



عنوان مقاله

تهیه، مطالعه چند هسته‌ای NMR و ساختار بلور ترکیب



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چکیده

واکنش جیوه(II) برماید با ترکیب نمک فسفونیوم نوع (۱) $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]\text{Br}$ در حلال متانول به نسبت مولی یکسان ترکیب با فرمول (۲) $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]_2[\text{Hg}_2\text{Br}_6]$ به دست می‌آید. شناسایی ترکیب به دست آمده توسط آنالیز عنصری، طیف‌سنجی IR و طیف‌سنجی NMR انجام گرفت. همچنین ساختار کمپلکس ۲ به وسیله بلور شناسی اشعه X تعیین گردید.

واژه‌های کلیدی: جیوه برماید (II)، بلور شناسی اشعه X، طیف‌سنجی NMR

Preparation, Multinuclear NMR study and Crystal Structure of $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]_2[\text{Hg}_2\text{Br}_6]$

Abstract

Mercury (II) boromid react with a phosphonium salt compound of the type $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]\text{Br}$ (1) in methanol as a solvent in equimolar ratios to give a compound of the formula $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]_2[\text{Hg}_2\text{Br}_6]$ (2). Characterization of the obtained compound was performed by elemental analysis, IR, ^1H , ^{13}C and ^{31}P NMR spectroscopy. Also the structure of 2 was determined by X-ray crystallography.

1. Introduction

Phosphorus compounds play an extraordinarily important role in living organisms, being the building components of nucleic acids. Due to a vast array of chemical species that may be formed by phosphorus, its compounds are also very frequently employed in organic synthesis [1]. Phosphorus compounds, such as phosphonium salts, phosphorus ylides and their transition metal complexes, notably palladium(II) metallacycle complexes, have been known for three decades. However,



recently they have attracted much more attention as exciting catalyst precursors for different types of cross coupling reactions [1–3]. Phosphonium salts and derivatives such as tetraphenylphosphonium (TPP) salts and triphenylmethylphosphonium (TPMP) salts have display much cancer-selective collection and cytotoxicity and they are proper of research as potential boron neutron capture therapy (BNCT) agents [5]. Because of applications and Enormous benefits phosphonium compound and their complexes a lot of research of these compounds has been that will briefly mention some of them. These compounds are present in a wide variety of organic compounds, functionalized types of branches and in several organic reactions such as oxidation used as a catalyst compound phosphonium able to move across the cell membrane [6]. More important than these factors is their new usage as an agent for imaging and diagnosing tumors, anticancer treatment and as a transport vector for targeting mitochondria [7,8].

2. Experimental

2.1 Materials and physical measurements

All reactions were carried out at room temperature using standard techniques. Reactants and reagents were obtained from Merck Chemical Company and used without further purification. The solvents were dried and distilled using standard methods. Melting points were measured on a Stuart SMP3 apparatus. IR spectra in the range 4000-400 cm^{-1} were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. ^1H , ^{31}P and ^{13}C NMR spectra were recorded on 300 MHz Bruker and 90 MHz Jeol spectrometers in DMSO- d_6 or CDCl_3 as solvent at 25 $^\circ\text{C}$. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid. Elemental analyses for C, H and N atoms were performed using a Perkin–Elmer 2400 series analyzer.

2.2. Synthesis

2.3.1. Synthesis of $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]\text{Br}$ (1)

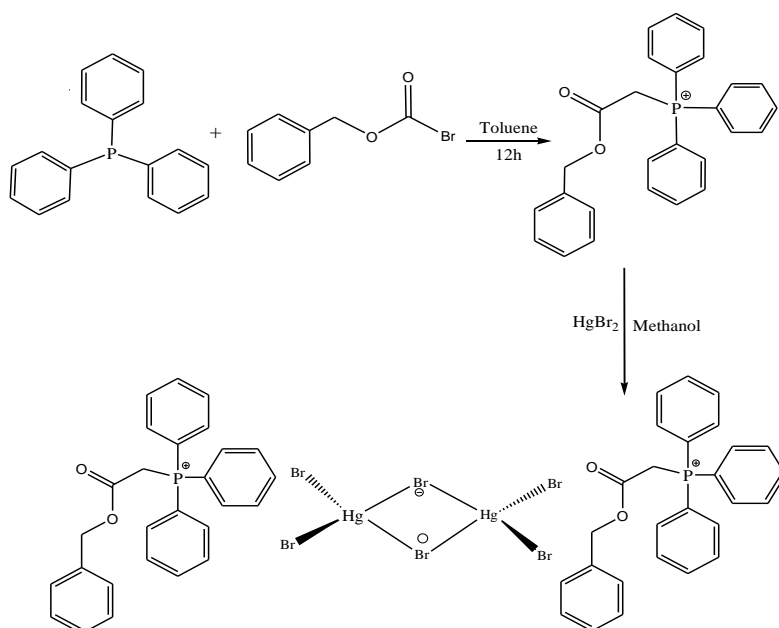
A solution consisting of triphenylphosphane (1.048 g, 4mmol) and then a solution (15ml) benzyl bromo acetate, $\text{BrCH}_2\text{COOCH}_2\text{C}_6\text{H}_5$ (0.917 g, 4 mmol) in toluene was stirred at room temperature for 12 h. The resulting suspension was filtered off, and the obtained precipitate washed with toluene, and then dried to give $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]\text{Br}$ (1) as a white powder. Yield: 1.27 g, 64%. M.p.: 132-134 $^\circ\text{C}$. Anal. Calc. for $\text{C}_{27}\text{H}_{24}\text{O}_2\text{P}$ (411.15 g/mol): C, 78.82; H, 5.88. Found: C, 78.3; H, 5.72%. IR (KBr disk, ν cm^{-1}): 1639 (CO), 650-900 (C-H in Ph), 1732 (COO), 1438 (P- CH_2). ^1H NMR (400 MHz, CDCl_3 , δ ppm): 5.48 (br, 2H, PCH_2); 7.05-7.80 (m, 20H, PPh_3). 4.87 (s, CH_2O); ^{13}C NMR (100 MHz, CDCl_3 , δ_c ppm): 68.41 (s, $\text{CH}_2\text{-O}$); 76.87, 77.51, (br, CDCl_3); 32.83-33.38 (br, PCH_2); 117.27, 118.15, 128.58, 128.70, 128.79, 130.20, 130.33, 133.86, 133.97, 134.19, 135.18, 135.21 (Ph); 164.13 (s, CO), $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , δ_p ppm): 20.68 (s, PPh_3).

2.3.2. Synthesis of $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]_2[\text{Hg}_2\text{Br}_6]$ (2)

To a solution of the compound $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]\text{Br}$, (0.437 g, 1mmol) in methanol (25 ml) HgBr_2 (0.271 g, 1 mmol) was added, and the resulting solution was stirred at room temperature for 36



h. The suspension that formed was filtered off, washed with diethyl ether and dried to give $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]_2[\text{Hg}_2\text{Br}_6]$ as a brown powder. Yield: 0.67 g, 85%. M.p.: 161 °C. Anal. Calc. for $\text{C}_{54}\text{H}_{48}\text{Br}_6\text{Hg}_2\text{O}_4\text{P}_2$ (411.15 g/mol): C, 38.07; H, 2.84. Found: C, 38.01; H, 2.72%. IR (KBr disk, ν cm^{-1}): 1736 (CO); 687-977 (C-H in Ph); 1588 (C=C in Ph); 1114, 1252 (C-O); 1438 (P-CH₂). ¹H NMR (400 MHz, CDCl₃, δ ppm): 5.62 (br, 2H, PCH₂); 7.08-7.9 (m, 20H, PPh₃). 4.91 (s, CH₂O); ¹³C NMR (100 MHz, CDCl₃, δ_C ppm): 68.41 (s, CH₂-O); 76.87, 77.51, (br, CDCl₃); 32.83-33.38 (br, PCH₂); 117.28, 118.15, 128.58, 128.70, 128.79, 130.20, 130.33, 133.86, 133.97, 134.19, 135.18, 135.21 (Ph); 164.13 (s, CO), ³¹P{¹H} NMR (162 MHz, DMSO-d₆, δ_P ppm): 20.72 (s, PPh₃).



Scheme 1. Synthesis of $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]_2[\text{Hg}_2\text{Br}_6]$.

2.3. X-ray crystallography

The single crystal X-ray diffraction data of suitable crystals of were collected on an Oxford Diffraction single-crystal x-ray diffractometer using mirror monochromated Mo K α radiation (0.71073 Å) at 298(2) K (Table 1). For Crystal White with dimensions of 0.40×0.30×0.25 mm, respectively, were mounted on a glass fiber and used for data collection. The data collection was performed using the ω -scans technique and using the STOE X-AREA software package [9], whereas data reduction was carried out using the program X-RED [10]. The molecular structure and packing of the triclinic system, lie across inversion centers in space group P-1 and the anion unit occupies a general position in space group. The structure was solved by direct methods and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares method using anisotropic displacement parameters. All hydrogen atoms were added in idealized positions. The atomic factors were taken from the International Tables for X-ray Crystallography. All refinements were performed using the X-STEP32 crystallographic software package [17].



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Table1. Crystal data and refinement details.

Empirical formula	(C ₂₇ H ₂₄ O ₂ P) ₂ (Hg ₂ Br ₆)
Formula weight	851.72
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P -1
a (Å)	10.953(2)
b (Å)	11.157(2)
c (Å)	13.167(3)
α (°)	99.68(3)
β (°)	114.11(3)
γ (°)	100.24(3)
Volume (Å ³)	1392.4(7)
Z	2
Absorption correction	Numerical
Absorption coefficient (mm ⁻¹)	9.911
Crystal size (mm ³)	0.40 × 0.30 × 0.25
Reflections collected	10167
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	0.913

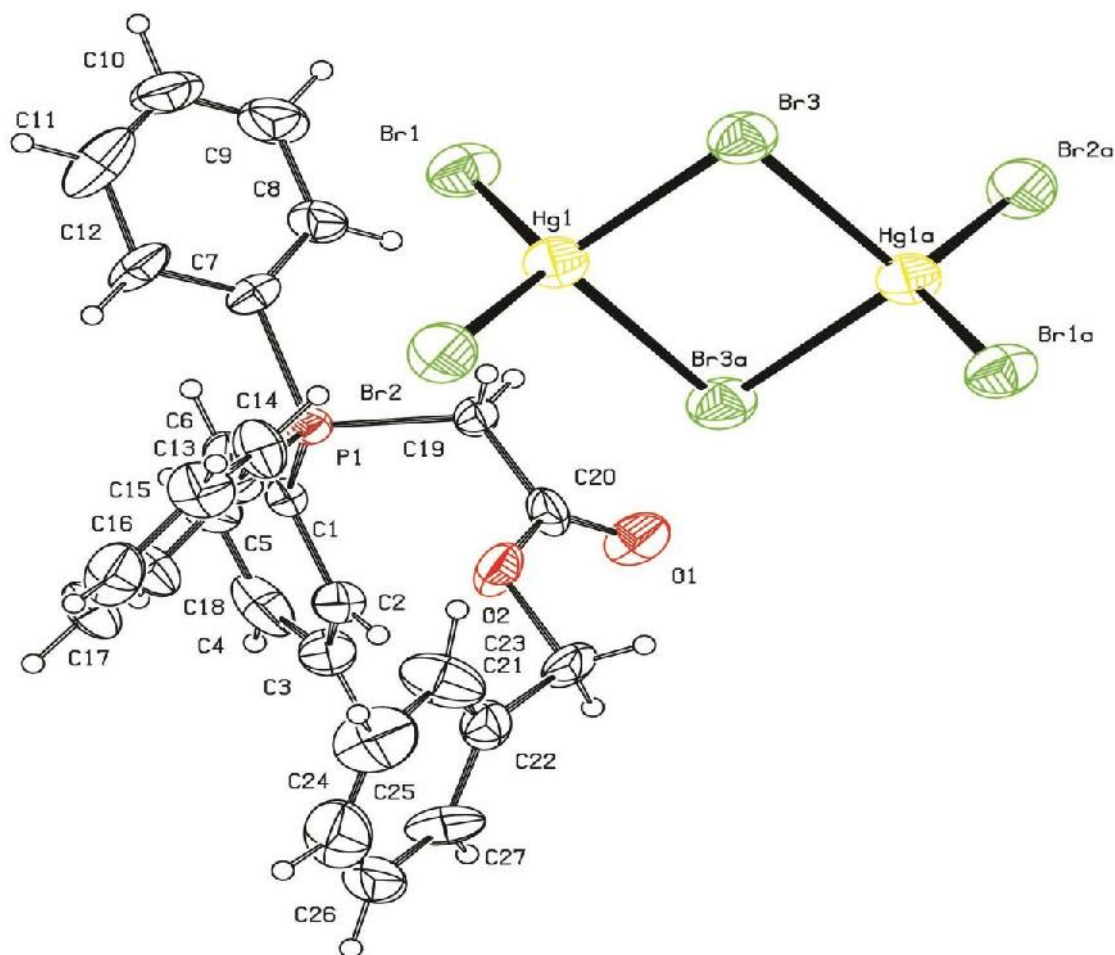


Figure 1. The structure of $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]_2[\text{Hg}_2\text{Br}_6]$.

3. Result and Discussion

We have reported previously the synthesis and structural characterisation of the compound bis [2-benzyloxy(2-oxoethyl)triphenylphosphonium]di- μ -bromo-bis[dibromomercury(II)], erived from the reaction between HgBr_2 and (Benzyloxycarbonylmethyl)triphenylphosphonium bromide. Crystallization of the product of the reaction results in white crystal for which X-ray crystallography reveals the structure $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{ph})_3]_2[\text{Hg}_2\text{Br}_6]$ (fig 1). The filtrate was evaporated to dryness and dissolved in dichloromethane, and the title product was crystallized by diffusion of diethyl ether into this solution. The structure of $[\text{Hg}_2\text{Br}_6]$ ion has been with triphenylphosphane (PPh_3) and with Benzyl bromoacetate ($\text{BrCH}_2\text{COOCH}_2\text{C}_6\text{H}_5$) determined as a counterions. The observed sharp and singlet peak at $\delta=20.72$ ppm by ^{31}P NMR confirmed the purity of the product. The IR spectrum 2 is represented by the bands of the cation dominated; they show no difference compared to the spectrum of $[\text{PhCH}_2\text{COOCH}_2\text{P}(\text{Ph})_3]\text{Br}$. The IR data shows that the CO absorption bands have not changed their vibrational frequency on going from the spectrum 1 to the spectrum 2 product. The compound



crystallizes in the non-centrosymmetric space group P-1 with one complete formula unit in the asymmetric unit. Selected bond distances and angles for the two autonomous but chemically identical molecules found in the unit cell of 2 are displayed in Table 2. Distances for the Hg₂Br₆ unit are as those seen before in other structure containing hexabromomercury(II). The crystal structure shows that there are no short interionic contacts and prove the coordination of P of the triphenylphosphine to C atom and mercury(II) not coordinated with them. Here we observed the same as previously reported that the [Hg₂(μ-Br)₂] core has a distorted square planar. To a slightly distorted square-planar geometry around the metal center, the Hg atom is surrounded by 4 bromide atoms. The crystal structure showed that in this molecule the diagram around the phosphorus atoms are close tetrahedral, and the O atoms are oriented cis to the in the vicinity of P atom.

Table 2. Selected bond lengths (Å) and bond angles (°).

Bond Lengths		Bond Angles	
Hg(1)-Br(2)	2.474(2)	Br(2)-Hg(1)-Br(1)	127.23(8)
Hg(1)-Br(3)	2.703(2)	Br(2)-Hg(1)-Br(3)	113.08(8)
Hg(1)-Br(1)	2.492(2)	Br(1)-Hg(1)-Br(3)	106.2 (7)
P(1)-C(13)	1.743(12)	C(1)-P(1)-C(19)	108.7(5)
P(1)-C(1)	1.778(12)	C(7)-P(1)-C(19)	106.5(6)
P(1)-C(7)	1.796(12)	C(13)-P(1)-C(19)	109.2(6)
P(1)-C(19)	1.822(12)	C(1)-P(1)-C(7)	109.5(5)
C(25)-C(26)	1.36(3)	C(13)-P(1)-C(7)	109.9(6)
O(1)-C(20)	1.187(15)	C(6)-C(1)-P(1)	122.2(9)
O(2)-C(20)	1.347(15)	C(6)-C(1)-C(2)	119.1(12)
C(23)-H(23)	0.932	C(20)-O(2)-C(21)	117.4(10)

4. Conclusions

This research examined the synthesis, characterization and antibacterial activity of some new phosphonium salt and Hg (II) complex. Characterization of the obtained compound was performed by elemental analysis, IR, ¹H, ¹³C and ³¹P NMR spectroscopy. Also the structure of 2 was determined by X-ray crystallography.

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Appendix A. Supplementary data

CCDC No. 1048125 contain the Supplementary crystallographic data for the compound. These data can be obtained free of charge via <http://www.ccdc.ac.uk/conts/retriving.html>, or from the Cambridge crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk



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