

Characterization and antibacterial study for synthesis binuclear complexes of Pd (II), Hg (II)

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ABSTRACT

This research includes synthesis and characterization of some Homogeneous and Heterogeneous binuclear complexes of Pd(II),Hg(II) with mixed ligands of dithiocarbamate derived from barbituric acid and tertiary phosphines. The formed complexes have the general formula of $[M_2 (BADTC)_2 (Phosphine)_n]$ Barbituric acid bis(dithiocarbamate) = (BADTC)M=Pd(II),Hg(II)n=2 or 4 mole. The synthesized complexes were identified using the micro elemental analysis (C.H.N), electrical molar conductivity, spectra methods (IR and ¹H, ³¹P-NMR). Antibacterial activity of ligands and complexes was evaluated with two types of bacteria *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative). According to the results obtained from the physical and spectral measurements, palladium (II) complexes have a square planer shape, and mercury (II) complexes have a tetrahedral arrangement.

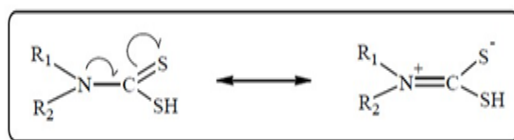
Keywords: dithiocarbamate, barbituric acid, tertiary phosphines.

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INTRODUCTION

Dithiocarbamates are S, N containing ligand, which display a rich and varied coordination chemistry with a wide range of transition and main group metal complexes [1]. The study of complexes containing sulfur as donor atoms has become an important subject in the field of coordination chemistry [2,]. Dithiocarbamate compounds are organic compounds (R \bar{R} NCSS), where R, \bar{R} are homogeneous or heterogeneous aliphatic or aromatic organic compounds which are stable with metal ions at high oxidation states due to the strength of the unique bond C-S. It has the electronic system S-C-S [3], and it is in a state of resonance, Where the flowing of additional electrons takes place from nitrogen to carbon from π orbitals [4] as in the following diagram:



Due to the significant importance of thiocarbamate derivatives which can be used as potent medicine against cancer and drugs [5]. In agriculture, industry, and biology, also they are used as antimicrobial and immunological regulatory materials [6,7]. And they are used as an intermediate in some reactions. Among the important reactions of dithiocarbamate is the oxidation to thiuram disulfide compounds [8]. Using oxidizing agents such as $K_3 [Fe (CN)_6]$, I_2 and hydrogen peroxide (H_2O_2), these types of ligands contain the active group S-S [9].

Such active group might react with metals through the cleavage or without cleavage of S-S bond. Phosphine and diphosphine are important ligands in transition-metal catalyzed reactions, and the electronic and steric effects of the phosphine have pronounced influence on the organic transformation that takes at the transition metal center [10,11].

While the Bis (diphenylphosphino) ethane and the Bis (diphenylphosphino) propane(dppp) behave as bidentate chelate [12], or behave as bridge ligands between two metal atoms [13,14], the complexes of phosphine with palladium used as assistant agent cyclic or heterocyclic by increase stability of medial compound [15].

In the present work, we report the synthesis and characterization of some new complexes obtained by the reaction of Pd(II), Hg(II) salts with mixed ligands of dithiocarbamate and a tertiary phosphine.

EXPERIMENTAL

IR-spectra were recorded on the (FTIR- 600 Spectrophotometer) in the (350-4000) cm^{-1} range using KBr discs. Micro elemental analysis (C.H.N) conducted by using (Euro EA 3000). Molar Conductivities for complexes were measured at 10^{-3} M solution in DMSO at 25°C using (Cond 7110). Melting points were obtained using (Electro thermal 9300). The ^1H - ^{31}P -NMR spectra were performed (solvent DMSO- d^6) on (Bruker 400MHz), at the University of Sinop, Turkey.

Starting materials

All chemicals and phosphine ligands were commercial products and were used as supplied.

Synthesis of ligand

Barbituric acid bis (dithiocarbamate) (BADTC) was prepared by a previously described method [16].

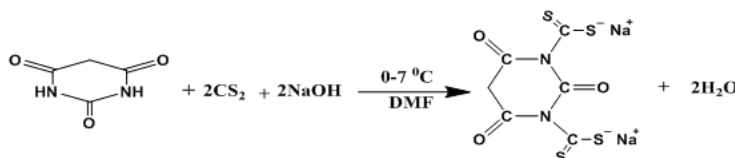


Table 1: chemical formula (CHN) analysis and some physical properties of the BADTC ligand

Chemical formula	color	Melting point/ $^\circ\text{C}$	Micro elemental analysis calculate (found)			
			C%	H%	N%	S%
324.31	Light orange	260-262	22.22	0.62	8.64	39.54
$\text{C}_6\text{H}_2\text{N}_2\text{Na}_2\text{O}_3\text{S}_4$			(22.61)	(0.55)	(8.12)	(38.91)

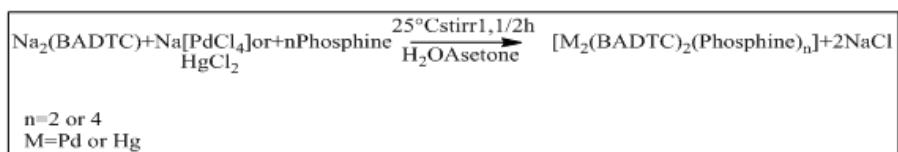
Synthesis of Dithiocarbamate complexes with phosphine

Synthesis of $[\text{Pd}_2(\text{BADTC})_2(\text{dppe})_2]$

This complex was synthesized by the following procedure:

A solution of $\text{Na}_2[\text{PdCl}_4]$ (0.045g, 0.000154mol) in distilled water (5ml) was added to a solution of Na_2BADTC (0.025g, 0.000154mol) in distilled water (5 ml), the mixture was stirred at room temperature for 1hour). The colour of the solution was changed from colorless to dark brown then a solution of dppe (0.0613g, 0.000145mol) in 5ml of acetone was added. The mixture was left stirring for half an hour, a light brown precipitate was formed, and it was filtered off and washed with a small amount of distilled water (3 times) and dried in an oven at 50°C .

The rest of the complexes listed in (Table 2) were synthesized in the same way as mentioned above using a proper number of moles of the metal salts and ligands.



RESULTS AND DISCUSSION

Physical and spectral techniques were used for the identification of synthesized complexes. The solid prepared complexes are soluble in most common solvents such as DMSO, DMF, THF. The molar conductivity values of all complexes in DMSO solvent of 10^{-3} M at 25°C (Table 2) indicate that complexes are non-electrolyte. This is consistent with the stoichiometry assumed for the complexes $[\text{M}_2(\text{BADTC})_2(\text{Phosphine})_n]$. The micro elemental analysis measurements for all complexes gave approximated values when are compared with theoretical values, (Table 2) includes some physical properties and (C.H.N) results for the synthesized complexes.

Table 2: Some physical properties, analytical, conductance data and yield % of the complexes

NO	Complexes	Color	M.P/ ^o C	yield%	Molar cond./ mole ⁻¹ , cm ⁻¹ hom	Micro elemental analysis calculated (found)		
						C%	H%	N%
1	[Pd ₂ (BADTC) ₂ (dppm) ₂]	Light brown	(210-212)*	70	1.01	58.40 (58.31)	4.09 (4.02)	2.51 (2.43)
2	[Pd ₂ (BADTC) ₂ (dppe) ₂]	Dark brown	(180-182)*	72	0.91	49.09 (49.08)	3.54 (3.35)	3.66 (3.58)
3	Pd ₂ (BADTC) ₂ (dppp) ₂]	Brown	(220-222)*	76	1.27	49.81 (49.72)	3.60 (3.54)	3.53 (3.51)
4]Pd ₂ (BADTC) ₂ (PPh ₃) ₄ [Brown	(170-172)*	66	0.82	55.55 (55.45)	3.61 (3.55)	3.11 (3.08)
5	Hg ₂ (BADTC) ₂ (dppm) ₂]	White	(300-302)	78	1.84	54.01 (53.91)	3.81 (3.72)	2.24 (2.25)
6	Hg ₂ (BADTC) ₂ (dppe) ₂]	Dark gray	(230-232)	80	2.49	43.88 (43.81)	3.03 (2.99)	3.22 (3.19)
7	Hg ₂ (BADTC) ₂ (dppp) ₂	Light gray	(280-282)	68	0.95	44.41 (44.47)	3.10 (3.17)	3.09 (3.14)
8]Hg ₂ (BADTC) ₂ (PPh ₃) ₄	White	(270-272)	77	1.07	50.30 (50.27)	3.25 (3.21)	2.8 3 (2.79)

decomposition*

Infrared spectra:-

The prominent infrared spectral data of prepared ligand and its complexes are given in (Table 3).

The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in bonding.

In BADTC, the infrared bands observed at 1662 cm⁻¹, 1430 cm⁻¹, (993) and (867) cm⁻¹ have been assigned to ν C=O, ν (C=S) and ν (C=S) respectively [16].

In IR spectra of all complexes, the C=O stretching vibration are shifted to higher values 1670-1705cm⁻¹, suggesting that the carbonyl group is not involved in bonding in coordination with central metal ion [17].

Also, the complexes spectra showed bands at 1550-1600 cm⁻¹ which is assigned to (C=N) group and those values, indicating that (C=N) group is not coordinated [18].

A noticeable shift to lower frequencies for bands of ν (C=S) (922-999) cm⁻¹, and (1101-1188)cm⁻¹ in the complexes were observed.

The (C=S) frequencies can be used for distinguishing between the mono and bidentate binding of dithiocarbamate ligand with the metal ion, the presence of two (C=S) bonds in spectra of the complexes refer to monodentate coordination of dithiocarbamate ligand with the metal ion [19].

The new bands in the region (507-528) cm⁻¹ and (1422-1429)cm⁻¹ were assigned to ν (P-C) and ν (P-Ph) respectively indicating that phosphine ligands are coordinated with metal center [13]

Table 3: IR data of synthesized complexes and ligands (cm⁻¹)

Compound	C-H (ν)		ν C=O	ν	ν	ν P-Ph	ν P-C
	Ar	Alph					
BADTC	-----	2887 _m	1662 _s	1520 _m	_s 1230 _m 1107	-----	-----
[Pd ₂ (BADTC) ₂ (dppm) ₂]	3049 _s	2948 _w	1679 _w	1550 _m	1099 _s 995 _w	1433 _s	505 _m
[Pd ₂ (BADTC) ₂ (dppe) ₂]	3051 _s	2916 _w	1704 _w	1556 _m	1099 _s 999 _w	1433 _s	515 _s
Pd ₂ (BADTC) ₂ (dppp) ₂]	3053 _s	2945 _w	1701 _w	1560 _w	1101 _s 995 _m	1434 _s	528 _s
[Pd ₂ (BADTC) ₂ (pph ₃) ₄]	3051 _s	2925 _w	1700 _w	1580 _m	1188 _s 993 _m	1434 _s	516 _s
Hg ₂ BADT) ₂ (dppm) ₂]	3051 _s	2925 _w	1697 _s	1572 _s	1101 _s 997 _m	1434 _s	509 _s
Hg ₂ (BADTC) ₂ (dppe) ₂]	3051 _s	2918 _w	1703 _s	1570 _s	1097 _s 995 _m	1433 _s	511 _s
[Hg ₂ (BADTC) ₂ (dppp) ₂]	3049 _w	2904 _w	1701 _w	1563 _w	1101 _s 995 _m	1434 _s	520 _s
[Hg ₂ (BADTC) ₂ (PPh ₃) ₄]	30 49 _m	2921 _w	1670 _w	1567 _s	1095 _s 991 _m	1429 _s	501 _s

NMR Results

¹H-NMR spectrum of BADTC:-

The ¹H-NMR spectrum of the ligand Barbituric acid bis (dithiocarbamate) showed singlet at δH(3.25) from the chemical shift and the integration this signal is assigned(to (CH₂) protons .

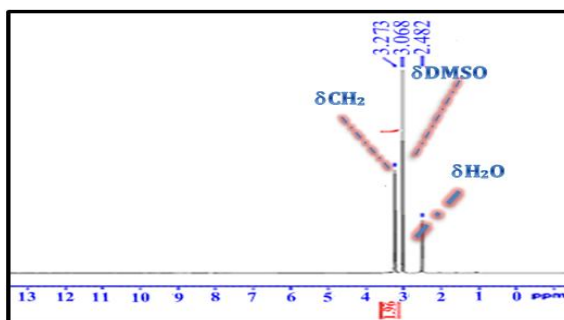


Figure 1: ¹H NMR spectrum of (Na₂BADTC)

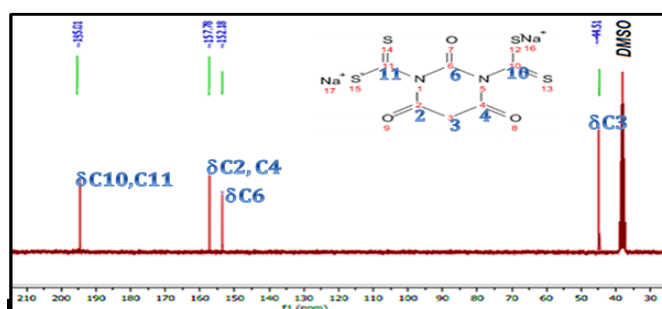


Figure 2: ¹³C NMR spectrum of (Na₂BADTC)

The ^1H and ^{31}P -NMR data for Some prepared complexes using DMSO-d_6 as a Solvent are given in (Table 4), and figures(1),(2) show the spectra for some of them. [20,21].

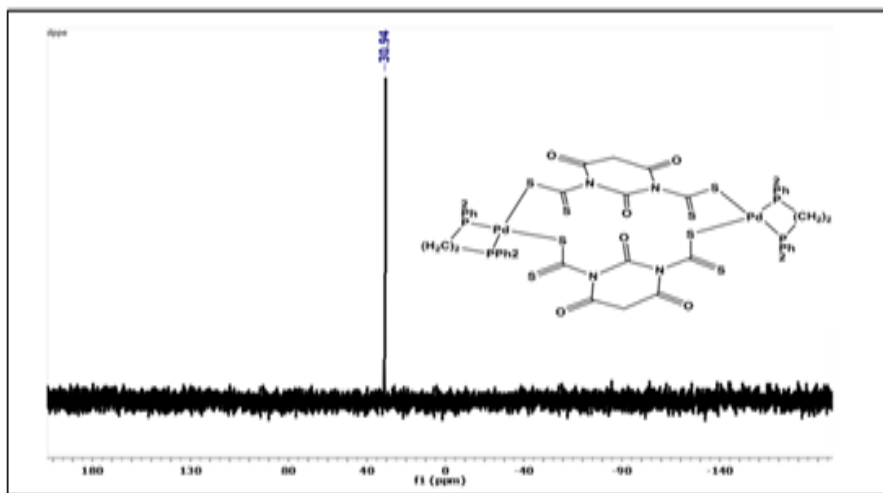


Figure 3: NMR spectrum of ^{31}P -NMR of complex $[\text{Pd}_2(\text{BADTC})_2(\text{dppe})_2]$

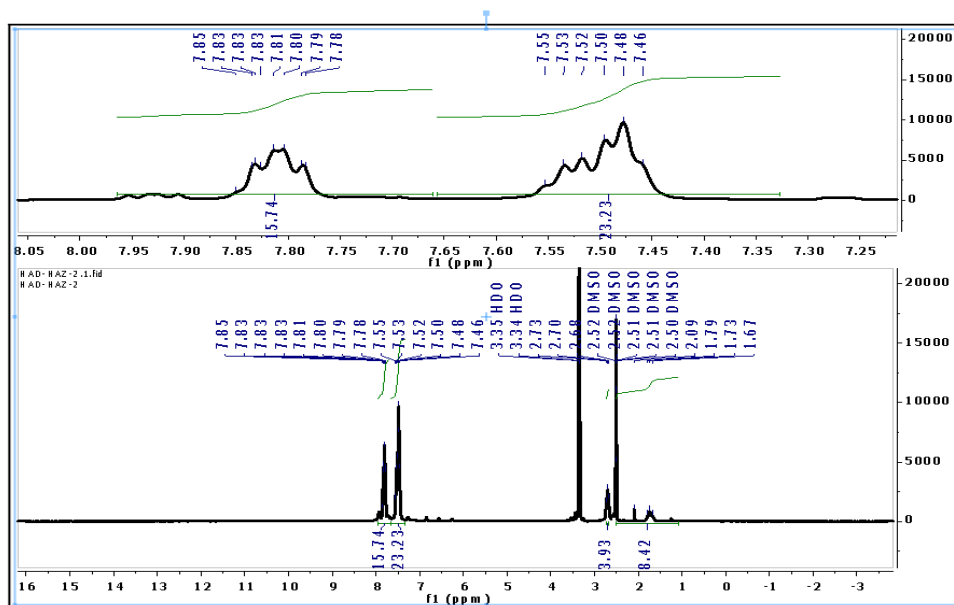


Figure 4: ^1H -NMR spectrum of the complex $[\text{Pd}_2(\text{BADTC})_2(\text{dppe})_2]$

Table 4: ^{31}P -NMR data $\delta^{31}\text{p}$ ppm of some prepared complexes are all singlet

N0	Complex	δP	
1	$[\text{Pd}_2(\text{BADTC})_2(\text{PPh}_3)_4]$	-26.69	P-free
2	$[\text{Pd}_2(\text{BADTC})_2(\text{dppm})_2]$	-23.77 53.11	P-free P-Pd
3	$[\text{Pd}_2(\text{BADTC})_2(\text{dppe})_2]$	30.94	P-free
4	$[\text{Pd}_2(\text{BADTC})_2(\text{dppp})_2]$	-26.29	P-free
5	$[\text{Pd}_2(\text{BADTC})_2(\text{dppp})_2]$	-29.90	P-free
6	$[\text{Hg}_2(\text{BADTC})_2(\text{dppp})_2]$	-29.90	P-free
7	$[\text{Hg}_2(\text{BADTC})_2(\text{dppe})_2]$	-53.25	P-free

Measured in CDCl_3^*

Table 5: ¹H-NMR spectral data for some complexes

N0	Complexes
3-	¹ H-NMR(DMSO-d ⁶): δ7.46-7.55(23H,Phos)and δ7.78-7.85(16H,Phos)for 8 cycle aromatic , δ1.73(8H,2CH ₂ ,ligand phos) , δ2.70(4H,CH ₂ ,ligandBADTC)ppm.
4-	¹ H-NMR (DMSO-d ⁶): δ7.49-7.49(26H,phos)and δ7.78-7.85(16H,phos)for 8 cycle aromatic , δ2.52(3CH ₂ , ligand dppp), δ2.63(CH ₂ ,ligand BADTC)ppm
5-	¹ H-NMR(DMSO-d ⁶): δ7.46-7.57(23H,phos)and δ7.57-7.81(16H-phos)for 8 cycle aromatic , δ1.95(2CH ₂ ,ligand dppp) δ2.92(CH ₂ ,ligand BADTC).ppm

Anti-bacterial activity:

The synthesized dithiocarbamate ligand and its complexes were tested against two types of bacteria *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative). DMSO was used as solvent and as a control. The concentration of the compound in this solvent were (1 x 10⁻⁴), (1 x 10⁻³) and (1 x 10⁻²) mg/ml. The disc sensitivity test method was used, the incubation was held for 24 hours at 37 °C. The measured inhibition zones against amounts of growth of two types of bacteria are summarized in (Table5) that displays the effect of synthesized compounds on bacterial strains.

The results revealed that some of the metal complexes have nearly the same activity or to be more active in comparison with the ligands and that means upon complexation may lead to slight increase of inhibition against bacteria. Antibiotics have been used are: Ciprofloxacin, Ampicillin, Amoxicillin.

Table 5: Results of antibacterial study of complexes and prepared ligands

Seq	Chemical formula	Conc mg/ml	Staphylococcus aureus	Escherichia coli
	BADTC	1 x 10 ⁻⁴ 1 x 10 ⁻³ 1 x 10 ⁻²	- - +	+ + +
1	[Pd ₂ (BADTC) ₂ (dppe) ₂]	1 x 10 ⁻³ 1 x 10 ⁻³ 1 x 10 ⁻¹	- + +++	+ ++ +++
2	[Pd ₂ (BADTC) ₂ (dppp) ₂]	1 x 10 ⁻³ 1 x 10 ⁻² 1 x 10 ⁻¹	+ ++ +++	+ + ++
3	[Pd ₂ (BADTC) ₂ (pph ₃) ₄]	1 x 10 ⁻³ 1 x 10 ⁻² 1 x 10 ⁻¹	- + +	- + ++
4	[Hg ₂ (BADTC) ₂ (dppm) ₂]	1 x 10 ⁻³ 1 x 10 ⁻² 1 x 10 ⁻¹	- - -	- + ++
5	[Hg ₂ (BADTC) ₂ (dppe) ₂]	1 x 10 ⁻³ 1 x 10 ⁻² 1 x 10 ⁻¹	- - +	+ + +
6	[Hg ₂ (BADTC) ₂ (dppp) ₂]	1 x 10 ⁻³ 1 x 10 ⁻² 1 x 10 ⁻¹	- + +++	+ ++ ++

(-) =There is no inhibition

(+) =Inhibition of 5 - 15 mm diameter

(++) =Inhibition of 2 - 15 mm diameter

(+++)=Inhibition of 25 to 35 mm diameter

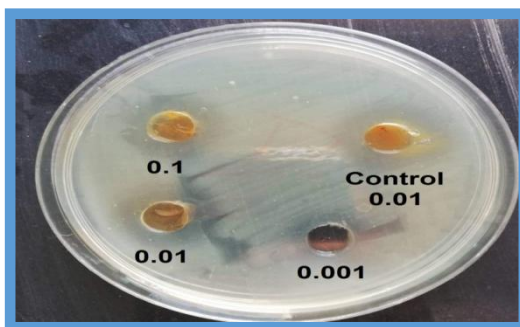


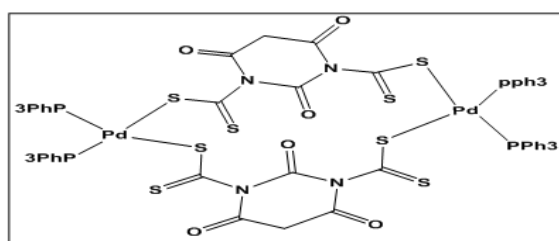
Figure (5): The inhibitory activity of the complex $[\text{Pd}_2(\text{BADTC})_2(\text{pph}_3)_4]$ against bacteria *Pseudomonas aeruginosa*

CONCLUSIONS

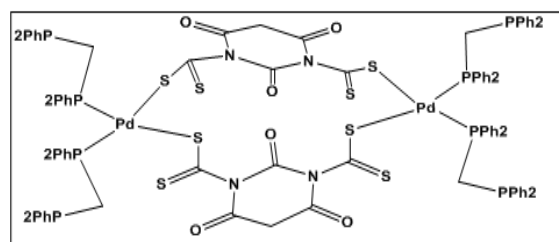
Based on analytical and spectral results, the BADTC acts as a monodentate ligand which is bonded with the metal ions through a single sulfur atom while phosphine ligands is coordinated with the metal ions in a different modes, pph_3 was coordinated as a monodentate ligand, dppm coordinate through one phosphine atom behaved and dppe and dppp behaved as a bidentate ligands.

The geometrical structures for synthesized complexes can be proposed as follows :

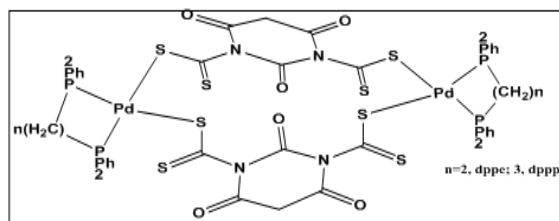
*Square planner structure for palladium complexes



$[\text{Pd}_2(\text{BADTC})_2(\text{PPh}_3)_4]$



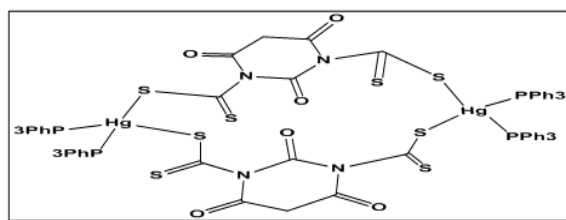
$[\text{Pd}_2(\text{BADTC})_2(\text{dppm})_2]$



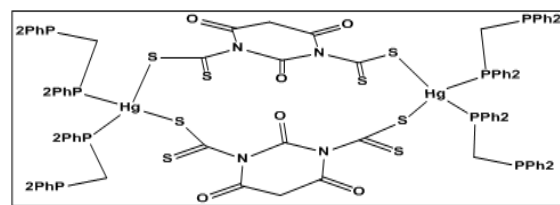
$[\text{Pd}_2(\text{BADTC})_2(\text{dppe})_2]$

$[\text{Pd}_2(\text{BADTC})_2(\text{dppp})_2]$

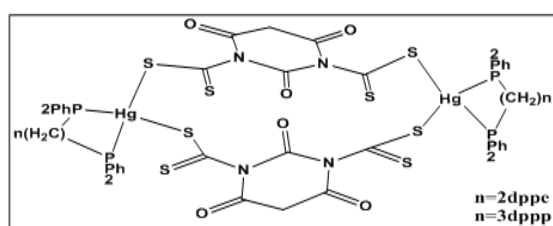
*Tetrahedral geometry for mercury complexes



[Hg₂(BADTC)₂(PPh₃)₄]



[Pd₂(BADTC)₂(dppm)₂]



**[Hg₂(BADTC)₂(dppe)₂]
[Hg₂(BADTC)₂(dppp)₂]**

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