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## Synthesis and Spectroscopic Characterization of bis{*O,O'*-di(4-chloro-3-methylphenyl) dithiophosphato} mercury(II).

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### ABSTRACT

*Synthesis of mercury(II) complex of di(4-chloro-3-methylphenyl)dithiophosphate has been carried out in aqueous medium by reacting mercury dichloride with sodium salt of di(4-chloro-3-methylphenyl)dithiophosphate in 1:2 molar ratio. The complex has been characterized by elemental analysis, infrared, heteronuclear nuclear magnetic resonance (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) and ESI-mass spectroscopic studies.*

### Keywords

*Mercury, Dithiophosphate, Environment, Sulphur*

### INTRODUCTION

It has been known since decades that the aquatic biosystems require sulphur-containing compounds. These compounds are biosynthesized by assimilation and reduction of sulphate ions [1]. Degradation of the organic matter releases several low molecular weight sulphur compounds into the environment. Some of them, such as H<sub>2</sub>S and thiols, form strong complexes with Hg<sup>2+</sup> and CH<sub>3</sub>Hg<sup>+</sup>. Soil contaminated by mercury or the redistribution of contaminated water has the potential to enter the food chain through plant and livestock [2]. Upon entering the food chain mercury can bioaccumulate causing adverse effects to human health [3]. Mercuric salts are more water soluble and toxic than elemental mercury. Mercuric salts are also easily absorbed by the gastrointestinal tract [4]. The most common form of organic mercury is methylmercury (MeHg), which is the major source of organic mercury found in the ecosystems [5]. MeHg is readily transported by water into the aquatic ecosystems. It is considered to be relatively more lipid soluble. MeHg is easily taken up by lower organisms, tends to work its way up the food chain and bioaccumulates in fish [6]. Mercury poisoning enters the terrestrial food chain through sea food diet. It is a serious matter of concern since the historical Minimata Bay mercury poisoning disaster of 1956. Mercury extraction by sulfur complexation is therefore an important aspect of removal of mercury from environment. The extraction of mercury by dithiophosphate ligands is being monitored [7]. In view of this a novel mercury dithiophosphate complex has been synthesized and characterized and discussed in this paper.

### EXPERIMENTAL

Commercial grade chemicals were used for synthetic purposes. Solvents were dried and distilled before use. The ligand, sodium salt of *O,O'*-di(4-chloro-3-methylphenyl)dithiophosphate, was prepared according to our report [8]. Mercury was estimated gravimetrically as Mercurysulfide and Chlorine was estimated by Volhard's method [9]. 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 4000–200 cm<sup>-1</sup> using pressed KBr pellets on a Perkin Elmer-spectrum RX1 FT-IR spectrophotometer. NMR samples were prepared in deuteriochloroform (CDCl<sub>3</sub>). The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX 300 (300 MHz) and reported relative to an internal reference of TMS.

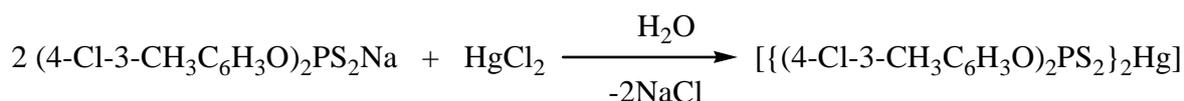
The  $^{31}\text{P}$  NMR spectra were recorded using  $\text{H}_3\text{PO}_4$  (85%) as external reference on a Bruker DRX 300 (300 MHz). The ESI mass spectra were recorded on ESQUIRE3000\_00037 spectrophotometer.

Synthesis of  $[\{(4\text{-Cl-3-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\}_2\text{Hg}]$

An aqueous solution (~10 mL) of  $\text{HgCl}_2$  (0.34 g, 1.25 mmol) was added dropwise to an aqueous solution (~30 mL) of  $[\{(4\text{-Cl-3-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\}\text{Na}]$  (1.00 g, 2.49 mmol) with constant stirring at room temperature. The reaction mixture was stirred for one hour followed by refluxing for one hour. The turbidity appeared due to the byproduct (sodium chloride) was removed by filtration using Buchner funnel which resulted the complex  $[\{(4\text{-Cl-3-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\}_2\text{Pb}]$ , as pale yellow crystalline in 87% yield. *Anal. Calc.* for  $\text{C}_{28}\text{H}_{24}\text{Cl}_4\text{O}_4\text{P}_2\text{S}_4\text{Hg}$ : C, 35.14; H, 2.53; S, 13.40; Cl, 14.82; Hg, 20.96, Found: C, 35.01; H, 2.24; S, 13.29; Cl, 14.71; Hg, 20.83; IR ( $\text{cm}^{-1}$ ) = 1209.1, s [ $\nu(\text{P})\text{-O-C}$ ], 938.8, s [ $\nu\text{P-O-(C)}$ ], 687.1, s [ $\nu\text{P-S}$ ], 561.5, m [ $\nu\text{P-S}$ ], 336.7, w [ $\nu\text{Hg-S}$ ]  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) = 2.1 (s, 12 H,  $\text{CH}_3$ ), 6.6 (d, 4 H, *ortho*,  $J = 8.1$ ), 6.7 (d, 4 H, *ortho'*,  $J = 8.1$ ), 6.8 (d, 4 H, *meta*,  $J = 8.1$ ) ppm;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) = 93.5 ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) = 17.4 ( $\text{CH}_3$ ), 114.2 (C-*ortho*), 128.6 (C- $\text{CH}_3$ ), 129.5 (C-*para*), 129.8-133.5 (C-*meta*), 148.6 (C-O) ppm.

## RESULTS AND DISCUSSION

Mercury dichloride reacted with sodium *O,O'*-di(4-chloro-3-methylphenyl)dithiophosphate, 1:2 molar ratio in aqueous medium yielding the title complex, bis{*O,O'*-di(4-chloro-3-methylphenyl)dithiophosphato} mercury(II).



### Scheme 1: Synthesis of bis{*O,O'*-di(4-chloro-3-methylphenyl)dithiophosphato} mercury(II).

This complex is soluble in common organic solvents (benzene, toluene, acetonitrile, methanol, chloroform), however, insoluble in solvents like *n*-hexane and carbon tetrachloride. This complex appears to be bit moisture sensitive but can be stored under anhydrous conditions for longer periods of time. This complex is non-volatile even under the reduced pressure. The elemental analyses (C, H, S and Hg) was found consistent with the molecular formula.

### Infrared spectra

IR spectrum was recorded in the range of 4000-200  $\text{cm}^{-1}$  as KBr pellets and the tentative assignments were made on the basis of relevant literature reports [10-11]. The comparison of IR spectrum with starting materials has also shown significant and characteristic changes and shifting of bands. Two strong intensity bands were observed at 1209.1  $\text{cm}^{-1}$  and 938.8  $\text{cm}^{-1}$ , which may be ascribed to the (P)-O-C and P-O-(C) vibrations of the diaryldithiophosphate moiety, respectively. The bands for P=S and P-S of the diaryldithiophosphate moiety were observed at 687.1  $\text{cm}^{-1}$  and 561.5  $\text{cm}^{-1}$ , respectively. The bands due to P=S and P-S vibrations have depicted a shift of 10-30  $\text{cm}^{-1}$  toward the lower frequency region in comparison to the parent dithiophosphate ligand. This shift of P-S vibration is perhaps due to bidentate mode of bonding by dithiophosphate ligand. The presence of a band for Hg-S at 336.7  $\text{cm}^{-1}$  in the spectra of these complexes is indicative of the formation of mercury-sulfur bond.

### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectrum recorded in  $\text{CDCl}_3$  showed the characteristic proton resonance of the corresponding aryl protons. In the  $^1\text{H}$  NMR spectra, the chemical shift for the methyl ( $-\text{CH}_3$ ) protons of the tolyl ring and were observed at 2.1 ppm as singlet. The chemical shifts for the aryl in the mercury(II) complex was observed

in the region 6.6-6.9 ppm as multiplet. These chemical shift values did not indicate any significant shift comparative to the parent dithiophosphate ligand.

### <sup>31</sup>P NMR spectra

Singlet for the dithiophosphate appeared at 93.5 ppm. Occurrence of a downfield shift (14-20 ppm) in comparison to the parent dithiophosphate ligand is indicative of the bidentate mode of linkage of the dithiophosphate ligand with mercury. A deshielding of this extent has been interpreted by different researchers to be consistent with the bidentate behavior of the dithiophosphate groups indicating the bidentate nature of the dithiophosphate ligand [10-12].

### <sup>13</sup>C NMR spectra

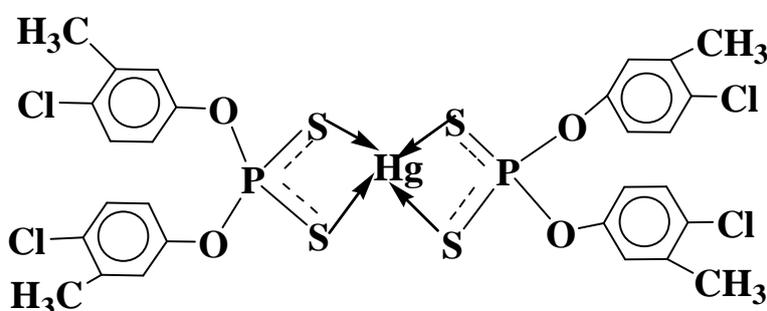
The <sup>13</sup>C NMR spectrum (in CDCl<sub>3</sub>) has been recorded, which show that the chemical shifts due to the carbon of aryl rings were found retained with a marginal shift in their values compared to the parent ligand. The chemical shift for the methyl (–CH<sub>3</sub>) carbon, attached to phenyl ring, was found at 17.4 ppm. The carbon nuclei of the aryl groups have displayed their resonance in the region 114.2-148.6 ppm. The chemical shifts for C–O carbon was found at 148.6 ppm

### Mass spectra

The mass spectrum of title complex depicted the molecular ion peak [M<sup>+</sup>] at 957.1 (m/z) In addition to molecular ion peak several other peaks of different fragments were observed, which were formed after consecutive dismissal of different groups. The chlorine isotopic abundance was exhibited by fragments containing chlorine atom, [4-Cl-3-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>O] being one with relative isotopic peaks at M value, 141.57 (m/z) and M+2 value, 143.57 (m/z). The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes.

### Structural Features

Literature survey [10-12] and observations based on elemental analysis, IR, NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P) and mass spectral studies indicated that the mercury atom is surrounded by the four sulfur atoms of dithiophosphate ligand in the probable square planar structure. The in the (P)–O–C, P–O–(C), P=S and P–S bands for dithiophosphate moiety in comparison to the parent dithiophosphate ligand indicates the formation of these complexes. Further, the appearance of new band ascribed to νHg–S is indicative of formation of mercury-sulfur bond. A singlet for the phosphorus atom of the dithiophosphato moiety indicates the bidentate mode of chelation by dithiophosphate ligand in addition to the equivalent nature of the phosphorus atom.



**Figure 1: Proposed four coordinated geometry for the complex, bis{O,O'-di(4-chloro-3-methylphenyl)dithiophosphato} mercury(II).**

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