

Synthesis and characterization of O,O'-bis-di- α -naphthyl dithiophosphate of lead(II).

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Abstract- O,O'-bis-di- α -naphthyl dithiophosphate of lead(II) corresponding to $[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Pb}$, has been synthesized by the reaction of PbCl_2 in 2:1 molar ratio with sodium salt of O,O'-di- α -naphthyl dithiophosphate in refluxing chloroform. This complex has been characterized by elemental analyses, C, H, S, Pb and further characterization by some spectroscopy analyses, namely, IR and NMR (^1H , ^{13}C and ^{31}P) has been carried out. Monomeric nature of this complex has been confirmed and lead atom is four coordinately bonded to two bidentate dithiophosphate ligands leading to a square planar geometry around the lead atom.

Key words- α -naphthyl, dithiophosphate, lead, phosphorus, sulfur

INTRODUCTION

Lead has been a significant element of historical significance. Markedly, the performance of engines has been boosted by increasing the octane number of gasoline by adding lead additives[1]. Tetraethyl lead (TEL) was the most important antiknocking agent but due to the poisonous effect of its combustion products its use has been discontinued. Lead compounds are important raw materials in paints, cosmetics and polymer industry [2-3]. Measures taken in the direction to decrease the concentration of lead ions in effluent wastewater are being explored[4]. A significant lead removal agent is sodium salt of diethyl dithiophosphate that removes lead(II) from waste water treatment under the brand name of DTP, 7 [5]. Chelation therapy using CaNa_2EDTA and dimercaprol as chelating agents is used to treat lead poisoning [6]. A vast amount of literature is present pertaining to the sulfur donor ligand complexes of lead(II) [7-11]. Therefore, development of new complexes of lead with sulfur donor ligands, particularly, dithiophosphates is an important field of investigation. Herein, the synthesis and characterization of a complex of lead with a new dithiophosphate ligand corresponding to, O,O'-bis-di- α -naphthyl dithiophosphate of lead(II) has been reported.

MATERIALS AND METHODS

Moisture free conditions were maintained applying standard schlenk's technique. Chloroform was dried by standard methods prior to their use. Sodium salt of di- α -naphthyl dithiophosphate was prepared by literature method [12]. Lead was estimated gravimetrically as PbO_2 [13]. Elemental analyses (C, H, N, S) were measured with the Elemental Analyser Vario EL-III, their results were found to be in good agreement ($\pm 0.3\%$) with the calculated values. Infrared spectra were recorded in the range of $4000\text{--}200\text{ cm}^{-1}$ using pressed KBr pellets on a Perkin Elmer-spectrum RX1

FT-IR spectrophotometer. NMR samples were prepared in deuteriochloroform (CDCl_3). The ^1H 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).

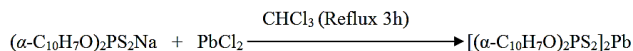
Synthesis of $[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Pb}$

For the synthesis of $[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Pb}$ chloroform solution (30ml) of PbCl_2 (0.34 g or 1.22 mmol) was taken in a 100 ml round bottom flask. To this solution, added (30ml) chloroform suspension of sodium salt of O,O'-bis-di- α -naphthyl dithiophosphate ligand, $(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2\text{Na}$ (1.00 g or 2.47 mmol) in a drop wise with constant stirring. Precipitation of sodium chloride took place. The contents were further refluxed for 3 hours. Then the contents were brought to room temperature and sodium chloride formed during the course of the reaction was filtered off through sintered glass crucible (G4 disc). Finally the excess of solvent was removed from the filtrate under reduced pressure, which yielded $[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Pb}$ as white solid in 89% yield. *Anal. Calc.* $\text{C}_{40}\text{H}_{28}\text{O}_4\text{P}_2\text{S}_4\text{Pb}$: C, 49.53; H, 2.91; S, 13.22; Pb, 21.36; Found: C, 49.32; H, 2.87; S, 13.18; Pb, 21.27; IR (KBr): $\nu = 1173$, s [$\nu(\text{P})\text{--O--C}$], 989, s [$\nu(\text{P--O--C})$], 861, s [$\nu(\text{P}=\text{S})$], 593, m [$\nu(\text{P--S})$], 392, w [$\nu(\text{Pb--S})$] cm^{-1} ; ^1H NMR (CDCl_3 , ppm): = 6.5-7.3 ppm; ^{13}C NMR (CDCl_3 , ppm): 125.2 (C_2), 123.1 (C_7), 121.1 (C_3), 121.5 (C_6), 113.1 (C_4), 119.2 (C_5), 134.2 (C_9), 132.1 (C_{10}), 152.0 ($\text{C}_1\text{--O}$); ^{31}P NMR (CDCl_3 , ppm): 84.3 (s). The ^{13}C NMR signals have been ascribed to the carbon atoms as depicted in Figure 1.

RESULTS AND DISCUSSION

The title complex has been prepared in good yield by the reaction of sodium salt of O,O'-di- α -naphthyl dithiophosphate ligand with PbCl_2 in 2:1 stoichiometric ratio

in refluxing chloroform (Scheme 1). The reaction requires refluxing conditions for completion.



Scheme 1: The synthesis of O,O'-bis-di- α -naphthyl dithiophosphate of lead(II).

This complex was obtained as white solid in 89% yield after the separation of sodium chloride. The elemental analyses (C,H,S, Pb) were found in close agreement with the molecular formula of the complexes. It has been further characterized by some other spectroscopic analyses, viz., IR and (^1H , ^{13}C and ^{31}P NM). This complex was obtained just about in quantitative yield.

Infrared spectroscopic analysis

The IR spectrum for the complex showed characteristic IR peaks which were assigned in comparison with the previously reported values [7, 10, 12]. On comparison with the free ligand slight shifting of bands in the IR spectra may be regarded as an evidence of the formation of this complex. The diagnostic vibrational frequencies are the two strong intensity bands, $\nu(\text{P})\text{-O-C}$, 1173 cm^{-1} ; $\nu\text{P-O-(C)}$, 989 cm^{-1} ; and two medium intensity bands, $\nu\text{P-S}$, 861 cm^{-1} ; $\nu\text{P-S}$, 593 cm^{-1} . From the above data, we observe that the $\nu(\text{PS}_2)$ signifies anisobidentate binding mode. Furthermore, the presence of a band for $\nu\text{Pb-S}$ at 392 cm^{-1} in the spectrum is indicative of the formation of lead-sulfur bond.

^1H NMR spectroscopic analysis

The ^1H NMR spectrum (CDCl_3) exhibited negligible shifting of the characteristic proton resonances of the corresponding aryl protons in the complex in comparison to the ligand protons. The chemical shifts for the aryl ring protons were observed in the region 6.5–7.3 ppm as multiplet.

^{13}C NMR spectroscopic analysis

No appreciable change was observed in the ^{13}C NMR spectrum of the complex and has about the same chemical shifts compared to corresponding carbons in the uncoordinated ligand. The carbon nuclei of the aryl ring have displayed their resonance in the region 113.1–152.0 ppm.

^{31}P NMR spectroscopic analysis

The phosphorus atom of the dithiophosphate moiety appears as a singlet at 84.3 ppm in the ^{31}P NMR spectrum indicating its equivalent nature. This value for ^{31}P nucleus present in these complexes is consistent with anisobidentate behavior of dithiophosphate moiety [7, 10, 14]

Structural Features

On the basis of the above observations and the comparison of relevant data from literature[7-12], it can be concluded that the complex has monomeric nature and the metal atom has four coordinate geometry where lead(II) is bonded to two anisobidentate dithiophosphato ligands leading to a square planar geometry around the lead atom. The proposed structure has been given in Figure 1.

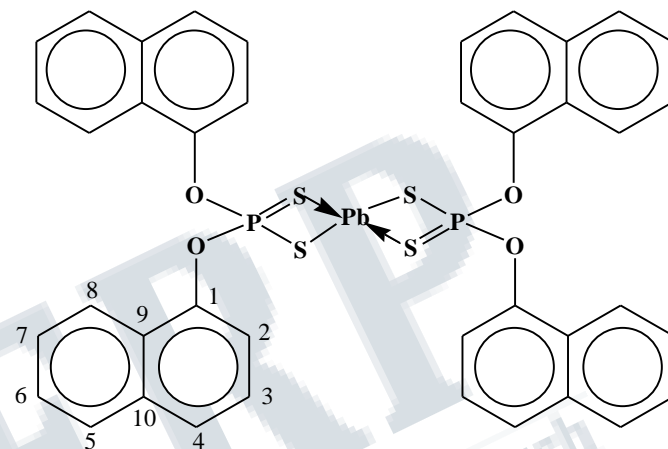


Figure 1: The proposed four coordinate geometry of Pb(II) in the complex $[(\alpha\text{-C}_{10}\text{H}_7\text{O})_2\text{PS}_2]_2\text{Pb}$.

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