36.21-36.29 ppm.

³¹P NMR 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 [15]. This behavior confirms the equivalent nature of phosphorus nuclei in the molecule and coordination to antimony(III).

IV. CONCLUSION

In this research new disubstituted diphenyldithiophosphates complexes of antimony(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 νSb-S bond has been formed. Furthermore, the the heteronuclear NMR spectra exhibit chemical resonances that predict a probable structure for these complexes. Each complex possibly forms a four-membered distorted chelate ring as a [SbS₄] unit. A trigonal bipyramidal geometry is proposed with antimony 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).

V. ACKNOWLEDGMENTS

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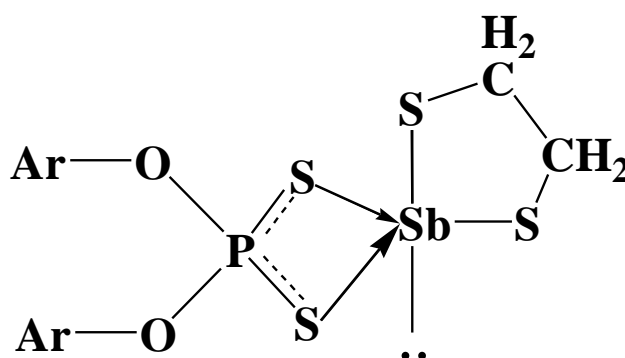


Figure 1: Proposed structure of mixed ligand antimony(III) complexes (Ar = 2,4-(CH₃)₂C₆H₃, 2,5-(CH₃)₂C₆H₃, 3,4-(CH₃)₂C₆H₃ and 3,5-(CH₃)₂C₆H₃)

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