



## Mixed Ligand Complexes of Hg-tetrazole-thiolate with phosphine, Synthesis and spectroscopic studies.

Osama'a A. Y. Al-Samrai<sup>1</sup>, Ahmed S. M. Al-Janabi<sup>2</sup>, Eman A. Othman<sup>1</sup>

<sup>1</sup> Department of Chemistry, College of Education, University of Samra'a, Samara, Iraq

<sup>2</sup> Department of Biochemistry, College of Veterinary Medicine, University of Tikrit, Tikrit, Iraq

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**Corresponding Author:**

**Name:** Ahmed S. M. Al-Janabi

**E-mail:**

[dr.ahmed.chem@tu.edu.iq](mailto:dr.ahmed.chem@tu.edu.iq)

**Tel :** +9647703765962

### ABSTRACT

Seven new complexes  $[\text{Hg}(\kappa^1\text{-ptt})_2]$  (1),  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppm})]$  (2),  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppe})]$  (3),  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppp})]$  (4),  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppb})]$  (5),  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppf})]$  (6), and  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{PPh}_3)_2]$  (7) have been synthesized and characterized. The reaction of two moles equivalent of 1-Phenyl-1*H*-tetrazole-5-thiol (Hptt) with one mole equivalent of  $\text{Hg}(\text{oAc})_2 \cdot x\text{H}_2\text{O}$  in ethanol solution afford  $[\text{Hg}(\kappa^1\text{-ptt})_2]$  (1). Treatment of (1) with one mole equivalent of diphos (diphos : dppm, dppe, dppp, dppb, dppf) or two moles equivalent of  $\text{PPh}_3$  afforded a complexes of the types  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{diphos})]$  (2-6) or  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{PPh}_3)_2]$  (7). The prepared complexes have been characterized by CHNS elemental analyses, molar conductivity, IR and NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P) spectroscopy. In all complexes, the ptt<sup>-</sup> ligand is bonded through the sulfur atom of deprotonated thiol group, whereas the diphosphine ligands bonded as bidentate chelating and  $\text{PPh}_3$  bonded as a monodentate, to afford a tetrahedral geometry around the  $\text{Hg}^{+2}$  ion.

### 1. Introduction

Tetrazole-thione ligands containing sulfur and nitrogen donor and their complexes are very important because of their different application in various field, such as medicine (including anti-bacterial, antifungal and anti-inflammatory), material science, photography, agricultural and industrial.[1-6]. "Hetero-aromatic chelators based on derivatives of tetrazole, such as mercapto-tetrazole {1-Phenyl-1*H*-tetrazole-5-thiol (Hptt)} are important ligands for inorganic complexes"[6-15].

Tetrazole-thiol exist as two tautomeric form, exhibiting thiol(I) and thione (II) isomers (Chart1). The deprotonation of (Hptt) leads to form (ptt<sup>-</sup>) anion, which is like 6π-electron ring system [16,17]. The (Hptt) can be binding to metal ions through its sulfur or nitrogen donor atoms as a monodentate ligands [18,19], or bonded through its S and N fashion as a bidentate (Chelating or bridging), or through sulfur atom only as bridging bidentate [6,10]. Recently, many studies were published including the complexes of metal ions with tetrazole - thione and phosphines or amines [5,8-15,20,21].

The present paper reports the preparation and spectroscopic studies of mercury(II) complexes of 1-Phenyl-1*H*-tetrazole-5-thiol(Hptt) containing

phosphines (dppm, dppe, dppp, dppb, dppf and  $\text{PPh}_3$ ) as co-ligands .

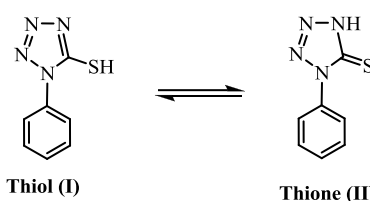


Chart 1: Tautomeric equilibrium of thione Hptt ligand.

### 2. Experimental

#### 2.1 Materials and methods

All chemical compounds and solvents used for synthesis were used as supplied without purification. CHNS analysis were conducted on a VarioEL CHNS elemental analyzer. The Nuclear magnetic resonance were measured on a Varian Unity 400 MHz spectrometer in  $\text{DMSO-d}_6$  as a solvent. The melting points of the prepared complexes were recorded on Automatic (SMP30) melting point apparatus. The infrared spectra of compounds were recorded as KBr disc using a Shimadzu FT-IR 8400S spectrophotometer in the 400-4000  $\text{cm}^{-1}$  range. The molar conductivity of  $10^{-3}$  M Freshly DMSO solution

of the prepared complexes were measured by using a digital conductivity meter.

## 2.2. Synthesis of complexes

### 2.2.1 Synthesis of $[\text{Hg}(\kappa^1\text{-ptt})_2]$ (1)

A solution of 1-Phenyl-1*H*-tetrazol-5-thiol (Hptt) (0.223g, 1.255mmole) in EtOH (10 ml) was added to a suspension of  $\text{Hg}(\text{oAc})_2 \cdot x\text{H}_2\text{O}$  (0.200g, 0.627mmole) in EtOH (10 ml). A white ppt. was formed directly. The mixture was stirred at room temperature for 1hr. The white product was filtered off, washed with EtOH, distal water, and dried in oven (Yield: 0.315g ; 90% ; m.p: 229-231 °C).

### 2.2.2 Synthesis of $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppm})]$ (2)

A solution of dppm (0.034g ; 0.090 mmole) in  $\text{CHCl}_3$  (10 ml) was added to a suspension of  $[\text{Hg}(\kappa^1\text{-ptt})_2]$  (0.05g; 0.090 mmole) in  $\text{CHCl}_3$  (10 ml). A clear solution was formed. The mixture was stirred at room temperature for (2hr). The clear solution was filtered off and set aside to evaporate the solvent at room temperature. The gum product treated with diethyl ether to produce a white solid which was dried in oven. (Yield: 0.082g ; 98% ; m.p: 101-103 °C).

### 2.2.3 Synthesis of $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppe})]$ (3)

To a suspension of complex (1) (0.050g; 0.090 mmole) in  $\text{CHCl}_3$  (10 ml), a solution of (dppe) ligand (0.035g; 0.090 mmole) in  $\text{CHCl}_3$  (10 ml) was added with stirring. A clear solution was formed. The solution was stirred for 2hr at room temperature then filtered off and set aside for slow evaporation to produce a white solid. The produced white solid was

collected and dried in oven (Yield: 0.083g ; 98% ; m.p: 224-225 °C).

The  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppb})]$  (4);  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppb})]$  (5) and  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppf})]$  (6) complexes were prepared and isolated by a similar method.

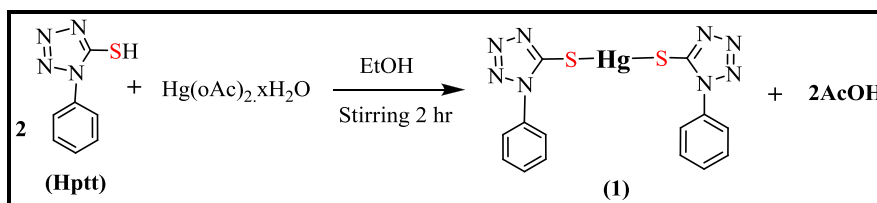
### 2.2.3 Synthesis of $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{PPh}_3)_2]$ (7)

A solution of  $\text{PPh}_3$  (0.047 g; 0.180 mmole) in  $\text{CHCl}_3$  (10 ml) was added to a suspension of  $[\text{Hg}(\kappa^1\text{-ptt})_2]$  (0.050 g; 0.090 mmole) in  $\text{CHCl}_3$  (10 ml), a clear solution was formed. The solution was stirred at room temperature for 2hr, then filtered off, and set aside for slow evaporation at room temperature. The produce white solid was collected and dried in oven (Yield: 0.094g ; 96% ; m.p: 185-187 °C).

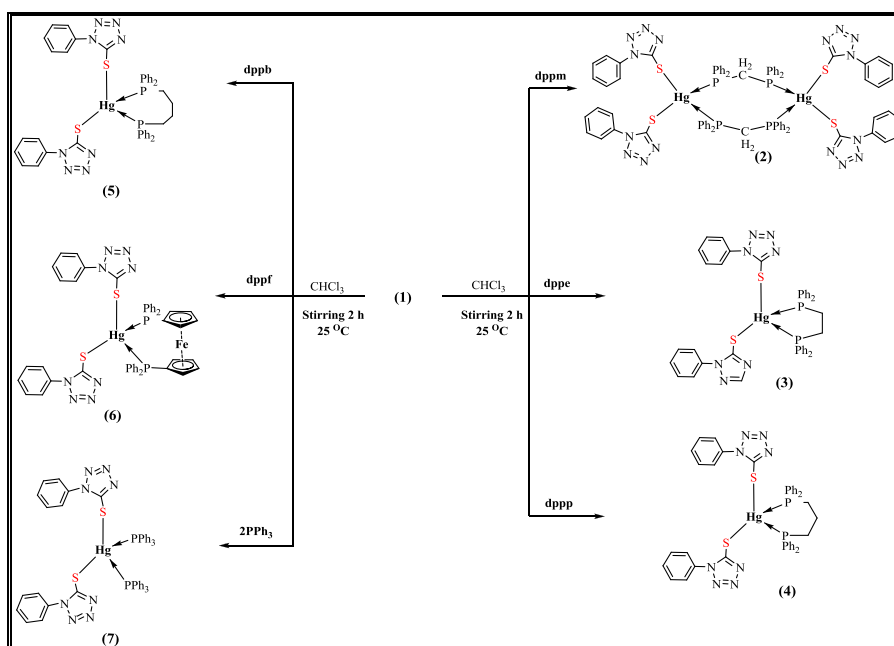
## 3. Result and Discussion

### 3.1 Synthesis of complexes (1-7)

Complex 1 was prepared by the treatment of one mole equivalent of mercuric acetate  $\text{Hg}(\text{oAc})_2 \cdot x\text{H}_2\text{O}$  in EtOH with two moles of 1-Phenyl-1*H*-tetrazol-5-thiol (Hptt) in EtOH at room temperature (Scheme 1). Reaction of an equal molar ratio of complex (1) with diphosphine (dppm, dppe, dppb, dppf) in  $\text{CHCl}_3$  as a solvent afforded complexes of the types  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{diphos})]$  (2-6) in good yields (94-98). while treatment of (1) with two equivalents of  $\text{PPh}_3$  afforded  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{PPh}_3)_2]$  (7) in good (96%) yield (Scheme 1). In all the complexes the 1-Phenyl-1*H*-tetrazol-5-thiol (Hptt) ligand was bonded as a monodentate ligand bonded through the sulfur atom of the deprotonated thiol group.



Scheme 1: Synthesis of complex 1



Scheme 2: Synthesis of complexes 2-7

### 3.2 Characterization of complexes (1-7)

All the prepared complexes are insoluble in methanol, absolute ethanol, distal water and diethyl ether, while soluble in chloroform, dichloromethane, dimethylsulfoxide and dimethylformide. The complexes have been characterized by infrared spectroscopy, elemental analysis (C.H.N.S), conductivity measurements, NMR spectroscopy

( $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$ ). The C.H.N.S analysis are listed in Table 1 and are in agreement with the suggested formula of the complexes. The molar conductivity of freshly prepared solution in DMSO ( $10^{-3}$ ) are listed in (Table 1). The molar conductivity are low, suggesting that complexes 1-7 are non- electrolytes [22].

**Table 1. Color, yield, m.p.(°C), and elemental analysis of the prepared complexes (1-7)**

Seq.	Complexes	Color	m.p.(°C)	Yield %	$\Lambda$ ( $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	Elemental analysis Found(cal)%			
						C	H	N	S
1	[Hg(ptt) <sub>2</sub> ]	White	229-231*	90	4.30	30.64 (30.30)	1.98 (1.82)	20.89 (20.19)	6.98 (11.55)
2	[Hg(ptt) <sub>2</sub> (dppm)]	White	101-103	98	4.28	50.21 (49.86)	3.81 (3.43)	12.23 (11.93)	7.12 (6.83)
3	[Hg(ptt) <sub>2</sub> (dppe)]	White	224-225	97	3.46	49.85 (50.39)	2.90 (3.59)	11.09 (11.75)	6.98 (6.73)
4	[Hg(ptt) <sub>2</sub> (dppp)]	White	213-215	98	3.26	51.45 (50.90)	3.05 (3.75)	11.07 (11.58)	6.95 (6.63)
5	[Hg(ptt) <sub>2</sub> (dppb)]	White	222-223	95	3.41	51.30 (51.40)	3.52 (3.90)	10.94 (11.42)	6.79 (6.53)
6	[Hg(ptt) <sub>2</sub> (dppf)]	Light orange	226-228*	95	18.94	51.43 (51.97)	3.07 (3.45)	9.63 (10.10)	6.05 (5.78)
7	[Hg(ptt) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	Yellowish white	185-187	96	3.25	55.97 (55.63)	3.89 (3.73)	10.95 (10.43)	6.19 (5.94)

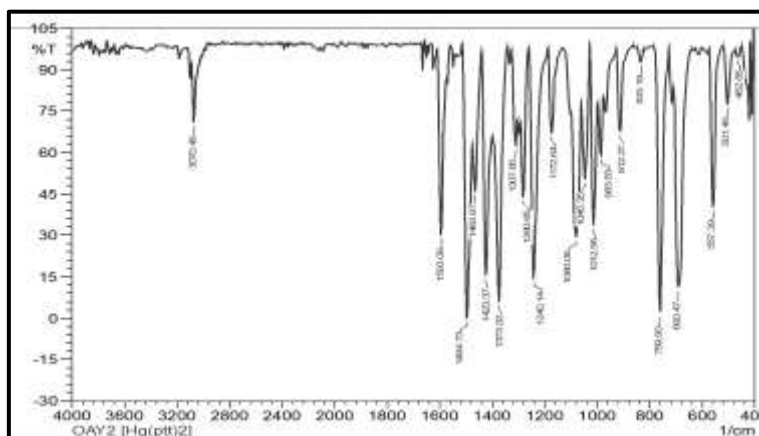
\* decommission.

### 3.3 Infrared spectra

The selected IR bands of the free ligand and its complexes (1-8) are presented in Table 2. The free (Hptt) ligand showed a bands at  $2540 \text{ cm}^{-1}$ ,  $1593 \text{ cm}^{-1}$ ,  $1493 \text{ cm}^{-1}$ ,  $1373 \text{ cm}^{-1}$  due to the frequencies of  $\nu(\text{S-H})$ ;  $\nu(\text{C=N})$ ;  $\nu(\text{C=C})$  and  $\nu(\text{N=N})$  respectively.

The IR spectrum of complex 1 (Fig 1a) showed the absence of a  $\nu(\text{S-H})$  band and the presence of a band at  $557 \text{ cm}^{-1}$  assign to  $\nu(\text{C-S})$ , indicating that 1-Phenyl-

1*H*-tetrazol-5-thiol (Hppt) deprotonated and present in the thiol form, bonded through the sulfur atom[23]. The IR spectra of complexes (2-7) showed new bands within ( $1433\text{-}1434 \text{ cm}^{-1}$  and ( $509\text{-}516 \text{ cm}^{-1}$  range attributed to the  $\nu(\text{P-Ph})$  and  $\nu(\text{P-C})$  respectively [24-26, 30-36], indicating the presence of the phosphine ligands in the prepared complexes. The other selected bands are listed in Table 2.



**Fig. 1: IR spectrum of complex 1**

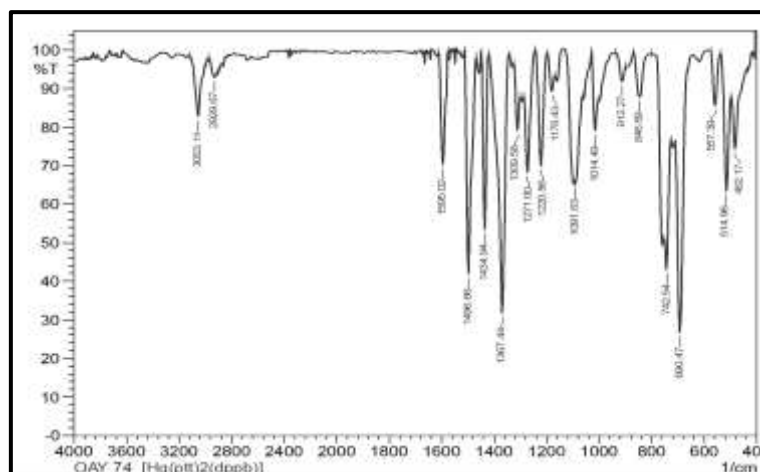


Fig. 2: IR spectrum of complex 5

Table 2 . Selected IR stretching vibration bands ( $\text{cm}^{-1}$ ) of the prepared complexes (1-7)

Seq.	Complex	$\nu(\text{C-H})$		$\nu(\text{C=N})$	$\nu(\text{Ph-P})$	$\nu(\text{N=N})$	$\nu(\text{N-N})$	$\nu(\text{C-S})$	$\nu(\text{P-C})$
		Ar.	Alph.						
ligand	Hppt	3034 m	-----	1593 m	-----	1356 s	1095 w	569 m	-----
1	$[\text{Hg}(\text{ppt})_2]$	3070 w	-----	1593 m	-----	1373 s	1080 m	577 m	-----
2	$[\text{Hg}(\text{ppt})_2(\text{dppm})]$	3053w	2879 w	1593 m	1433 m	1369 s	1093 s	555 w	509 m
3	$[\text{Hg}(\text{ppt})_2(\text{dppe})]$	3053 w	2904 w	1593 m	1434 m	1369 s	1095 m	557 w	511 m
4	$[\text{Hg}(\text{ppt})_2(\text{dppp})]$	3053 w	2902 w	1593 m	1433 s	1369 s	1095 m	557 w	511 m
5	$[\text{Hg}(\text{ppt})_2(\text{dppb})]$	3053 w	2929 w	1595 m	1434 m	1367 s	1091 m	557 w	514 m
6	$[\text{Hg}(\text{ppt})_2(\text{dppf})]$	3055 w	-----	1595 m	1434 m	1369 s	1095 m	559 w	509 m
7	$[\text{Hg}(\text{ppt})_2(\text{PPh}_3)_2]$	3051 m	-----	1593 m	1433 m	1367 s	1095 s	557 m	516 s

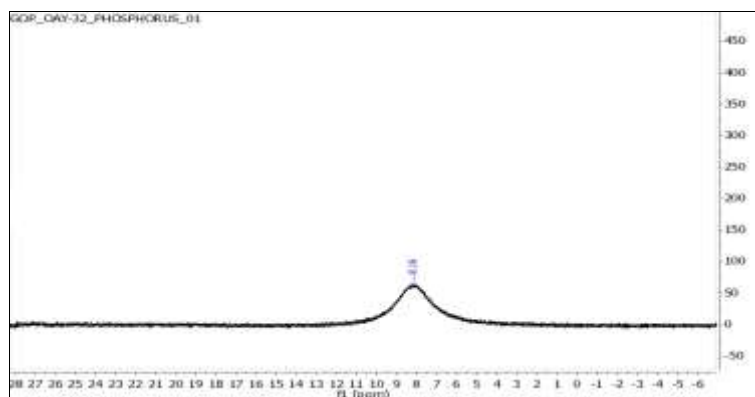
s = strong, m= medium, w= weak , Ar.= Aromatic , Alph.=Aliphatic

### 3.4 $^1\text{H}$ and $^{31}\text{P}$ NMR spectra

The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of the prepared complexes (2-7) (Fig 3 and 4), displayed a singlet peak at (8.16), (30.26), (31.13), (29.95), (39.84) and (25.53) ppm, This clearly showed that the phosphorus atoms are equivalent [27-29]. The positive value of the  $\delta\text{P}$  of (dppm) complex 2 (Fig 3) indicate that (dppm) ligand behaves as bidentate bridging to afford a binuclear complex [27-30]. This has been supported by  $^1\text{H}$  NMR spectrum of complex 2 which showed a broad singlet at  $\delta\text{H}=(4.03)\text{ppm}$  for the methylene group of the bridging (dppm) (Fig 6) [30-34]. The  $^1\text{H}$ -NMR spectra of complexes (2-7), were clearly

showed the protons of diphosphines ligands as well as the (ptt') ligand (see Fig 5 and 6) (data are given in Table 3).

The  $^{13}\text{C}$ -NMR spectrum of  $[\text{Hg}(\kappa^2\text{-ppt})_2]$  complex is in a good agreement with the suggest structure, ptt' has five different types of carbon atoms (see Fig. 7), the important peaks in the  $^{13}\text{C}$  NMR spectrum are the C7 peaks of C=S group at  $\delta 155.91\text{ppm}$  and C-N (C1) at  $\delta 134.19\text{ppm}$ . whereas the C4, C3,5 and C2,6 appeared at  $\delta 130.58$ ,  $130.22$ ,  $125.19$  ppm respectively.

Fig. 3:  $^{31}\text{P}\{-^1\text{H}\}$  nmr spectrum of  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppm})]$  (2) in  $\text{DMSO-d}_6$

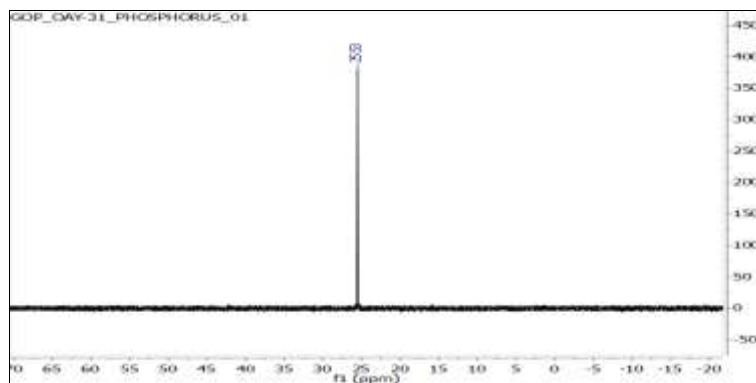


Fig. 4:  $^{31}\text{P}\{-^1\text{H}\}$  nmr spectrum of  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{PPh}_3)_2]$  (7) in  $\text{DMSO-d}^6$

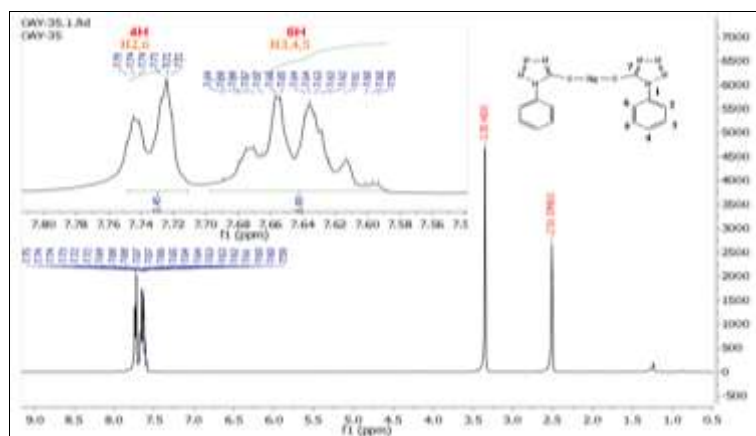


Fig. 5: The  $^1\text{H}$ -NMR spectrum of  $[\text{Hg}(\kappa^1\text{-ptt})_2]$  (1) in  $\text{DMSO-d}^6$

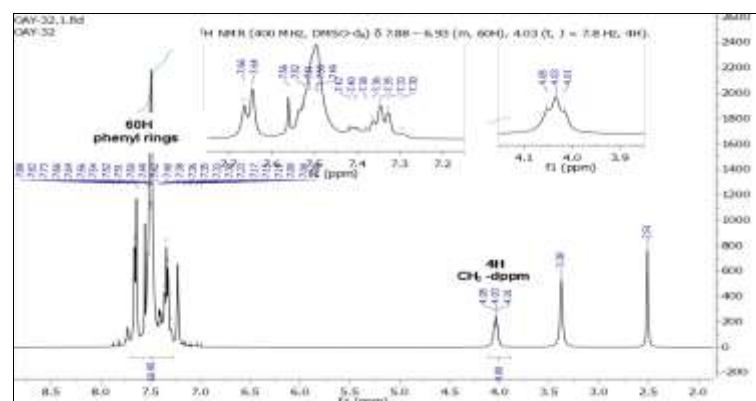


Fig. 6: The  $^1\text{H}$ -NMR spectrum of  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{dppm})]$  (2) in  $\text{DMSO-d}^6$

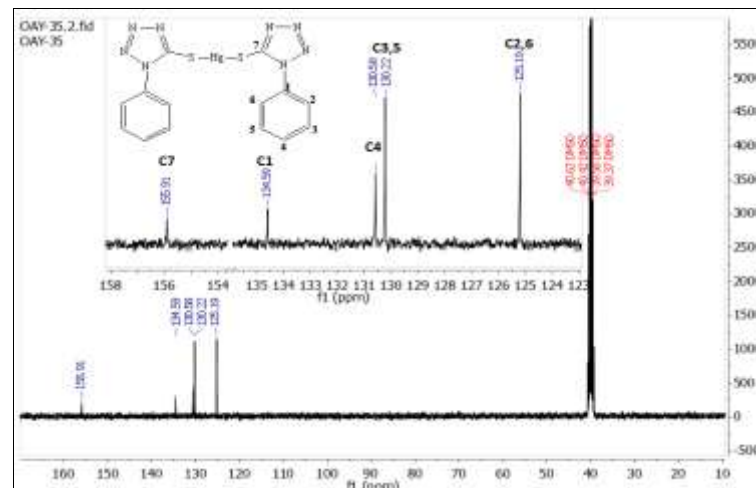


Fig. 7: The  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum of  $[\text{Hg}(\kappa^1\text{-ptt})_2]$  in  $\text{DMSO-d}^6$

**Table 3:  $^1\text{H}$  and  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR chemical shifts ( $\delta$  ppm) and coupling constant (Hz) for the prepared complexes (1-7) measured in  $\text{DMSO-d}^6$**

Seq.	Complexes	$\delta\text{P}$ (ppm)	$\delta\text{H}^*$ (ppm)
1	$[\text{Hg}(\text{ptt})_2]$	-----	7.72 – 7.75 (m, 4H), 7.59 – 7.69 (m, 6H).
2	$[\text{Hg}(\text{ptt})_2(\text{dppm})]$	8.16 b	6.93 – 7.88 (m, 30H, Ar-H), 4.03 (t, $^3J_{\text{P-H}} = 7.8$ Hz, 2H, $\text{CH}_2\text{-dppm}$ ).
3	$[\text{Hg}(\text{ptt})_2(\text{dppe})]$	30.26	7.72 – 7.34 (m, 30H, H-Ar), 3.09 (b s, 4H, $\text{CH}_2\text{-dppe}$ ).
4	$[\text{Hg}(\text{ptt})_2(\text{dppp})]$	30.13	7.76 – 7.35 (m, 30H, H-Ar), 3.18 (t, $^3J_{\text{HH}} = 5.5$ Hz, 4H, $\text{CH}_2^1\text{-dppp}$ ), 1.97 (p, $^3J_{\text{HH}} = 8.5$ , 1.51 Hz, 2H, $\text{CH}_2^2\text{-dppp}$ ).
5	$[\text{Hg}(\text{ptt})_2(\text{dppb})]$	29.95	7.76 – 7.23 (m, 30H, H-Ar), 2.86 (b s, 4H, $\text{CH}_2^1\text{-dppb}$ ), 1.67 (b s, 4H, $\text{CH}_2^2\text{-dppb}$ ).
6	$[\text{Hg}(\text{ptt})_2(\text{dppf})]$	39.84	7.98 – 7.13 (m, 30H, H-Ar), 4.70 (b s, 8H, $2\text{Cp-dppf}$ ).
7	$[\text{Hg}(\text{ptt})_2(\text{PPh}_3)_2]$	25.53	7.65 – 7.38 (m, 40H, H-Ar).

#### 4. Conclusions

In summary, we have synthesized seven new tetrazole-5-thiol Hg(II) complexes by the reaction of the Hptt ligand with mercury (II) acetate to afford complex of the type  $[\text{Hg}(\kappa^1\text{-ptt})_2]$ . Treatment of complex (1) with phosphine ligands gave complexes of the types  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{diphos})]$ (2-6) or  $[\text{Hg}(\kappa^1\text{-ptt})_2(\text{PPh}_3)_2]$  (7). The prepared complexes have been

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## معقدات حاوية على مزيج من الليكاندات للزئبق (II) - تترازول-ثايوليت مع الفوسفينات، تحضير، دراسة طيفية

أسامة أحمد ياسين السامرائي<sup>1</sup>، احمد شاكر مرموص الجنابي<sup>2</sup>، ايمان عبد الواحد عثمان<sup>1</sup>

<sup>1</sup> قسم الكيمياء ، كلية التربية جامعة سامراء ، سامراء ، العراق

<sup>2</sup> جامعة تكريت ، كلية الطب البيطري، فرع الكيمياء الحياتية، تكريت، العراق

### الملخص

حضرت وشُخصت سبعة من سلسلة من المعقدات الجديدة ذات الصيغ  $[Hg(\kappa^1-pta)_2]$  (1) و  $[Hg(\kappa^1-pta)_2(dppm)]$  (2)، و  $[Hg(\kappa^1-pta)_2]$  (3) من تفاعل ليكاند 1-فنيل-1H-تترازول-5-ثايول ( $Hpta$ ) مع خلاص الزئبق الثنائي في مذيب الايثانول مع التحريك بدرجة حرارة المختبر ليعطي المعقد (1)، وان معاملة المعقد (1) مع مول واحد من ليكاندات  $dppf$ ,  $dppb$ ,  $dppp$ ,  $dppe$ ,  $dppm$  أو مولين من  $PPh_3$  اعطى المعقدات من (2-7). شُخصت المعقدات المحضرة بواسطة التحليل الدقيق للعناصر، التوصيلية المولارية الكهربائية، مطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي للبروتون، الفسفور والكربون، حيث أظهر ليكاند ( $pta$ ) في جميع المعقدات سلوك احادي السن يرتبط عن طريق ذرة الكبريت لمجموعة الثايول الفاقدة للبروتون، فيما ارتبطت ليكاندات الفوسفين الثنائية ( $diphos$ ) بشكل ثنائي السن الجسري مع ليكاند ( $dppm$ ) او المخلبي بقية الفوسفينات الثنائية، أما ( $PPh_3$ ) فقد ارتبط بشكل احادي السن، لتعطي معقدات ذات بنية رباعي السطوح حول الأيون الفلزي في جميعها.