

New mercury (II) complexes containing the mixed ligands 5-phenyl -1,3,4-oxadiazole-2-thione, and diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n=1-4$ or triphenyl phosphine

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Abstract

Reaction $[\text{HgX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) with one mole proportion of thione ligand 5-phenyl -1,3,4-oxadiazole-2-thione (AH) gave tetrahedral complexes of the type $[\text{HgX}_2(\text{AH})_2]$. But reaction of $[\text{Hg}(\text{OAc})_2]$ with two mole proportion of AH in the presence Et_3N gave linear complex of the type $[\text{HgA}_2]$. Treatment of $[\text{HgA}_2]$ with two mole proportion of PPh_3 or one mole proportion of the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1-4$) gave tetrahedral complexes of the type $[\text{HgA}_2(\text{PPh}_3)_2]$, $[\text{HgA}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$, $[\text{HgL}_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]$ $n=2-4$ respectively. The prepared complexes were characterized by elemental analysis, IR spectra, ^1H , ^{13}C - $\{^1\text{H}\}$ and ^{31}P - $\{^1\text{H}\}$ n.m.r. data.

Key words: Mercury(II), Phosphine, thione/ thionate complexes.

Introduction

1,3,4-oxadiazole and their complexes have attracted much attention because of their biological activity served 1,3,4-oxadiazole derivatives exhibit analgesic¹ antiproteolytic, anticonvulsive, anti-inflammatory^{2,3} or fungicidal⁴ properties. There is considerable interests in the coordination chemistry of mercury(II) with heterocyclic thione^{1,2} because of the important of such complexes as models in biological system as solid state complexes³⁻⁵. The chemical interest of these thiones lies in the fact that they are potentially ambidentate or multi- functional donors with exocyclic S and heterocyclic N available for coordination, and their biological interest arises from their structural analogy to thiolated nucleosides⁶⁻⁷. Some paper involving platinum(II) or platinum(IV), gold(II) and ruthenium(II) with tertiary phosphines as a co-ligands have been published⁸⁻¹⁰. There have been several papers concerning study the coordination modes of the heterocyclic thiones ambidentate, 5-phenyl-1,3,5-oxadiazole-2-thione¹¹, 4,5-diphenyl-1,2,4-triazole-3-thione¹², with palladium(II) or platinum(II) in the presence of their tertiary mono phosphines. The prepared complexes have been used effectively to prepare heterobimetallic complexes¹³.

In the presence work, we report a study of the linkage of thione ligands with mercury(II) halide and pesidohalides $[\text{HgX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ and SCN) and reaction between mercury (II) acetate with thione ligands in the presence of Et_3N , and subsequent treatment with the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1-4$) and triphenyl phosphines.

Experimental

General

The ^1H - and ^{13}C - n.m.r spectra were recorded on Varian unity 500 and Gemini 2000 spectrometers respectively with CDCl_3 as solvent and Me_4Si as internal reference. ^{31}P - n.m.r spectra were recorded on Gemini 200 spectrometer with CDCl_3 as solvent and H_3PO_4 (85%) as external reference. Elemental analysis were carried out on a CHN analyzer type 1106 (Carlo-Erba). The n.m.r. spectra and CHN analysis were determined at the Institute fur

Anorganische chemie, Martin – Lurher-Univasitat Halle- Witten-berg, Germany. IR spectra were recorded on a Shimadzu FT.IR. 8400 spectrometer in the 200 – 4000 cm^{-1} range using CsI discs. Melting points were measured on an electro-thermal 9300 melting point apparatus.

Starting materials

The compounds $[\text{HgX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$ or OAc), PPh_3 , dppm, dppe, dppp, dppb were commercial products and were used as supplied, the ligand 5-phenyl-1,3,4-oxadiazole-2-thione (AH), was prepared according literature methods¹⁴⁻¹⁵.

Preparation of complexes

$[\text{HgCl}_2(\text{AH})]$ (1)

A solution of $[\text{HgCl}_2]$ (0.3g, 1.12mmol) in EtOH (10cm^3) was added to a solution of 5-phenyl-1,3,4-oxadiazole-2-thione (AH) (0.2g, 1.12mmol) in EtOH (10cm^3). The mixture was stirred at room temperature for 2h. The white solid thus formed was filtered off washed with EtOH , dried under vacuum and recrystallized from DMSO and EtOH (yield 84%). The following complexes $[\text{HgX}_2(\text{AH})]$ ($\text{X} = \text{Br}, \text{I}, \text{SCN}$) (2,3 and 4) respectively, were prepared and isolated by a similar method.

$[\text{Hg}(\text{A})_2]$ (5)

A solution of $[\text{Hg}(\text{OAc})_2]$ (0.522g, 1.82mmol) in EtOH (15cm^3) was added to solution of (AH) ligand (0.646g, 3.64mmol) in EtOH (10cm^3) in the present Et_3N (0.37g, 3.64mmole) The mixture was stirred at room temperature for 2h. The white solid formed was filtered off washed with EtOH , dried under vacuum and recrystallized from DMSO (yield 62%).

$[\text{Hg}(\text{A})_2(\text{dppm})]$ (6)

A solution of dppm (0.07g, 0.18mmol) in CHCl_3 (10cm^3) was added to a warm solution of $[\text{Hg}(\text{A})_2]$ (5) (0.11g, 0.18mmol) in EtOH (10cm^3). The mixture was stirred at room temperature for 1.5h. The white solid thus formed was filtered off washed with hot EtOH , dried under vacuum and recrystallized from CHCl_3 (yield 73%). The following complexes $[\text{HgA}_2(\text{dppe})]$ (7), $[\text{HgA}_2(\text{dppp})]$ (8), $[\text{HgA}_2(\text{dppb})]$ (9), were prepared and isolated by a similar method.

$[\text{Hg}(\text{A})_2(\text{PPh}_3)_2]$ (10)

A solution of PPh_3 (0.195g, 0.72mmol) in CHCl_3 (10cm^3) was added to a warm solution of $[\text{Hg}(\text{A})_2](12)$ (0.2g, 0.36mmol) in EtOH (10cm^3). The mixture was stirred at room temperature for 2h. The white solid thus formed was filtered off washed with EtOH , dried under vacuum and recrystallized from CHCl_3 , (yield 90%).

Results and discussion

Synthesis of complexes

Reaction of $[\text{HgX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) with heterocyclic thione ligand (5-phenyl-1,3,4-oxadiazole-2-thione(AH)) in ethanol solvent (1:1) molar ratio gave tetrahedral complexes of the type $[\text{HgX}_2(\text{AH})_2]$ (see Figure1). The halogen ligands coordinated as bidentate bridging and monodentate to mercury(II) ions, while the heterocyclic thione (AH) behaves as a monodentate ligand bonded via sulfur atoms to mercury(II) ion.

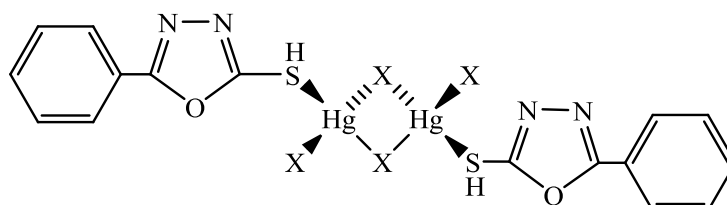


Fig 1: The structure formula of the complexes $[\text{HgX}_2(\text{AH})_2]$ when $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$

However treatment of mercury(II) acetate $[\text{Hg}(\text{OAc})_2]$ with two mole proportion of the thione ligand in the present Et_3N as a base gave linear complexes of the type $[\text{HgA}_2]$ (see Figure2), the anionic thionate ligands are coordinated as monodentate ligands via sulfur atoms to mercury(II) ion.

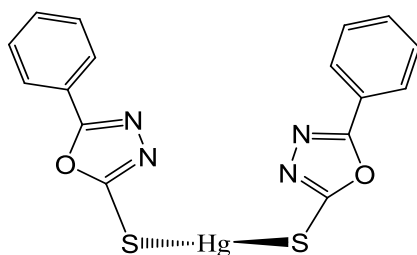


Fig 2: The structure formula of the complex $[\text{HgA}_2]$

Treatment of the linear mercury(II) complex of the type $[\text{HgA}_2](5)$ with one mole proportion of the diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-4$) or two mole proportion of PPh_3 , gave tetrahedral complex of the type $[\text{HgA}_2(\eta\text{-Ph}_2\text{CH}_2\text{PPh}_2)]_2(6)$ (see Figure 3) $[\text{HgA}_2(\text{diphos})]$ (7,8 and 9) (see Figure 4a) or the $[\text{HgA}_2(\text{PPh}_3)_2]$ (10) (see Figure 4b).

The anionic thionate ligands are coordinated as monodentate ligands, via sulfur atoms to mercury(II) ion binding ligand, while $\text{Ph}_2(\text{CH}_2)_n\text{PPh}_2$ ($n=2-4$) were coordinated as bidentate chelate. PPh_3 coordinated as monodentate ligands. But the $\text{Ph}_2\text{CH}_2\text{PPh}_2$ ligand was coordinated a bidentate bridging ligand with mercury(II) ion.

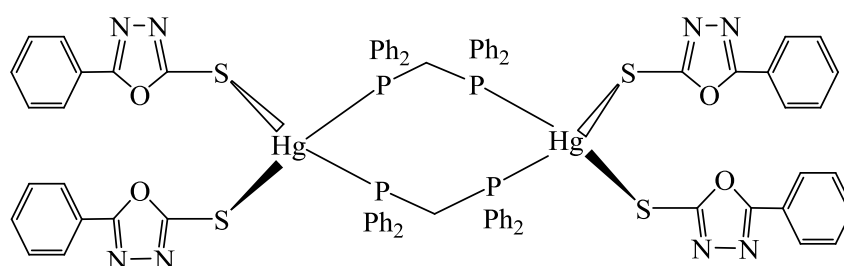


Fig 3: The structure formula of the complex $[\text{HgA}_2(\mu\text{-Ph}_2\text{CH}_2\text{PPh}_2)]_2$

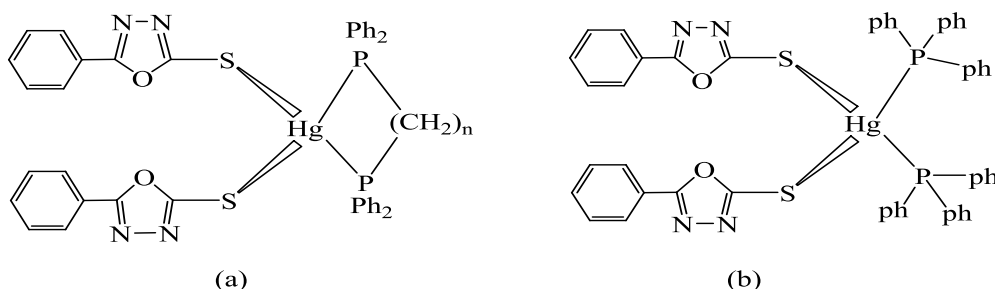


Fig 4: The structure formula of the complexes a- $[\text{HgA}_2(\text{diphos})](n=2-4)$; b- $[\text{HgA}_2(\text{PPh}_3)_2]$

Characterization of complexes

The prepared complexes were identified by elements analysis, IR spectra, and some them by ^{31}P - $\{^1\text{H}\}$, ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. spectra and their data are listed in Tables 1-3.

Infrared spectra

The infrared spectra of complexes(1-10) recorded in the $4000 - 250 \text{ cm}^{-1}$ range reveals some characteristics bands due to four thioamide, $(\text{C}-\text{O}-\text{C})_{\text{sy/asy}}$, NH bands required by the present of the heterocyclic thione ligands. All of the thioamide bands (I – IV) are shifted to some degree on complexation. The most significant change is observed in the thioamide band (IV). This bands has largest proportion of $(\text{C}=\text{S})$ band activity and negative shift ($11-75 \text{ cm}^{-1}$) range for AH ligand in all complexes, suggesting that coordination occurs through the thione $-\text{S}$ atom to the corresponding metal (II) ion^{2,17}.

The IR spectra of the $[\text{Hg}(\text{SCN})_2(\text{AH})_2]$ complex shown two strong band at 2069 cm^{-1} and 2113 cm^{-1} was assigned to SCN terminal and bridging bond, respectively¹⁸.

The position of IR bands due to oxadiazolyl group($\text{C}-\text{O}-\text{C}$)_{sy/asy}, do not change in the complexes indicated non-coordination of oxygen atom¹⁹. Moreover the spectra of complexes under investing containing $\nu(\text{Hg}-\text{P})$ stretching vibrations observed in the ($327 - 376 \text{ cm}^{-1}$) range²⁰ and $(\text{P}-\text{C})$ stretching vibrations observed in the ($485-505 \text{ cm}^{-1}$) range²¹ signify the coordination of phosphines ligands.

Nuclear magnetic resonance

The ^{31}P - $\{^1\text{H}\}$, ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. data of some the prepared complexes are given in Table 3. The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra of $[\text{HgA}_2(\mu\text{-dppm})]_2$ complex showed a singlet peak at $\delta\text{P} = 22.024 \text{ p.p.m.}$ The

singlet peak indicate the presence a single compound in which the two phosphorus atoms are equivalent and the positive values of the δP indicate that dppm behaves as a bidentate bridging²²⁻²⁴. This has been supported by ^1H n.m.r. spectra of $[\text{HgA}_2(\mu\text{-dppm})]_2$ complex which showed a triplet at $\delta\text{H} = 2.8 \text{ p.p.m.}$ for the methylene group of the bridging dppm, coupled to two equivalent phosphorus atoms²⁴⁻²⁵.

While reaction one mole of diphosphines $\text{Ph}_2(\text{CH}_2)_n\text{PPh}_2$ ($n = 2-4$) gave mono nuclear chelated-diphosphine complexes, The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra of complexes $[\text{HgA}_2(\text{diphos})]$ showed a singlet peak for (7,8 and 9) complexes (Table 3) these single peak indicated the presence a single compound each²¹⁻²³.

These conclusions have been supported by CHN analysis (Table 1), ^1H and ^{13}C - $\{^1\text{H}\}$ n.m.r. data are shown in Tables 3. On the basis of these data and other identification data given in Tables1 and 2 the tetrahedral structures shown in figure 4a have been suggested for these complexes.

The ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra of $[\text{HgA}_2(\text{PPh}_3)_2](10)$ complex shown a singlet peak at $\delta\text{P} = 5.196 \text{ p.p.m.}$ The singlet peak indicate the presence a single compound in which the two phosphorus atoms are equivalent^{18,25}. On the basis of these data and other identification data given in Tables1-3 the tetrahedral structures shown in figure 4b have been suggested for these complexes.

Acknowledgements

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Table 1 . Color, Yield, M.p. and CHN analysis for complexes (1-10)

Seq.	Complexes	Color	M.p. °C	Yield	CHN Cacl.(Found)%		
					C	H	N
1-	$[\text{HgCl}_2(\text{AH})]$	White	184-185	84	21.41(21.34)	1.12(1.10)	6.24 (6.22)
2-	$[\text{HgBr}_2(\text{AH})]$	White	178-181	78	17.87(17.76)	0.94(0.92)	5.21 (5.13)
3-	$[\text{HgI}_2(\text{AH})]$	White	155-159	65	15.21(15.23)	0.80(0.79)	4.44 (4.43)
4-	$[\text{Hg}(\text{SCN})_2(\text{AH})]$	White	184-188	70	24.32(24.12)	1.02(0.99)	11.34(11.28)
5-	$[\text{HgA}_2]$	White	211-214	62	34.63(34.66)	1.82(1.81)	10.09(10.01)
6-	$[\text{HgA}_2\text{dppm}]$	White	132-134	73	52.42(52.33)	3.43(3.45)	5.96(5.87)
7-	$[\text{HgA}_2\text{dppe}]$	White	105-107	90	52.91(52.67)	3.59(3.57)	5.88(5.87)
8-	$[\text{HgA}_2\text{dppp}]$	White	136-138	83	53.38(53.87)	3.75(3.45)	5.79(5.67)
9-	$[\text{HgA}_2\text{dppb}]$	White	231-233	78	53.85(53.83)	3.90(3.87)	5.71(5.70)
10-	$[\text{HgA}_2(\text{PPh}_3)_2]$	White	123-126	92	57.85(57.65)	3.73(3.66)	5.19(5.12)

Table 2 . IR. spectra data (cm⁻¹) of the ligand and complexes (1-10)

Seq.	Thioamide				v(N-H)	v(C-H)	v(Hg-P)	v(P-C)	v(N-N)	v (C-O-C) _{asy}
	I	II	III	IV						
AH	1608s	1340m	985m	765s	3108w	2960w			1486m	1086m, 890s
(1)	1612m	1352s	1000s	745s	3210w	3066w			1476m	1100w, 870w
(2)	1608s	1338m	1010s	754s	3188w	3062w			1490m	1085m, 880w
(3)	1621m	1331s	1008m	743m	3190w	3042w, 2890w			1475m	1080m, 857s
(4)	1612s	1340m	980m	732m	3156w	3076w			1470m	1093m, 860w
(5)	1550m	1342m	1000s	702s		3051w			1500w	1077m, 900m
(6)	1600m	1318m	1000m	731m		3050w	335w	500m	1488m	1076m, 865s
(7)	1601s	1323s	980m	732		3066w	345m	505s	1490m	1085m, 890s
(8)	1605m	1327s	996m	698m		2960w		500m	1500m	1090w, 850w
(9)	1612m	1342m	1006m	690m		3058w	327m	504m	1504w	1085w, 867s
(10)	1621	1323s	1014m	723		2900w		500s	1469s	1095s, 865s

w=weak, m=medium , s= strong.

Table (3) The ³¹P-{¹H} and ¹H-{³¹P} n.m.r. data(δ p.p.m) of some the prepared complexes ^a

Complexes	Seq.	δP	δCH ₂	δ Phenyl
[HgA ₂ dppm]	6	22.024	2.800	7.238-7.800
[HgA ₂ dppe]	7	16.560	2.381	7.192-8.082
[HgA ₂ dppp]	8	21.621	2.061(2H); 2.326(4H)	7.191-8.082
[HgA ₂ dppb]	9	23.269	1.388(4H); 3.075(4H)	7.241-7.872
[HgB ₂ (PPh ₃) ₂]	10	5.196		7.091-7.677

a- Measured inCDCl₃ unless stated otherwise.

References

- 1- P. A. Ochoa, M. I. Rodriguiz-Tapiador, S. S. Alxexadre, C. Pastor, F. Zamora, *J. Inorg. Biochem.* **99**, 1540(2005).
- 2- H. Fleischer, *Coord. Chem. Rev.*, **249**, 799(2005).
- 3- Ahmed, S., Isad, A. A., Ali, S., Al-Arfaj, A. R., *Polyhedron*, **25**, 1646(2006).
- 4- T. S. Lobanna, R. J. Butcher, A. D. Hunter, M. Zeller, *Polyhedron*, **25**, 2775(2006).
- 5- Raper, E. S., *Coord. Chem. Rev.*, **61**, 115(1985).
- 6- Raper, E. S., *Coord. Chem. Rev.*, **129**, 91(1997).
- 7- E. S. Raper, *Coord. Chem. Rev.*, **213**, 181(2001).
- 8- Beheshti, A., Brooks, N. R., Clegg, W. and Hyvadi, R., *Acta. Crystallogr. Sec.*, **E 61**, 1383(2005).
- 9- Popovic, Z., Soldin, Z., Calogovic, D. M., Povlovic, C. G., Giester, G., and M. Rajic, *Europ. J. Inorg. Chem.*, **2002**, 171(2001).
- 10- P. A. Dean, *Prog. Inorg. Chem.*, **24**, 109(1978).
- 11- D. P. Graddon, *Rev. Inorg. Chem.*, **4**, 211(1982).
- 12- N. A. Bell, C. William, C. P. Constable, J. C. Siman, H. W. Ross, B. Michael, E. L. Mark, E. S. Raper, C. S. Sammon, *Inorg. Chim. Acta.* **357**, 2091(2004).
- 13- M. I. M. Wazeer, A. A. Isab, M. Fettouhi, *Polyhedron*, **26**, 1725(2007).
- 14- C. Pert and G. Tosi, *Can. J. Chem.*, **55**, 1407 (1977).
- 15- Z. Popovic, D. Matkovic- Galogolovic, Z. Soldin, G. Povlovic, N. Davidovic and D. Vikić- Topic, *Inorg. Chim. Acta.*, **72**, 360(2001).
- 16- Z. Zugaj, Z. Popovic and D. Mrvos-Seemek, *Bell-Czech, Crystalllogr. Association*, **5**, 322(1998).
- 17- Chatt J. and Duncanson L.A., *Nature*, **97**, 178 (1956).
- 18- Al-Janabi, A. S. M., Abdullah, B. H., Al-Jibori, S. A., *Orient. J. Chem.*, **25**(2) 277(2009).
- 19- R. W. Mitchell, J. D. Ruddirck and G. A. Wilkinson, *J. Chem. Soc. A*, **3224** (1971).
- 20- Al-Jibori, S. A., Al-Zaub, A. S. S., Mahammed, M. Y. and T. A. A. Al-Allaf, *Trans. Met. Chem.*, **27**, 281(2007).
- 21- S. K. Hadjikakou and M. Kubicki, *Polyhedron*, **19**, 223(2000).
- 22- T. Kamei, T. Fujli and M. Saotome, *Jap. Appl. Chem. Abst.*, **107**, 220333d (1987).
- 23- C. T. Hunt and A. L. Balch, *Inorg. Chem.*, **20**, 2267(1981).
- 24- S. A. Al-Jibori, I. A. Abdullah, and T. A. K. Al-Allaf, *Trans. Met. Chem.*, **32**, 398(2007).
- 25- L. J. Al-Hayaly, B. H. Abdullah, A. A. N. Al-Dulaimi and S. A. Al-Jibori, *Orient. J. Chem.*, **24** (2), 38(2008).

معقدات جديدة للزئبق (II) الحاوي على مزيج من ليكاندات (5-فنيـل-4,3,1-او كساديازول-2-ثايون، وثنائية الفوسفينات $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ حيث $n = (1-4)$ ثلاثي فنيـل فوسفين

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الملخص

تفاعل هاليدات الزئبق $[\text{HgX}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) مع مول مكافئ واحد من ليكاند الثايون (5-فنيـل-4,3,1-او كساديازول-2-ثايون، (AH) أعطت معقدات رباعية السطوح من النوع $[\text{HgX}_2(\text{AH})]_2$. ولكن عندما تتفاعل خلاص الزئبق مع مولين من ليكاند الثايون (AH) بوجود ثلاثي اثيل أمين (Et_3N) كقاعدة تعطي معقد خطي من النوع $[\text{HgA}_2]$ ، وعند معاملة $[\text{HgA}_2]$ مع مولين من ثلاثي فنيـل فوسفين (PPh_3) أو مول واحد من ثنائي الفوسفين $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n=1-4$) يعطي معقدات رباعية السطوح من النوع $[\text{HgA}_2(\mu - [\text{HgA}_2(\text{PPh}_3)_2]$ ، $[\text{HgA}_2(\text{PPh}_3)_2]$ ، $[\text{HgL}_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)]$ ($n=2-4$) على التوالي. شخضت المعقدات المحضرة بواسطة التحليل الدقيق للعناصر، طيف الأشعة تحت الحمراء، أطياف الرنين النووي المغناطيسي ^1H ، ^{13}C ، ^{31}P .
كلمات الدلالة: الزئبق (II)، الفوسفين، الثايون، معقدات الثايونات.