



Synthesis and characterization of new mixed ligand complexes of Zn (II) and Hg (II) with dithiocarbamate and phosphines

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ABSTRACT

Complexes of the type $[M(Et_2DTC)_2]$ [$M = Zn(1)$ or $Hg(2)$] were prepared from the reaction of mercury acetate or zinc acetate with sodium diethyldithiocarbamate trihydrate ($NaEt_2DTC \cdot 3H_2O$) in (1:2) molar ratio (metal: ligand) in mixture of MeOH and H_2O as a solvent. Treatment equal molar of (1) or (2) with diphosphine ligands {where diphos: bis (diphenylphosphino) methane (dppm), 1,2-bis (diphenylphosphino) ethane (dppe) and 1,3-Bis (diphenylphosphino) propane (dppp)} afforded complexes of the type $[Zn(Et_2DTC)_2(dppeO)]$ (3); $[Zn(Et_2DTC)_2(dpppS)]$ (4a); $[Zn(Et_2DTC)_2(dppp)]$ (4b); $[Hg(Et_2DTC)_2(dppm)]$ (6a); $[Hg(Et_2DTC)_2(\mu-dppm)]_2$ (6b); $[Hg(Et_2DTC)_2(dppe)]$ (7) and $[Hg(Et_2DTC)_2(dppp)]$ (8), or with two moles of triphenylphosphine (PPh_3) afforded a complexes of the type $[M(\kappa^1-Et_2DTC)_2(PPh_3)_2]$ (5a, 9a) and $[M(\kappa^2-Et_2DTC)_2(PPh_3)_2]$ (5b, 9b) $\{M = Zn, Hg\}$. The prepared complexes were fully characterized by different technics such as IR, NMR (1H and ^{31}P) spectroscopy, elemental analysis, and molar conductivity. Characterization data showed that the (Et_2DTC) ligand in all of the prepared complexes was coordinated with metal through the sulfur atoms of CSS^- group. The geometry of the complexes (1-9) were tetrahedral around the $Zn(II)$ and $Hg(II)$ ions, except isomers 5b and 9b are octahedral geometry. .

1. Introduction

Diethyldithiocarbamate is known as a {diethyldithiocarbamic acid, or diethyldithione, (Et_2DTC) }. Dithiocarbamate chemistry has been attracted more attention because both DTCs derivatives and their complexes are very important in the biological field [1,2], industrial [3,4] and inorganic analysis [5, 6]. Moreover; diverse functions of dithiocarbamates were used as antidotes against metal poisoning in cisplatin or carboplatin toxicity [7]. (Et_2DTC) ligand can be showed bridge coordination fashion to metal ions and acts as the ability to bonding as a bidentate fashion through sulfur atoms [8,9]. Complexes of diethyldithiocarbamate or their derivatives with metal ions such as $Tc(II)$, $Pt(II)$, $Hg(II)$, $Cd(II)$, and other ions have been recently been synthesized and characterized [10-13]. Herein, we describe the preparation of mixed ligand $Zn(II)$ and $Hg(II)$ diethyldithiocarbamate (Et_2DTC) complexes with phosphine. The prepared complexes were characterized by spectroscopic and physical methods.

2. Experimental

2.1 Materials and Methods:

All chemical compounds and solvents ($Zn(OAc)_2 \cdot xH_2O$, $Hg(OAc)_2 \cdot xH_2O$, sodium diethyldithiocarbamate trihydrate ($NaEt_2DTC \cdot 3H_2O$), phosphines, chloroform ($CHCl_3$) and methanol ($MeOH$)) were supplied and used without further purification. IR spectra were recorded on Shimadzu 8400 S FTIR spectrophotometer as KBr disc in 4000-400 cm^{-1} range. NMR spectra (1H - $\{^{31}P\}$ and ^{31}P - $\{^1H\}$) were recorded on Bruker av 400 NMR spectrometer in $DMSO-d_6$, except the (^{31}P - $\{^1H\}$) for $Zn(II)$ complexes which were recorded on Bruker av 300 NMR spectrometer in $DMSO-d_6$. Melting points were recorded on SMP40 - Stuart company. The conductivity of the prepared complexes solution ($10^{-3}M$) in $DMSO$ were measured on digital conductivity meter 730.

2.2. Preparation of $[Hg(Et_2DTC)_2]_2$ (2)

A methanolic solution of $NaEt_2DTC \cdot 3H_2O$ (1.000g; 4.4383mmole) in (15ml) was added to an aqueous

solution of $\text{Hg}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ (0.7072g; 2.2192mmole) in (10ml) in (2:1) (ligand: metal) molar ratio with stirring. The mixture was stirred at room temperature for two hours. The green precipitate formed and then the product was filtered off and dried under vacuum (Yield: 1.030g; 94%; m.p: 141 °C).

Complex $[\text{Zn}(\text{Et}_2\text{DTC})_2]$ (**1**) was prepared and isolated in a similar method. (colour : white; Yield: 0.763g ;95% ;m.p: 182 °C).

2.2.2 Preparation of $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppm})]$ (**6**)

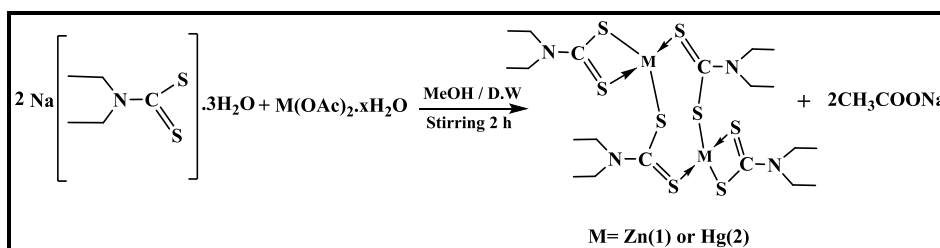
A solution of bis (diphenylphosphino) methane (dppm) (0.1144g; 0.4023mmole) in CHCl_3 (10ml) was added to a solution of $[\text{Hg}(\mu\text{-Et}_2\text{DTC})_2]$ (0.2001g; 0.4025 mmole) in CHCl_3 (10ml) with stirring. The mixture was stirred for 24 hours at room temperature. The creamy solution was filtered off and then filtrate was left aside at room temperature until the solvent evaporate. The gummy product was washed with diethyl ether and n-hexane several times. The yellow precipitate was collected and dried under vacuum. (Yield: 0.2128g; 60%; m.p: 86 °C).

The following complexes $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppeO})]$ (**3**), $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppp})]$ (**4**), $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppm})]$ (**6**), $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppe})]$ (**7**) and $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppp})]$ (**8**) were prepared same procedure as mentioned above, while the $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ (**5**) and $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ (**9**) complexes were prepared and isolated in a similar method, but the molar ratio was (1:2) (complex : phos).

3. Results and Discussion

3.1 Synthesis

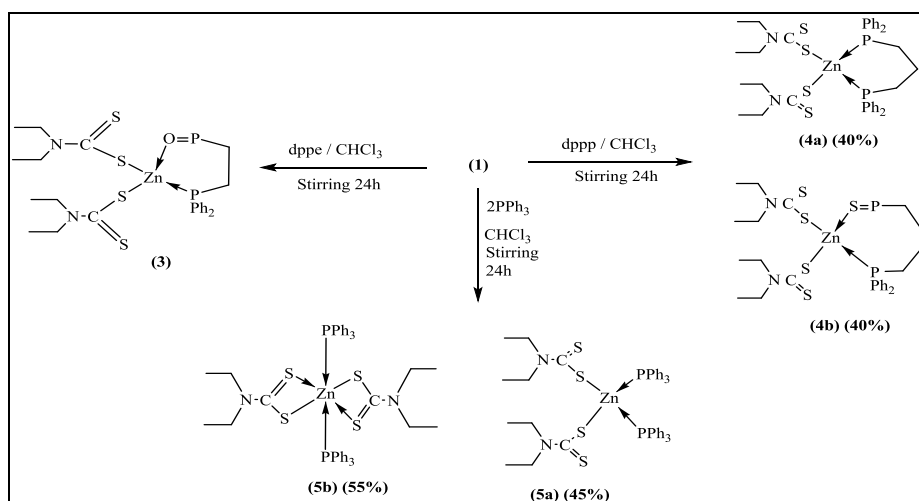
The reaction of zinc (II) acetate or mercury (II) acetate with two equivalents of sodium diethyldithiocarbamate trihydrate ($\text{NaEt}_2\text{DTC} \cdot 3\text{H}_2\text{O}$) in absolute methanol and distilled water, gave complex of the type $[\text{M}(\text{Et}_2\text{DTC})_2]$ ($\text{M} = \text{Zn}$ (**1**), Hg (**2**)) (See Scheme 1). The Et_2DTC ligand was coordinated as bridged bidentate and bidentate chelating ligand through the sulfur atoms of CSS^- group to afford a tetrahedral geometry around the central atom ion, in binuclear complexes.



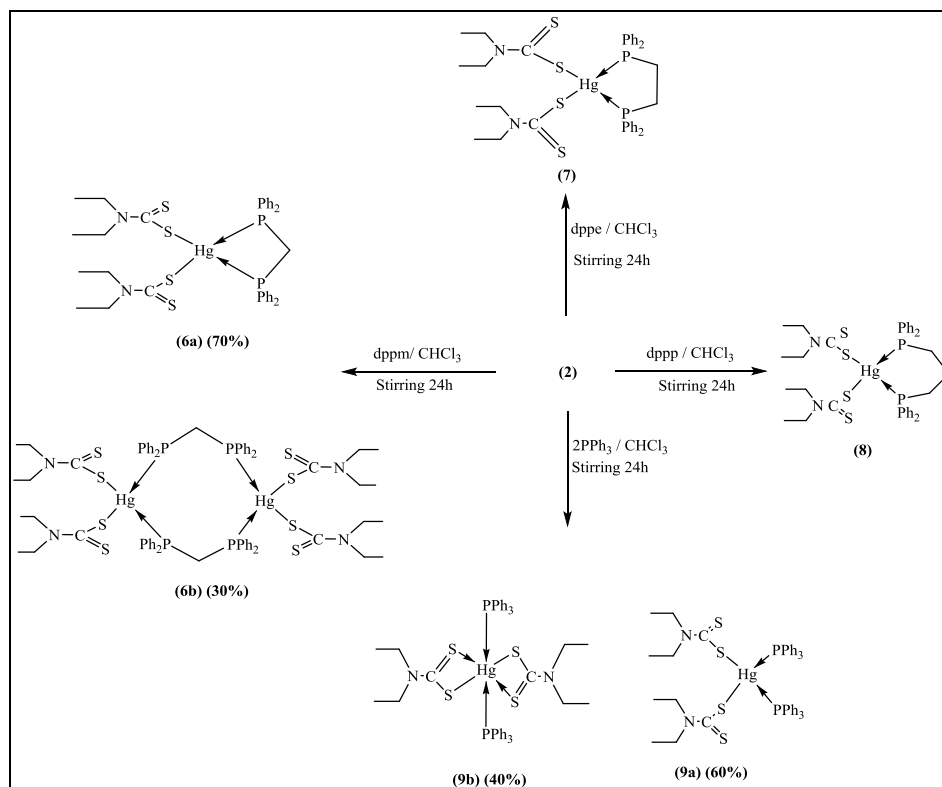
Scheme 1: preparation of $[\text{Zn}(\mu\text{-Et}_2\text{DTC})_2]$ and $[\text{Hg}(\mu\text{-Et}_2\text{DTC})_2]$ complexes

Treatment equal molar of diphosphine ligands (dppm, dppe and dppp) with $[\text{M}(\mu\text{-Et}_2\text{DTC})_2]$ [$\text{M} = \text{Zn}$ (**1**) or Hg (**2**)] in chloroform as a solvent afforded complexes of the types $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppeO})]$ (**3**); $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dpppS})]$ (**4a**); $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppp})]$ (**4b**); $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppm})]$ (**6a**); $[\text{Hg}(\text{Et}_2\text{DTC})_2(\mu\text{-dppm})_2]$ (**6b**); $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppe})]$ (**7**) and $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppp})]$ (**8**). The dithiocarbamate ligand was bonded as monodentate ligands through the sulfur atom of the thioureide group, while the diphosphine ligands were bonded as a bidentate chelating ligand. The reaction of one mole of the

complex $[\text{M}(\mu\text{-Et}_2\text{DTC})_2]$ [$\text{M} = \text{Zn}$ (**1**) or Hg (**2**)] with two moles of PPh_3 , afforded yellow precipitate characterized as $[\text{M}(\kappa^1\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ (**5a**, **9a**) and $[\text{M}(\kappa^2\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ (**5b**, **9b**), which exist as a mixture of two inseparable products was resulted as shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Scheme 2 and 3). In complex (**5a**, **9a**) the (Et_2DTC) ligand behaved as monodentate ligand through a sulfur atom of thioureide group, whereas in complex (**5b**, **9b**) act as bidentate chelating ligand through the sulfur atoms of CSS^- group.



Scheme 2: preparation of complexes (3-5)



Scheme 3: preparation of complexes (6-9)

All prepared complexes are air stable in solid state and insoluble in diethyl ether, n-hexane, methanol and distilled water, but they are soluble in CHCl_3 , CH_2Cl_2 , DMSO and DMF. The elemental analyses are listed in **Table (1)** and they agreed with the theoretical analysis. The conductivity of freshly prepared complexes solution were measured in

DMSO at room temperature and that the complexes are non-electrolyte [14]. The prepared complexes were characterization by many technical IR, NMR spectroscopy (^1H and ^{31}P), CHNS analysis and molar conductivity. All the data are mentioned in Tables (1 - 3).

Table (1), Color, yield%, m.p. (°C) and elemental analysis of prepared complexes (1-10)

Se q.	Complexes	Color	m.p.(°C)	Yield %	Λ ($\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$)	Elemental analysis Found(cal.) %			
						C	H	N	S
1	$[\text{Zn}(\mu\text{-Et}_2\text{DTC})_2]_2$	White	182	95	1.65	33.2 (33.19)	5.59 (5.57)	7.73 (7.90)	35.44 (35.43)
2	$[\text{Hg}(\mu\text{-Et}_2\text{DTC})_2]_2$	Green	141	94	0.46	24.18 (24.16)	4.10 (4.06)	5.62 (5.64)	25.79 (25.80)
3	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppm})]$	Creamy	100	89	7	56.51 (56.33)	5.79 (5.67)	3.80 (3.75)	17.15 (17.18)
4	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppe})]$	Creamy	125	65	12.3	56.93 (56.87)	5.87 (5.83)	3.65 (3.68)	16.95 (16.87)
5	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppp})]$	Creamy	138	92	15.4	57.46 (57.39)	6.18 (5.99)	3.70 (3.62)	16.54 (16.56)
6	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$	Creamy	157	50	15.5	62.45 (62.33)	5.68 (5.69)	3.25 (3.16)	14.55 (14.47)
7	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppm})]$	Yellow	86	60	7.4	47.79 (47.69)	4.73 (4.80)	3.30 (3.18)	14.59 (14.55)
8	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppe})]$	Creamy	155	79	15	48.20 (48.28)	4.99 (4.95)	3.16 (3.13)	14.35 (14.32)
9	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppp})]$	Creamy	82	77	21.7	48.93 (48.86)	4.98 (5.10)	3.05 (3.08)	14.20 (14.10)
10	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$	Yellow	112	70	25	54.20 (54.08)	5.20 (4.93)	2.69 (2.74)	12.58 (12.55)

3.2 Spectroscopic studies

3.2.1 Infrared spectra

The IR selected bands of dithiocarbamate and its complexes are listed in **Table (2)** and **Fig (1 and 2)**. The IR spectrum of dithiocarbamate showed bands at

(2929), (987), (1068) and (1477) cm^{-1} which due to $\nu(\text{CH})_{\text{alpha}}$, $\nu(\text{C-S})$, $\nu(\text{C=S})$ and $\nu(\text{C-N})$ respectively. In the IR spectra of complexes (1), (2) showed two bands at (983, 1070), (983,991) cm^{-1} and (1070, 1072) cm^{-1} assigned to $\nu(\text{C-S})$ and $\nu(\text{C=S})$

respectively, these two bands indicates the thioureide group was coordinated with Hg^{+2} and Zn^{+2} ions through the sulfur atoms as bridge and chelate bidentate [15, 16]. The spectra of complexes (3-10) showed the $\nu(\text{C-S})$ and $\nu(\text{C=S})$ within (985-995) and (1066-1072) cm^{-1} range respectively, and displayed a

new bands at (1427-1433) cm^{-1} , (501-540) cm^{-1} , (1182) cm^{-1} and (694) cm^{-1} range assigned to $\nu(\text{P-Ph})$, $\nu(\text{P-C})$ [17-28], $\nu(\text{P=O})$ [29] and $\nu(\text{P=S})$ [30] indicating the phosphine ligand was coordinated with the metal ions.

Table 2: Selected IR stretching vibration bands (cm^{-1}) of the prepared complexes (1-10)

Seq.	Compounds	$\nu(\text{C-H})$ Ar.	$\nu(\text{C-H})$ alpha.	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{C=S})$	$\nu(\text{P-Ph})$	$\nu(\text{P-C})$	Others
*	$\text{NaEt}_2\text{DTC} \cdot 3\text{H}_2\text{O}$	---	2929w	1477s	987w	1068w	---	---	---
1	$[\text{Zn}(\text{Et}_2\text{DTC})_2]$	---	2976w 2872w	1502s 1271m	991m	1072w	---	---	---
2	$[\text{Hg}(\text{Et}_2\text{DTC})_2]$	---	2976w 2866w	1496s 1269m	983m	1070w	---	---	---
3	$[\text{Zn}(\text{Et}_2\text{DTC})_2\text{dppm}]$	3061w	2978w 2872w	1504s 1271s	993m	1072w	1431s	503m	Zn-P 474w
4	$[\text{Zn}(\text{Et}_2\text{DTC})_2\text{dppe}]$	3064w	2978w 2872w	1502s 1271m	993m	1072w	1433s	507w	P=O 1182m Zn-P 472w
5	$[\text{Zn}(\text{Et}_2\text{DTC})_2\text{dppp}]$	3053w	2978w 2870w	1502s 1271m	995m	1070w	1431m	511w	P=S 694m Zn-P 547w
6	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$	3057m	2976w 2870w	1502s 1271m	991m	1070w	1431m	540w	Zn-P 505w
7	$[\text{Hg}(\text{Et}_2\text{DTC})_2\text{dppm}]$	3049w	2976w 2870w	1494s 1267m	985m	1068w	1427m	505w	Hg-P 474w
8	$[\text{Hg}(\text{Et}_2\text{DTC})_2\text{dppe}]$	3051w	2972w 2868w	1483s 1269m	989m	1072w	1433w	509w	Hg-P 472w
9	$[\text{Hg}(\text{Et}_2\text{DTC})_2\text{dppp}]$	3051w	2972w 2870w	1483s 1267s	985m	1066w	1433m	511m	Hg-P 478w
10	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$	3051w	2978w 2868w	1496s 1269m	985m	1070w	1429m	501w	Hg-P 474w

s: strong, m: medium, w : weak

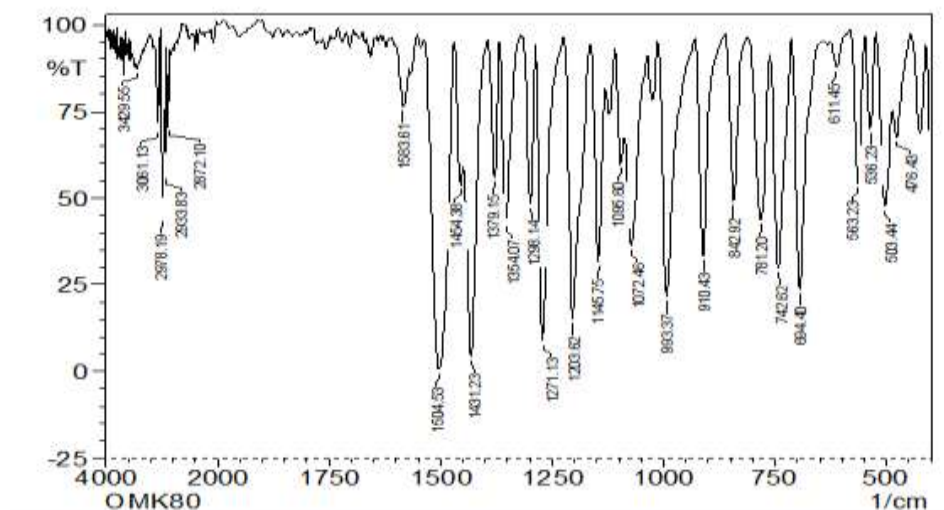


Fig. 1: IR spectrum of complex (3)

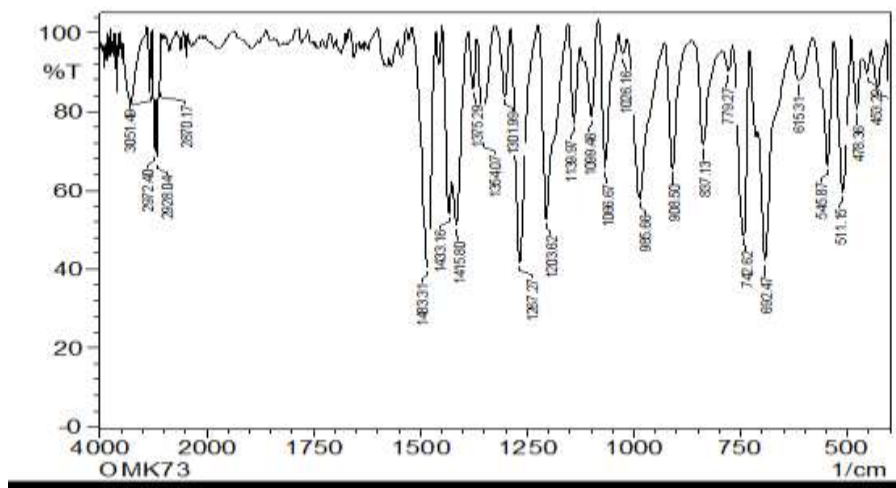


Fig. 2: IR spectrum of complex (9)

3.3 NMR spectra

The ^1H and ^{31}P chemical shifts are listed in Table (3). The ^1H -NMR spectrum of complex (2) measured in CHCl_3 (Fig 3) showed two peaks, a triplet peak at $\delta\text{H}=1.33$ ppm with coupling constant ($^3J_{\text{HH}} = 20$ Hz)

assign to 4CH_3 groups, and a quartet peak at $\delta\text{H} = 3.83$ ppm with coupling constant ($^3J_{\text{HH}} = 16$ Hz) assign to 4CH_2 groups. The same peaks were observed for complex (1).

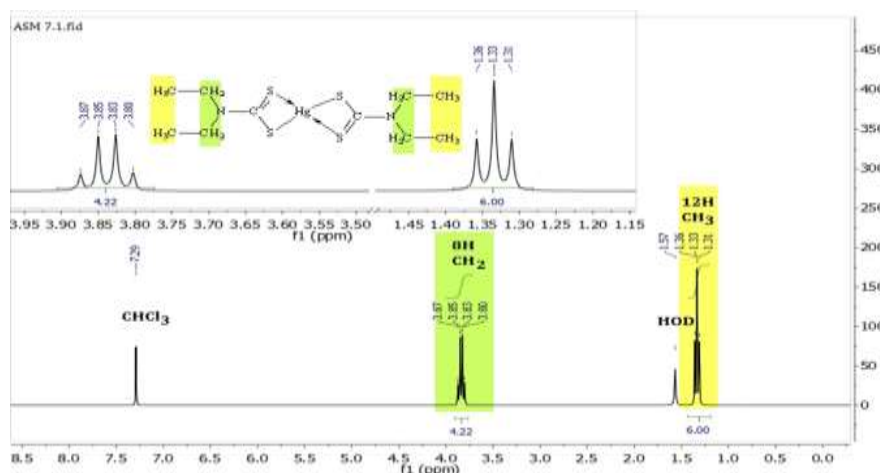
Fig. 3: ^1H -NMR spectrum of complex (2) in CHCl_3

Table 3 : ^1H and ^{31}P - $\{^1\text{H}\}$ NMR chemical shifts (δ ppm) for the prepared complexes (1-10) measured in DMSO-d_6

Seq	Complexes	δP (ppm)	δH^a (ppm)
1	$[\text{Zn}(\mu\text{-Et}_2\text{DTC})_2]_2$	---	1.19 (t, $^3J_{\text{H-H}} = 8$ Hz, 12H); 3.80 (q, $^3J_{\text{H-H}} = 8$ Hz, 8H)
2	$[\text{Hg}(\mu\text{-Et}_2\text{DTC})_2]_2$	---	1.33 (t, $^3J_{\text{H-H}} = 20$ Hz, 12H); 3.84 (q, $^3J_{\text{H-H}} = 16$ Hz, 8H)
3	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppe})]$	38.43 (dd); -2.84 (dd)	1.20 (t, $^3J_{\text{H-H}} = 12$ Hz, 12H); 3.81 (q, $^3J_{\text{H-H}} = 12$ Hz, 8H); 2.04 (s, 4H, $\text{CH}_2\text{-dppe}$); 7.48 (m, 20H)
4	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppp})]$	Isomer (a) (24.66) (s) (40%) Isomer (b) (35.37) (dd); (-6.94) (dd) (60%)	1.21 (t, $^3J_{\text{H-H}} = 12$ Hz, 12H); 3.81 (q, $^3J_{\text{H-H}} = 8$ Hz, 8H); 2.64 (s, 4H, $\text{CH}_2\text{-dppp}$); 1.68 (s, 2H, $\text{CH}_2\text{-dppp}$); 7.49 (m, 20H)
5	$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$	Isomer (a) 34.10 (s) (45%) Isomer (b) 37.46 (s) (55%)	1.20 (t, $^3J_{\text{H-H}} = 12$ Hz, 12H); 3.81 (q, $^3J_{\text{H-H}} = 12$ Hz, 8H); 7.64 (m, 30H)
6	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppm})]$	Isomer (a) (-1.56) (bs) (70%) Isomer (b) (26.81) (s) (30%)	1.25 (t, $^3J_{\text{H-H}} = 12$ Hz, 12H); 3.76 ($^3J_{\text{H-H}} = 16$ Hz, q, 8H); 3.69 (s, 2H, $\text{CH}_2\text{-dppm}$); 7.46 (m, 20H)
7	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppe})]$	10.54 (bs)	1.22 (t, $^3J_{\text{H-H}} = 16$ Hz, 12H); 3.78 (q, $^3J_{\text{H-H}} = 16$ Hz, 8H); 2.64 (s, 4H, $\text{CH}_2\text{-dppe}$); 7.51 (m, 20H)
8	$[[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppp})]$	13.09 (s)	1.23 (t, $^3J_{\text{H-H}} = 12$ Hz, 12H); 3.77 (q, $^3J_{\text{H-H}} = 12$ Hz, 8H); 2.81 (s, 4H, $\text{CH}_2\text{-dppp}$); 1.70 (s, 2H, $\text{CH}_2\text{-dppp}$); 7.52 (m, 20H)
9	$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{PPh}_3)_2]$	Isomer (a) 22.63 (s) (60%) Isomer (b) 23.52 (s) (40%)	1.25 (t, $^3J_{\text{H-H}} = 8$ Hz, 12H); 3.77 (q, $^3J_{\text{H-H}} = 12$ Hz, 8H); 7.56 (m, 30H)

The $^{31}\text{P}\{-^1\text{H}\}$ nmr spectrum of $[\text{Zn}(\text{Et}_2\text{DTC})_2(\kappa^2\text{-dppeO})](\mathbf{3})$ (Fig. 4) showed only one signal, as a doublet of doublets peak at $\delta\text{P} = (38.43)$ and (-2.84) ppm for $(\text{P}=\text{O})$ and (P) atom respectively, with coupling constant ($J_{\text{PP}}=78.0\text{Hz}$), this indicate the two phosphorus atoms are un-equivalent. and dppeO ligands was bonded as chelating bidentate ligand,

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of the product indicated that it is a mixture of two compounds; 1st compound, namely $[\text{Zn}(\text{Et}_2\text{DTC})_2(\kappa^2\text{-dpppS})](\mathbf{4a})$ (60%) [$^{31}\text{P}\{-^1\text{H}\}$ NMR a doublet of doublets peak at $\delta\text{P} = (38.43)$ and (-2.84) ppm for $(\text{P}=\text{O})$ and (P) atom respectively, this indicate the two phosphorus atoms are un-equivalent.] and 2nd compound, namely $[\text{Zn}(\text{Et}_2\text{DTC})_2(\kappa^2\text{-dppp})](\mathbf{4b})$ (40%) [$^{31}\text{P}\{-^1\text{H}\}$ NMR: δ 24.66 ppm (s), this indicate the two phosphorus atoms are equivalent].

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of the product of the reaction of dppm with $[\text{Hg}(\mu\text{-Et}_2\text{DTC})_2]$ showed two signal, broad at $\delta\text{P} = (-1.56)$ ppm for the isomer (a) $[\text{Hg}(\kappa^1\text{-Et}_2\text{DTC})_2(\kappa^2\text{-dppm})]$ (70%) dppm bonded as chelating bidentate ligand, and the second isomer (b)

showed a singlet peak at $\delta\text{P} = (26.81)$ ppm, due to the complex $[\text{Hg}(\kappa^1\text{-Et}_2\text{DTC})_2(\mu\text{-dppm})]_2$ (30%), and the positive value of δP refer to the dppm bonded a bridge bidentate ligand.

The $^{31}\text{P}\{-^1\text{H}\}$ nmr spectra of $[\text{Hg}(\kappa^1\text{-Et}_2\text{DTC})_2(\kappa^2\text{-dppe})]$ and $[\text{Hg}(\kappa^1\text{-Et}_2\text{DTC})_2(\kappa^2\text{-dppp})]$ showed only one signal at δ (10.54) ppm and (13.09) ppm respectively, indicating the presence of a single isomer.

The $^{31}\text{P}\{-^1\text{H}\}$ nmr spectra of complexes (**6a**, **6b**) showed a two single peaks at $\delta\text{P} = (34.10)$ (45%) and (37.46) (60%) ppm attributed to complexes $[\text{Zn}(\kappa^1\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ and $[\text{M}(\kappa^2\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ respectively. And the $^{31}\text{P}\{-^1\text{H}\}$ nmr spectra of complexes (**9a**, **9b**) also, showed a two single peaks at $\delta\text{P} = (22.63)$ (60%) and (23.52) (40%) ppm attributed to complexes $[\text{Hg}(\kappa^1\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ and $[\text{Hg}(\kappa^2\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ respectively.

The ^1H - NMR of complexes (**3-9**) (Fig 6 and 7) showed the expected signals for the dithiocarbamate ligand as well as and the phosphine ligands.

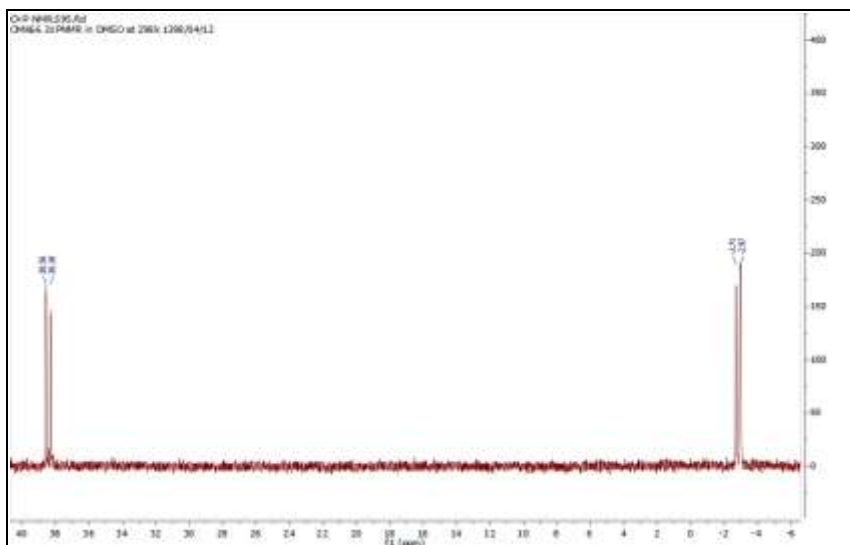


Fig. 4: $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex (**3**) in DMSO-d^6

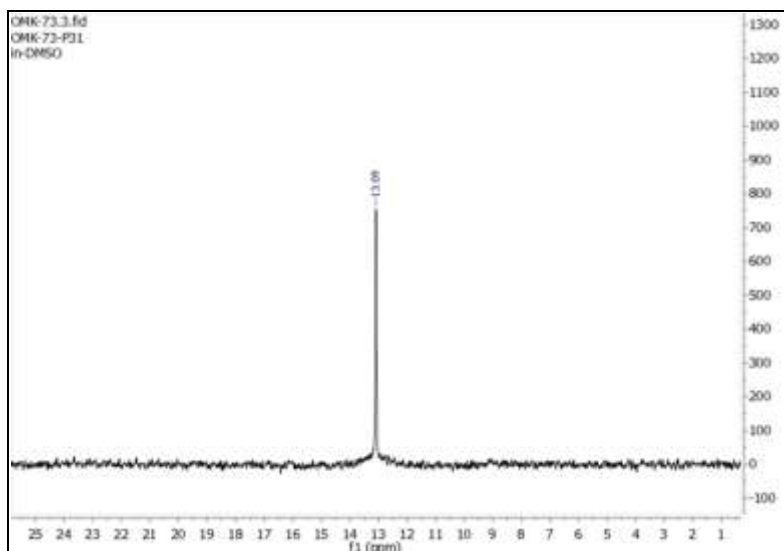
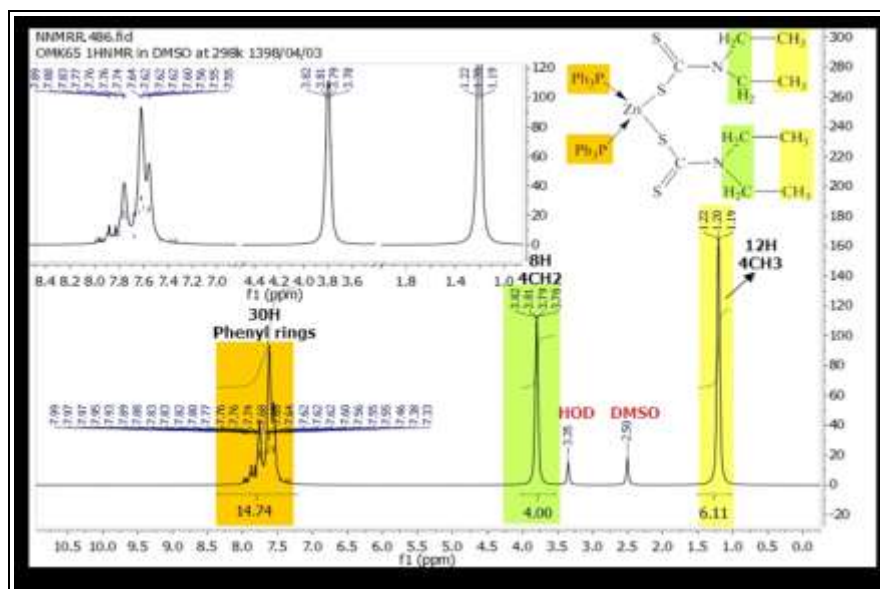
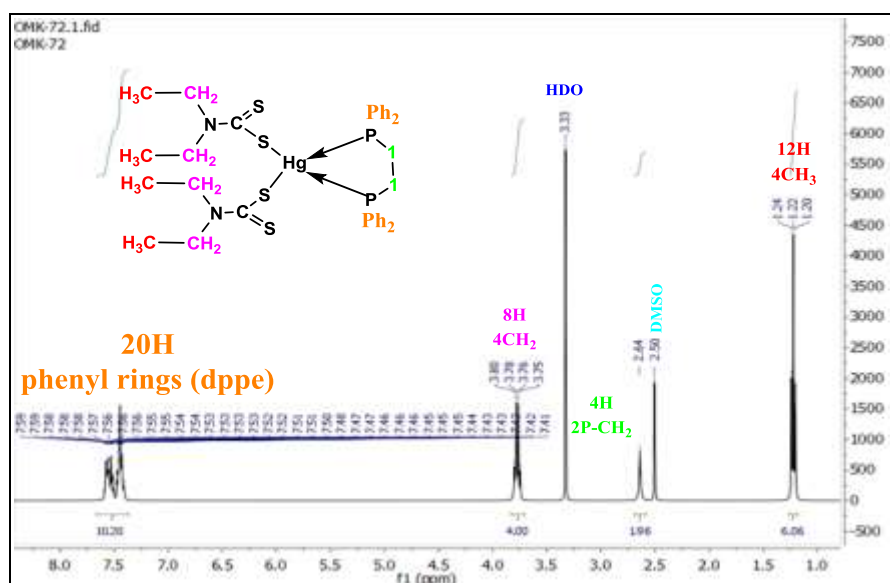


Fig. 5: $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex (**8**) in DMSO-d^6

Fig. 6: $^1\text{H}\text{-}\{^{31}\text{P}\}$ NMR spectrum of complex (6) in DMSO-d^6 Fig. 7: $^1\text{H}\text{-}\{^{31}\text{P}\}$ NMR spectrum of complex (8) in DMSO-d^6

4. Conclusions

In summary, we have synthesis and characterization new Zn(II) or Hg(II) dithiocarbamate complexes with phosphine ligands as co-ligands. A complexes of the type $[\text{M}(\kappa^2\text{-Et}_2\text{DTC})_2]$ $[\text{M} = \text{Zn}(1), \text{Hg}(2)]$ were prepared and characterized. The complex (1) or (2) was treated with equal molar of phosphine ligands to afford complexes of the type $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppeO})]$ (3); $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dpppS})]$ (4a); $[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppp})]$ (4b); $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppm})]$ (6a); $[\text{Hg}(\text{Et}_2\text{DTC})_2(\mu\text{-dppm})_2]$ (6b); and $[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppe})]$ (7)

$[\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppp})]$ (8). Or with two moles of PPh_3 , afforded yellow precipitate characterized as $[\text{M}(\kappa^1\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ (5a, 9a) and $[\text{M}(\kappa^2\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2]$ (5b, 9b). The dithiocarbamate ligand was bonded as monodentate ligands through the sulfur atom of the thioureide group in complexes (1-9) except, the complexes (5b, 9b) was bonded as bidentate chelating ligands the two sulfur atoms of CSS^- group. The prepared complexes have been characterized by IR, NMR (^1H , and ^{31}P) spectroscopy, molar conductivity and C.H.N.S elemental analyses.

References

- [1] Ogasawara, M., Nagano, T., & Hayashi, T. (2005). A New Route to Methyl (R, E)-(-)-Tetradeca-2, 4, 5-trienoate (Pheromone of *Acanthoscelides obtectus*) Utilizing a Palladium-Catalyzed Asymmetric Allene Formation Reaction. *The Journal of Organic Chemistry*, **70**(14), 5764–5767.
- [2] Trevisan, A., Marzano, C., Cristofori, P., Venturini, M. B., Giovagnini, L., & Fregona, D. (2002). Synthesis of a palladium (II)-dithiocarbamate complex: biological assay and nephrotoxicity in rats. *Archives of Toxicology*, **76**(5–6), 262–268.
- [3] Malik, W. U., Bembi, R., & Bhardwaj, V. K. (1980). Metal-complexes with sulfur donor ligands. I. preparation and characterization of some mixed-ligand complexes containing bidentate tertiary-amines and ethyl xanthate. *Journal of the Indian Chemical Society*, **57**(1), 35–38.
- [4] Chaurasia, M. R., Sharma, A. K., & Sharma, S. K. (1981). Synthesis of some new dithiocarbamates as potential insecticides and agricultural and garden fungicides. *Chemischer Informationsdienst*, **12**(49), no-no.
- [5] Stephen, W. I. (1966). *J. Stry, The solvent extraction of metal chelates: Pergamon Press, Oxford, 1964, xiv+ 240 pp., price 60 s.* Elsevier.
- [6] Iwasaki, H. (1973). The crystal structure of dimeric and monomeric forms of mercury (II) N, N-diethyldithiocarbamate, $\text{Hg}_2(\text{S}_2\text{CNEt}_2)_4$ and $\text{Hg}(\text{S}_2\text{CNEt}_2)_2$. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, **29**(10), 2115–2124.
- [7] Cvek B, Dvorak Z. (2007). Targeting of nuclear factor- κ B and proteasome by dithiocarbamate complexes with metals. *Curr Pharm Des*, **13**(30), 3155–3167.
- [8] Iwasaki, H. (1973). The crystal structure of dimeric and monomeric forms of mercury (II) N, N-diethyldithiocarbamate, $\text{Hg}_2(\text{S}_2\text{CNEt}_2)_4$ and $\text{Hg}(\text{S}_2\text{CNEt}_2)_2$. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, **29**(10), 2115–2124.
- [9] Tiekink, E. R. T. (2000). Redetermination of the crystal structure of dimeric bis (N, N-diethyldithiocarbamate) zinc, $[\text{Zn}(\text{S}_2\text{CNEt}_2)_2]_2$. *Zeitschrift für Kristallographie-New Crystal Structures*, **215**(3), 445–446.
- [10] Wessel, W., Tyrre, W., & Naumann, D. (2001). Synthese und Eigenschaften von Diethyldithiocarbaminsäureperfluororganylestern, $(\text{C}_2\text{H}_5)_2\text{NC}(\text{S})\text{SRf}$ ($\text{Rf} = \text{CF}_3$, C_2F_5 , $i\text{-C}_3\text{F}_7$, $n\text{-C}_4\text{F}_9$, C_6F_5). *Zeitschrift Für Anorganische Und Allgemeine Chemie*, **627**(6), 1264–1268.
- [11] Abrahams, B. F., Dakternieks, D., Hoskins, B. F., & Winter, G. (1988). Syntheses and NMR-Studies of Cationic Mercury Xanthate, Dithiophosphate and Dithiocarbamate Tricyclohexylphosphine Adducts-the Crystal and Molecular-Structures of $[\text{Hg}(\text{S}_2\text{CNEt}_2)(\text{P}(\text{C-C}_6\text{H}_{11})_3)_2]+(\text{CF}_3\text{SO}_3)^-$ [Hg(S2copri)(P(C-C6h11)3)2]+(ClO4)-. CH_2Cl_2 And $[\text{Hg}(\text{S}_2\text{p}(\text{Opri})_2)(\text{P}(\text{C-C}_6\text{H}_{11})_3)_2]+(\text{CF}_3\text{SO}_3)^-$. *Australian Journal of Chemistry*, **41**(5), 757–771.
- [12] Faraglia, G., Sindellari, L., & Sitran, S. (1990). Thermal S-demethylation in palladium (II) and platinum (II) complexes with S-methyl N, N-dialkyldithiocarbamates. *Thermochimica Acta*, **161**(1), 63–73.
- [13] Rochon, F. D., Melanson, R., & Kong, P.-C. (1992). Rearrangement of tetramethylthiourea to dimethyldithiocarbamate and crystal structures of $[\text{Tc}(\text{O})(\text{C}_5\text{H}_{12}\text{N}_2\text{S})_2((\text{CH}_3)_2\text{NCSS})](\text{PF}_6)_2$ and $[\text{Tc}(\text{dppe})_2((\text{CH}_3)_2\text{NCSS})](\text{PF}_6)$. *Inorganica Chimica Acta*, **194**(1), 43–50.
- [14] Geary, W. J. (1971). The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coordination Chemistry Reviews*, **7**(1), 81–122.
- [15] Georgieva, I., & Trendafilova, N. (2007). Bonding analyses, formation energies, and vibrational properties of M–R2dtc complexes (M= Ag (I), Ni (II), Cu (II), or Zn (II)). *The Journal of Physical Chemistry A*, **111**(50), 13075–13087.
- [16] Gupta, S. K., & Srivastava, T. S. (1970). Infrared and ^1H NMR spectra of five co-ordinate complexes of the bis (N, N'-diethyldithiocarbamate) zinc with the pyridine and other related nitrogen donors. *Journal of Inorganic and Nuclear Chemistry*, **32**(5), 1611–1615.
- [17] Bigotto, A., Costa, G., Galasso, V., & De Alti, G. (1970). Infra-red spectra and normal vibrations of bis-dimethylglyoximates of transition metals. *Spectrochimica Acta Part A: Molecular Spectroscopy*, **26**(9), 1939–1949.
- [18] Kuchen, W., & Buchwald, H. (1958). Zur Kenntnis der Organophosphorverbindungen, II. Das Tetraphenyldiphosphin. *Chemische Berichte*, **91**(12), 2871–2877.
- [19] Al-Jibori, S. A., Abdullah, A. I. and Al-Allaf, T. A. K. (2007). Mononuclear and heterobimetallic palladium(II) and platinum(II) complexes containing the mixed ligands N-(2-pyridyl or 2-pyrimidyl) acetamide and tertiary diphosphines. *Transition Metal Chemistry*, **32**(3): 398–406.
- [20] Al-Janabi A.S. M., Abdullah B.H., and Al-Jibori S.A., (2009). Synthesis, crystal structure and spectral studies of mercury(II) complexes containing the mixed ligands benz-1,3-imidazoline -2-thione, benz-1,3-oxazoline -2-thione, benz-1,3-thiazoline -2-thione, and diphosphines. *Oriental Journal Chemistry*, **25**(2):277–286.
- [21] Al-Janabi, A. S. M. Ahmed, S. A. and Ahmed, S. A. O., (2017). Synthesis and characterization of mercury(II) mixed ligands complexes derived from 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione with tertiary phosphines ligands. *Kirkuk University Journal / scientific studies*. **12**(2):9–21.

- [22] Al-Janabi, A. S. M. Jerjes, H. M. and Salah, M. H., (2017). Synthesis and characterization of new metal complexes of thione and phosphines Ligands. *Tikrit Journal of Pure Science*, **22**(9): 53-61.
- [23] Ahmed S. A. and Al-Janabi A. S. M., (2018), Synthesis, Spectroscopic characterization of Co(II), Ni(II) and Cu(II) complexes with 2-mercapto-5-(2,4-dinitrophenyl)-1,3,4-oxadiazole or 2-mercapto-5-((4-(dimethylamino) benzylidene)amino)-1,3,4-thiadiazole ligands. *Oriental Journal Chemistry*, **34**(4):787-784.
- [24] Al-Janabi, A. S. M., Irzoqi A. A., and Ahmed S. A.O., (2016). Synthesis and characterization of mixed ligands cadmium (II) complexes with N-hydroxymethylsaccharinate and diphosphines. *Tikrit Journal of Pure Science*, **21**(3):54-60.
- [25] Al-Jibori, S. A., Barbooti, M. M., Al-Janabi, A. S. M., Ali A.H., Sami N., Aziz B. K., and Basak-Modi S., (2017). Synthesis, characterization and thermal studies of mixed ligand mercury(II) complexes of N-hydroxymethylsaccharin (Sac-CH₂OH) and phosphine or heterocyclic amine co-ligands, *Research Journal of Chemical Sciences*. 7(10):1-5.
- [26] Al-Jibori, S. A., Al-Janabi, A. S. M., Basak-Modi, S., Mohamed, S. S., and Schmidt, H. (2015). Mixed ligand palladium (II) complexes of N-hydroxymethylsaccharin (Sac-CH₂OH): synthesis, characterization and biological studies. *Transition Metal Chemistry*, **40**(8):917-921.
- [27] Al-Doori, M. E. A. and Al-Janabi, A. S. M., (2019). New Salicylanilide-Hg(II) complexes with phosphine ligands, Synthesis and spectroscopic investigation. *Tikrit Journal of Pure Science*, **24**(5):31-37.
- [28] Al-Doori, M. E. A., Al-Janabi, A. S. M. and Othman, E. A. (2019). Mixed Ligand Complexes of Hg-tetrazole-thiolate with phosphine, Synthesis and spectroscopic studies. *Tikrit Journal of Pure Science*, **24**(5):10-17.
- [29] Grushin, V. V. (2001). Synthesis of Hemilabile Phosphine– Phosphine Oxide Ligands via the Highly Selective Pd-Catalyzed Mono-oxidation of Bidentate Phosphines: Scope, Limitations, and Mechanism. *Organometallics*, **20**(18), 3950-3961.
- [30] Breshears, A. T., Behrle, A. C., Barnes, C. L., Laber, C. H., Baker, G. A., & Walensky, J. R. (2015). Synthesis, spectroscopy, electrochemistry, and coordination chemistry of substituted phosphine sulfides and selenides. *Polyhedron*, **100**, 333-343.

تحضير وتشخيص معقدات الخارصين (II) والزنك (II) الحاوية على مزيج من ليكاندات الثنائي ثايوكارباميت والفوسفينات

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الملخص

حضرت المعقدات ذات الصيغة $[M(\mu\text{-Et}_2\text{DTC})_2] [M=\text{Hg}(1), \text{Zn}(2)]$ من تفاعل خلاات الزنك (1) او الخارصين (2) مع ليكاند صوديوم ثنائي اثيل ثنائي ثايوكارباميت المائي $[\text{NaEt}_2\text{DTC} \cdot 3\text{H}_2\text{O}]$ في الميثانول المطلق والماء المقطر بنسبة مولية (2:1) . ثم تم مفاعلة المعقد (1),(2) مع مول واحد من الفوسفينات الثنائية حيث ان

Bis (diphenylphosphino) methane (dppm), 1,2-Bis (diphenylphosphino) ethane (dppe), 1,3-Bis (diphenylphosphino) propane (dppp)

بنسبة مولية (1:1) لينتج معقدات ذات صيغة

$[\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppeO})] (3); [\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dpppS})] (4a); [\text{Zn}(\text{Et}_2\text{DTC})_2(\text{dppp})] (4b); [\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppm})] (6a); [\text{Hg}(\text{Et}_2\text{DTC})_2(\mu\text{-dppm})]_2(6b); [\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppe})] (7) \text{ and } [\text{Hg}(\text{Et}_2\text{DTC})_2(\text{dppp})](8)$

بينما ينتج معقدات من النوع $[\text{M}(\kappa^1\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2] (5a, 9a)$ و $[\text{M}(\kappa^2\text{-Et}_2\text{DTC})_2(\text{PPh}_3)_2] (5b, 9b)$ عند التفاعل مع مولين من ثلاثي فنيل فوسفين.

شُخصت المعقدات المحضرة بتقنيات مختلفة مثل الاشعة تحت الحمراء، الرنين النووي المغناطيسي (^1H , ^{31}P)، تحليل الدقيق العناصر و التوصيلية المولارية. وظهرت النتائج أن ليكاند (Et_2DTC) في جميع المعقدات المحضرة تناسقت مع الفلز من خلال ذرة الكبريت. الشكل الهندسي للمعقدات (1-9) رباعي السطوح ما عدا المعقدين (5b, 9b) تظهر كل ثنائي السطوح حول الايون المركزي.