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Characteristic Studying and Biological Effect of Synthesized Complexes Pd(II) and Hg(II) with Uracil dithiocarbamate and Phosphine's

Qader Abdullah Shannak[1], Mawlood Khalid mawlood[2], Hamza Raid Hebeb[3]
[1]Biotechnology and environmental center/ University of Fallujah/Iraq
[2]Samarra University/ Quality and Performance Department/Iraq
[3]Salahuddin Education Directorate/MOE/Iraq
Corresponding aurhor:
Qader Abdullah Shannak
E-mail: qaderabdullahah@uofallujah.edu.iq

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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 Uracil and tertiary phosphines . The formed complexes have the general formula of [M2 (U-DTC)$_2$ (Phosphine)n] Uracil bis(dithiocarbamate) = (-DTC) M = Pd(II),Hg(II) n=2 or 4 mole. The synthesized complexes were identified using the micro elemental analysis (C.H.N.S), electrical molar conductivity, spectra methods (IR and ^{1}H, ^{31}P-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, tertiary Phosphine, Uracil bis(dithiocarbamate)

Correspondence:
Qader Abdullah Shannak
Biotechnology and Environmental Center, University of Fallujah, Iraq
E-mail: qaderabdullahah@uofallujah.edu.iq

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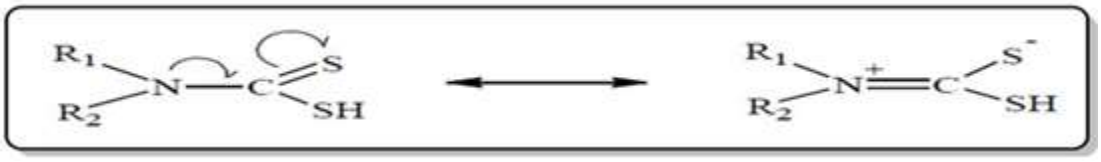
INTRODUCTION

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 RNCSS), where R, 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)], I2 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 (diphenyphosphino) ethane and the Bis (diphen yphosphino) 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-1range using KBr discs. Micro elemental analysis (C.H.N.S) conducted by using (Euro EA 3000). Molar Conductivities for complexes were measured at10-3 M solution in DMSO at 25° C using (Cond 7110). Melting points were obtained using (Electro thermal 9300). The ^{1}H- ^{31}P-NMR spectra were performed (solvent DMSO-d^6) on (Brucker 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

Uracil bis(dithiocarbamate) (U-DTC) was prepared by a previously described method [16].

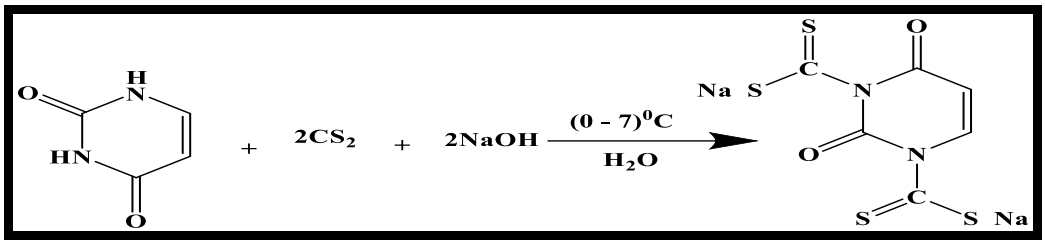


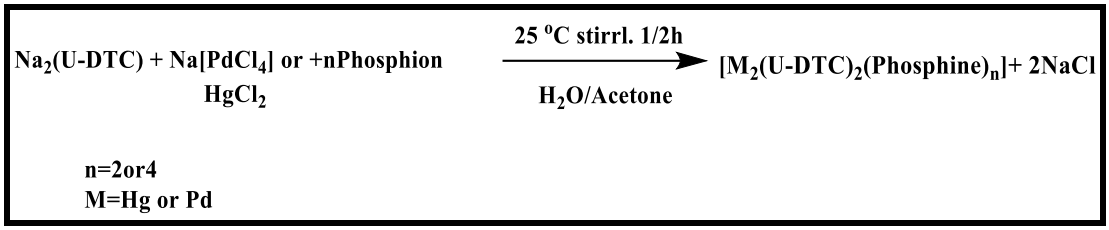
Table 1: Chemical formula (CHNS) analysis and some physical properties of the U-DTC ligand

Chemical formula	Color	Melting point/°C	Micro elemental analysis calculate (found)			
			S%	N%	H%	C%
$C_6H_2N_2Na_2O_2S_4$ 307.88	Light orange	358-359	41.59 (41.49)	(9.00) 9.09	(0.60) 0.65	23.37)(32.32

Synthesis of Dithiocarbamate complexes with phosphine.

Synthesis of $[Pd_2(T\text{-}DTC)_2(dppe)_2]$.

This complex was synthesized by the following procedure: A solution of $Na_2[PdCl_4]$(0.018g,0.000062mol) in distilled water(5ml) was added to a solution of Na_2U-DTC (0.021g,0.000062mol) 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 (0.025g, 0.000062mol) 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 wate (3 Ntimes) 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 [M (U-DTC)2(Phosphine)n]. The micro elemental analysis measurements for all complexes gave approximated values when are compared with theoretical values,(Table2) includes some physical properties and (C.H.N.S) results for the synthesized complexes.

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

No.	Complexes	Color	M.P/ ^{0}C	yield %	Molar cond./ mole^{-1}, cm^{-1} hom	Micro elemental analysis calculated (found)			
						C%	H%	N%	S%
1.	$[pd_2(U\text{-}DTC)_2(dppm)_2]$	Light orange	139138-	66	0.13	17.03 17.21) (	3.72 3.70) (	3.71 3.77) (	49.44 49.50) (
2.	$[pd_2(U\text{-}DTC)_2(pph_3)_4]$	orange	210-212	71	0.27	14.36 14.62) (	3.14 3.22) (	3.68 3.68) (	56.47 56.56) (
3.	$[pd_2(U\text{-}DTC)_2(dppe)_2]$	Light orange	-191190	69	0.26	50.74 (50.63)	3.61 (3.53)	3.59 (3.40)	16.42 (16.20)

4.	$[pd_2(U\text{-}DTC)_2(dppp)_2]$	brouwn	144-146	76	0.54	16.42 16.62) (	3.59 3.62) (	3.41 3.43) (	50.74 50.68) (
5.	$[Hg_2(U\text{-}DTC)_2(dppm)_2]$	white	271270-	62	0.78	……	……	……	……
6.	$[Hg_2(U\text{-}DTC)_2(pph_3)_4]$	Gray	-229228	68	0.73	12.80 12.85) (	2.80 2.78) (	3.42 3.20) (	)51.57 (51.32)
7.	$[Hg_2(U\text{-}DTC)_2(dppe)_2]$	Light gray	241-243	60	0.16	……	……	……	……
8.	$[Hg_2(U\text{-}DTC)_2(dppp)_2]$	Dark gray	255-257	58	0.19	45.92 (45.68)	3.40 (3.33)	3.15 (2.98)	14.42 (14.28)

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 U-DTC, the infrared bands observed at 1687 cm^{-1}, 1479 cm-1, (1118) and (993) cm^{-1} have been assigned to υ C=O, υ (C-N), υ (C=S) and(C-S) respectively [16]. In IR spectra of all complexes , the C=O stretching vibration are shifted to higher values 1653-1691cm^{-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 1435-1487 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 (C-S) (891-1001) cm^{-1}, and (1101-1188)cm^{-1} in the complexes were observed .

The υ (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 bonds in spectra of the complexes refer to υ (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 (692-700) $cm^{-1}$and (1429-1438)cm^{-1} were assigned to υ (P-C) and υ (P-Ph) respectively indicating that phosphine ligands are coordinated with metal center [13].

Table 3: IR data of synthesized complexes and ligands (cm^{-1})

Complexes	υ (C-H) Alph. Ar.	υ (C=C)	C=O)(υ	υ (C-N)	υ (C=S) υ (C-S)	υ (P-Ph)	υ (C-Ph)
U-DTC	2951 ……..	1595	1687	1479	1118 993	……..	……..
$[pd_2(U\text{-}DTC)_2(dppm)_2]$	**2937 3070**	**1597**	1683	**1477**	**1074**	1431	**700**
$[pd_2(U\text{-}DTC)_2(pph_3)_4]$	**2974 3057**	**1620**	1685	**1479**	**1093 997**	**1433**	**694**
$[pd_2(U\text{-}DTC)_2(dppe)_2]$	**2937 3063**	**1577**	1671	**1475**	**1074 995**	**1431**	**694**
$[pd_2(U\text{-}DTC)_2(dppp)_2]$	**2937 3057**	**1626**	**1696**	**14783**	**1014 964**	**1429**	**696**
$[Hg_2(U\text{-}DTC)_2(dppm)_2]$	**2970 3053**	**1604**	**1681**	**1467**	**1097**	**1433**	**692**
$[Hg_2(U\text{-}DTC)_2(pph_3)_4]$	**2922 3023**	**1622**	**1691**	**1479**	**1022 997**	**1429**	**694**
$[Hg_2(U\text{-}DTC)_2(dppe)_2]$	**2987 3059**	**1620**	**1685**	**1479**	**1031 993**	**1435**	**696**
$[Hg_2(U\text{-}DTC)_2(dppp)_2]$	**2941 3059**	**1606**	**1676**	**1481**	**1095 997**	**1433**	**696**

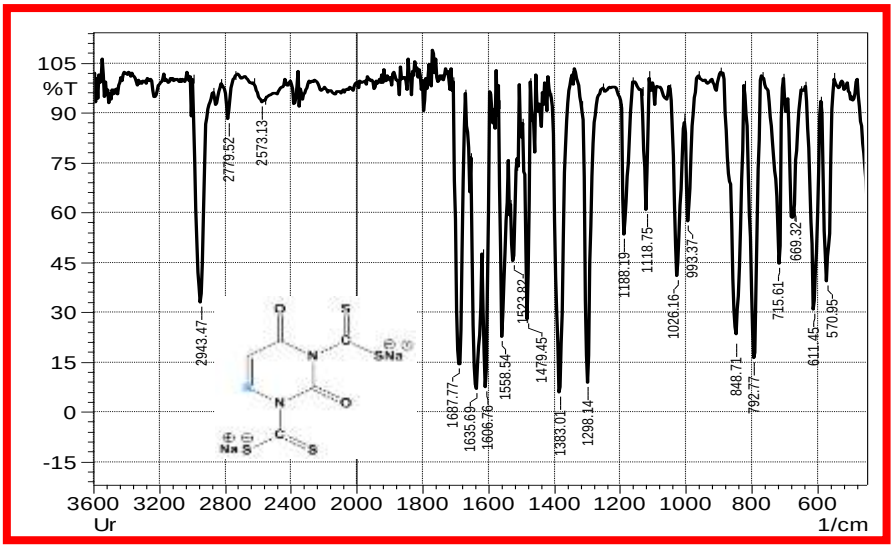


Figure 1: Infrared spectrum (U-DTC)(

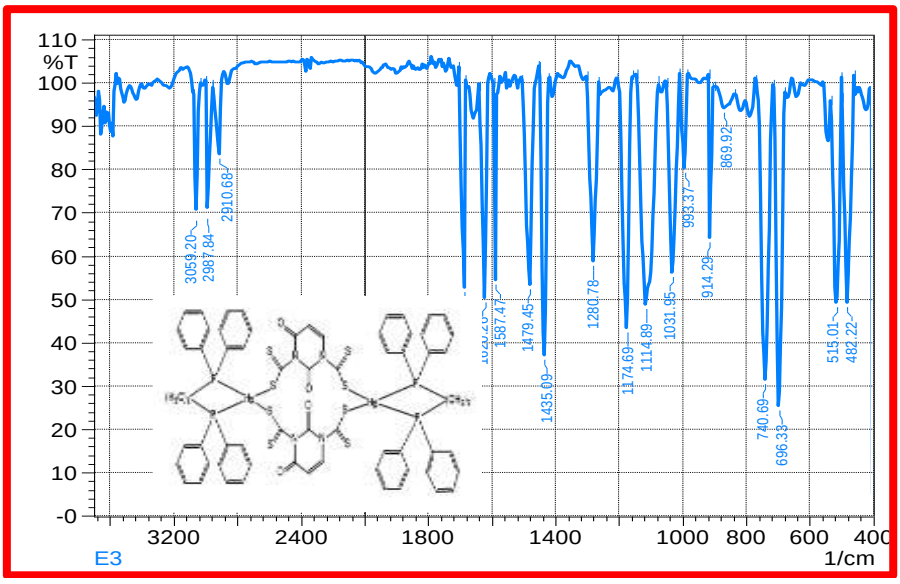


Figure 2: Infrared spectrum [Hg_2(U-DTC)$_2$(dppe)$_2$](

NMR RESULTS

^{1}H-NMR spectrum of U-DTC

The ^{1}H-NMR spectrum of the prepared ligand (Na_2U-DTC) in a dimethyl sulfoxide compensated by deuterium a two-signal at the site (δH = 5.21 ppm), one proton correspondence, and a binary signal at the site (δH = 7.41 ppm), One proton corresponded to as inferred from the complementarity, these two signals were attributed to the CH group. Which returns to the carbon atoms of the solvent as in Figure (3)

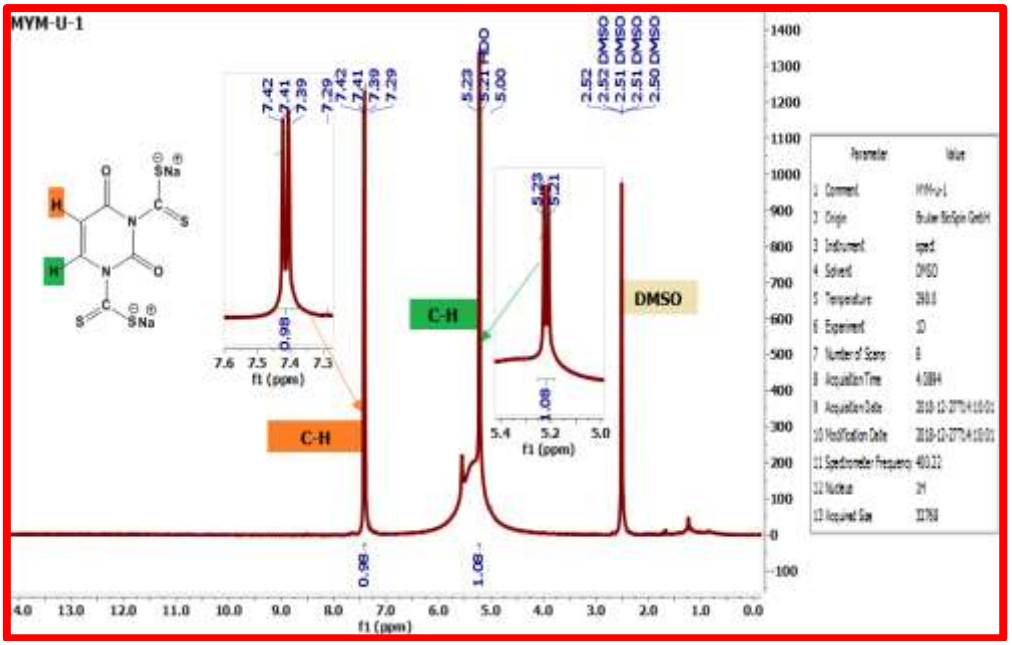


Figure 3: ^{1}H-NMR spectrum of (Na_2U-DTC)

The H-NMR NMR spectrum of the complex [Hg_2 (U-DTC) $_2$ (dppe) $_2$] illustrated in Figure 4 showed a multiple signal in the range δH =(7.37 - 7.77 ppm) and with an integration corresponding to 40 protons, the integrity of these signals indicates that they correspond to protons Eight aromatic rings, found in the dppe ligand, and the spectrum showed a mono signal at the location =H = (7.21) ppm belonging to the protons of the group (2C-H linked to the nitrogen of the ring nitrogen in the ligand (U-DTC) and with an complement that corresponds to two protons in the 2C-H groups The spectrum also showed a signal at the location δH = (5.42) ppm, attributed to (2C-H) protons bound to the L-carbonyl group (U-DTC), and by complementarity corresponding to two protons in the 2C-H groups as A The spectrum showed a mono signal at the chemical displacement δH = (2.37) ppm, whose integrity indicates that they correspond to eight protons that were induced to the protons of a group of 4CH_2 in ligand dppe, and a mono signal at the chemical displacement δH = (2.51 ppm) where the mono signal indicates solvent protons if These values indicate the presence of ligand dppe with ligand U-DTC.

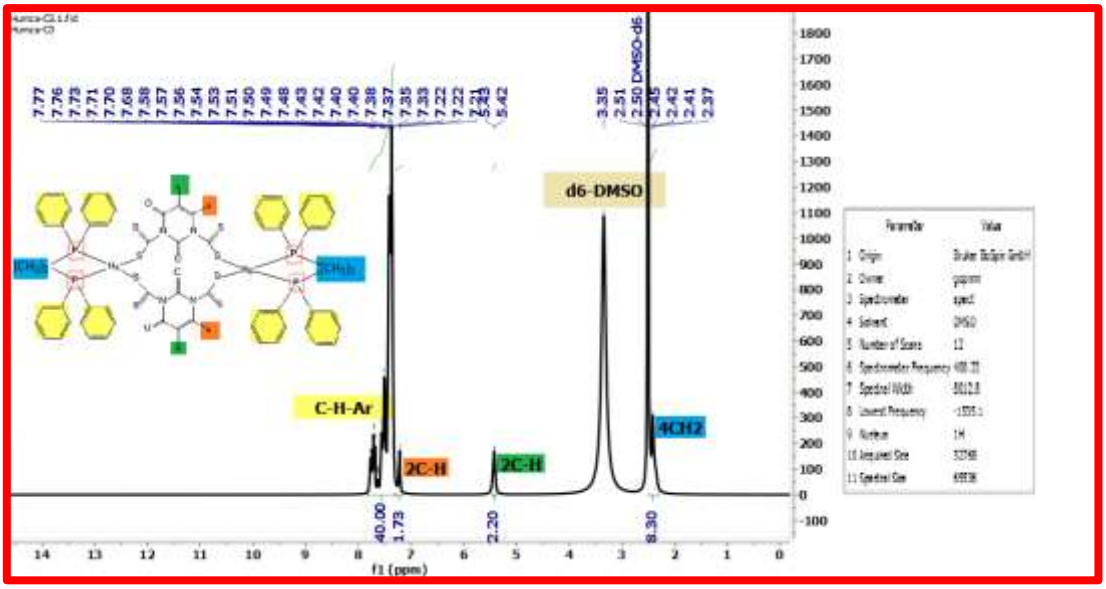


Figure 4: ^{1}H-NMR spectrum of the complex [Hg_2(U-DTC)$_2$(dppe)$_2$]

The ^{31}P-NMR data for Some prepared complexes using DMSO-d6 as a Solvent are given in (Table 4), and figures(3)show the spectra for some of them. [20,21].

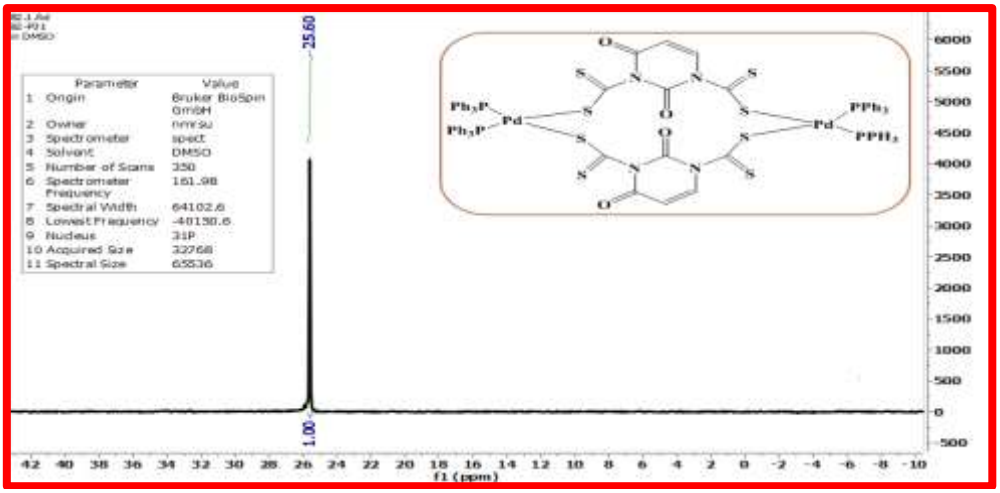


Figure 5: NMR spectrum of 31P-NMR of complex $[Hg_2(U\text{-}DTC)_2(dppp)_2]$

Table 4: ^{31}P-NMR data δ ^{31}P ppms of some prepared complexes are all singlet

No.	Complex	δp
1.	$[Hg_2(\ U\text{-}DTC\ )_2(\ dppp)_2]$	24.08
2.	$[Hg_2(\ U\text{-}DTC\ )_2(\ dppe)_2]$	30.19
3.	$[pd_2(\ U\text{-}DTC\ )_2(\ pph_3)_4]$	25.60
4.	$[pd_2(\ U\text{-}DTC\ )_2(dppm)_2]$	48.52

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

No.	Complex
5.	^{1}H-NMR(DMSO-d^6): δ7.30-7.54(40H,Phos) for 8 cycle aromatic , δ3.01(4H,CH_2, ligand dppm), δ2.09(6H,2CH_3,ligand phos), 7.77(2H,2CH,ligand phos) dppm
6.	H-NMR(DMSO-d^6): δ7.31-7.67(60H,Phos) for 12 cycle aromatic , δ1.37(6H,2CH_3,ligand phos) , δ3.01(4H,CH2,ligandU-DTC)ppm., 7.26(2H,2CH,ligand phos) PPh_3

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^{-3}), (1 x 10^{-2}) and (1 x 10^{-1}) mg/ml. The disc sensitivity test method was used, the incubation was held for 24 hours at 37 ^{0}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: Ampicillin, Amoxicillin.

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

No.	Complexes	Conc.mg/ml	*staphylococcus aureus*	*Pseudomonas aeruginosa*
1.	U-DTC	1 x 10^{-3} 1 x 10^{-2} 1 x 10^{-1}	+ + +++	- + ++
2.	$[Pd_2(U\text{-}DTC)_2(dppm)_2]$	1 x 10^{-3} 1 x 10^{-2} 1 x 10^{-1}	- - +	+ + +++
3.	$[Pd_2(U\text{-}DTC)_2(dppp)_2]$	1 x 10^{-3} 1 x 10^{-2} 1 x 10^{-1}	- + ++	+ ++ +++
4.	$Pd_2(\ U\text{-}DTC)_2(pph_3)_4]$[	1 x 10^{-3} 1 x 10^{-2}	- +	- +

		1×10^{-1}	+	++
5.	]Pd_2(U -DTC)$_2$(dppe)$_2$[	1×10^{-3} 1×10^{-2} 1×10^{-1}	- - -	- + ++
6.	[Hg_2(U-DTC)$_2$(dppm)$_2$]	1×10^{-3} 1×10^{-2} 1×10^{-1}	- - -	- + +
7.	[Hg_2(U-DTC)$_2$(dppp)$_2$]	1×10^{-3} 1×10^{-2} 1×10^{-1}	+ ++ +++	- + ++
8.	Hg_2(U-DTC)$_2$(pph_3)$_4$][	1×10^{-3} 1×10^{-2} 1×10^{-1}	+ + ++	- + ++
9.	]Hg_2(U-DTC)$_2$(dppe)$_2$[	1×10^{-3} 1×10^{-2} 1×10^{-1}	+ ++ ++	- + ++

(-) = There is no inhibition
(+) =Inhibition of 5 - 15 mm diameter
(++) =Inhibition of 2 - 15 mm diameter
(+++)=Inhibition of 25 to 35 mm diameter

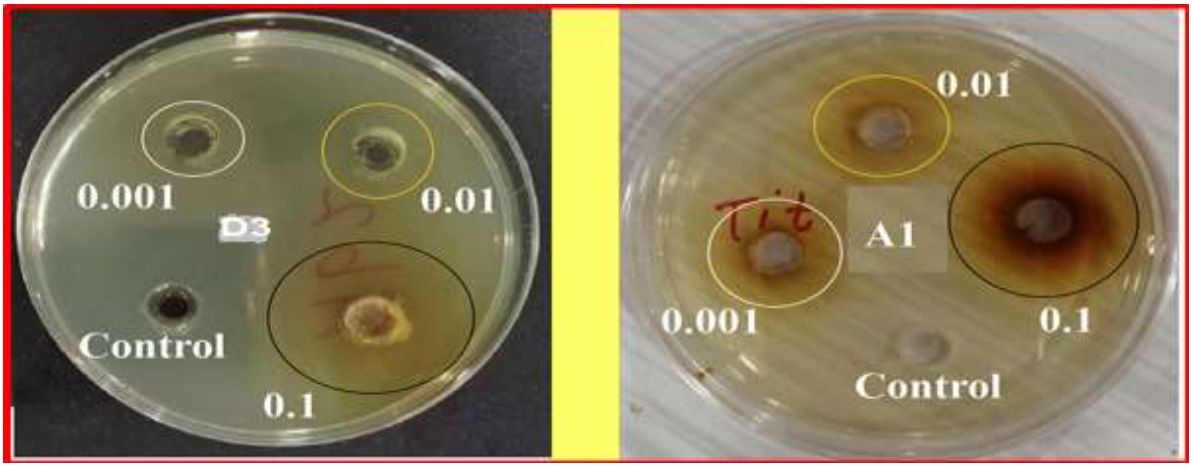
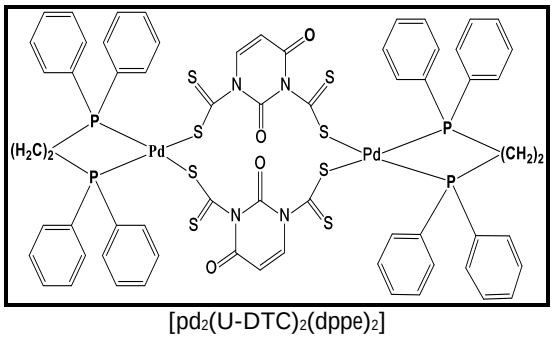


Figure 6: The inhibitory activity of the complex [Hg_2 (U-DTC) $_2$ (dppe) $_2$] and [Pd_2 (U-DTC)$_2$ (dppm)$_2$] against bacteria *Pseudomonas aeruginosa*

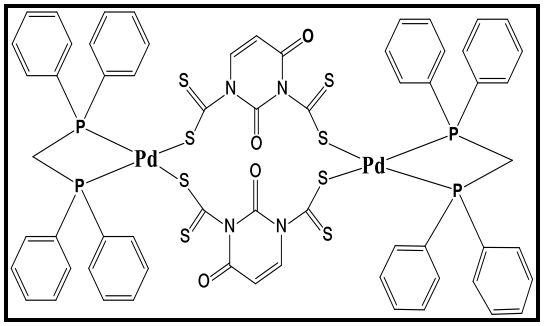
CONCLUSIONS

Based on analytical and spectral results, the U-DTC 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_3wascoordinated as amonodentate 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

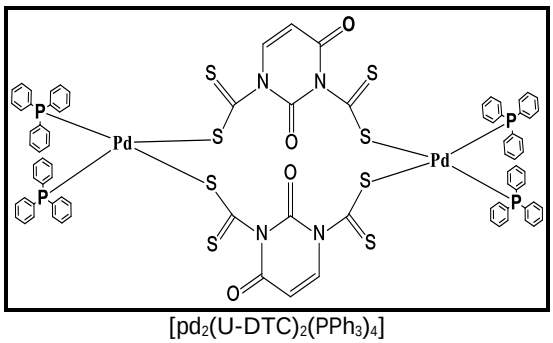
*SQUARE PLANNER STRUCTURE FOR PALLADIUM COMPLEXES



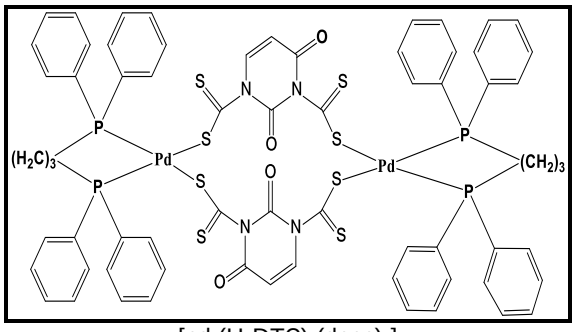
[pd_2(U-DTC)$_2$(dppe)$_2$]



[pd$_2$(U-DTC)$_2$(dppm)$_2$]

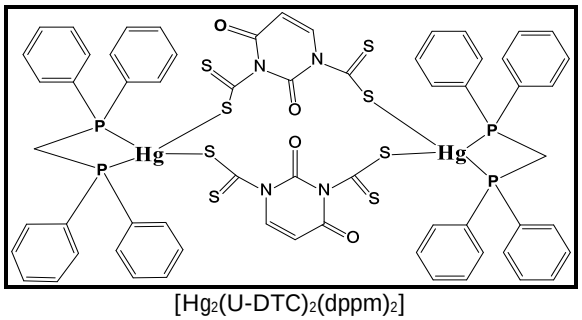


[pd$_2$(U-DTC)$_2$(PPh$_3$)$_4$]

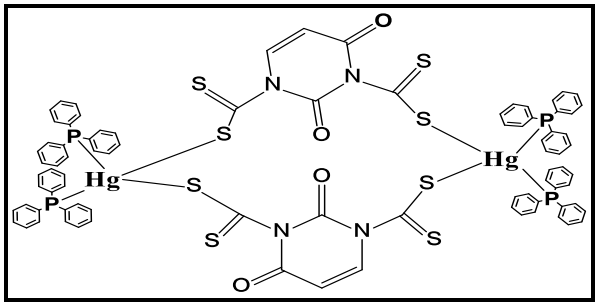


[pd$_2$(U-DTC)$_2$(dppp)$_2$]

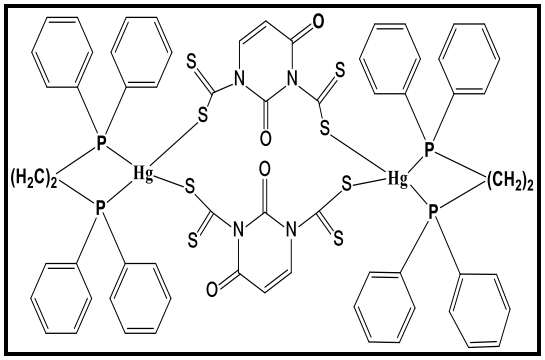
*TETRAHEDRAL GEOMETRY FOR MERCURY COMPLEXES



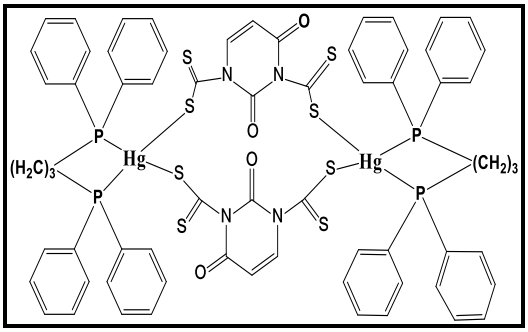
[Hg$_2$(U-DTC)$_2$(dppm)$_2$]



[Hg$_2$(U-DTC)$_2$(PPh$_3$)$_4$]



[Hg$_2$(U-DTC)$_2$(dppe)$_2$]



[Hg$_2$(U-DTC)$_2$(dppp)$_2$]

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