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Spectroscopic studies of piperidine dithiocarbamate-Hg(II) mixed ligand complexes

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ABSTRACT

Treatment two moles of sodium piperidine dithiocarbamate (NaPipDT) with one mole of mercuric acetate afforded complex of the type $[\text{Hg}(\kappa^2\text{-PipDT})](1)$ as a white ppt. Further reaction of complex (1) with two moles of monodentate ligand (L) afforded complexes of the type $[\text{Hg}(\kappa^1\text{-PipDT})(\text{L})_2]$ (**2-8**) {triphenyl phosphine (Ph_3P), triphenyl phosphine oxide (Ph_3PO), triphenyl phosphine sulfide (Ph_3PS), 2-aminopyridine (2Apy), 3-aminopyridine (3Apy), 2-aminopyrimidine (2Apmy) and Pyridine (Py)}. Different spectroscopic methods were used to identify the synthesized complexes. In complex (**1**), the PipDT^- was joined as bidentate mode through the S atoms of the N-CSS group, whereas in complex (**2-8**) coordinated as monodentate mode via S atom. The monodentate amine ligand {2Apy, 3Apy, 2Apmy and Py} coordinate through the N atom of the amine ring as monodentate mode.

Keywords: dithiocarbamate, mercury, amine, phosphine, piperidine, complex.

1. Introduction

Ligands containing sulfur and nitrogen atoms have been commonly utilized to prepare stable complexes [1-5]. These ligands are mostly known for their monoanionic characteristic such as dithiocarbamate ligands [6]. Dithiocarbamates or 1,1-dithiolate compounds are very interesting ligands due to their multi-coordination types [7-11] (Fig. 1).

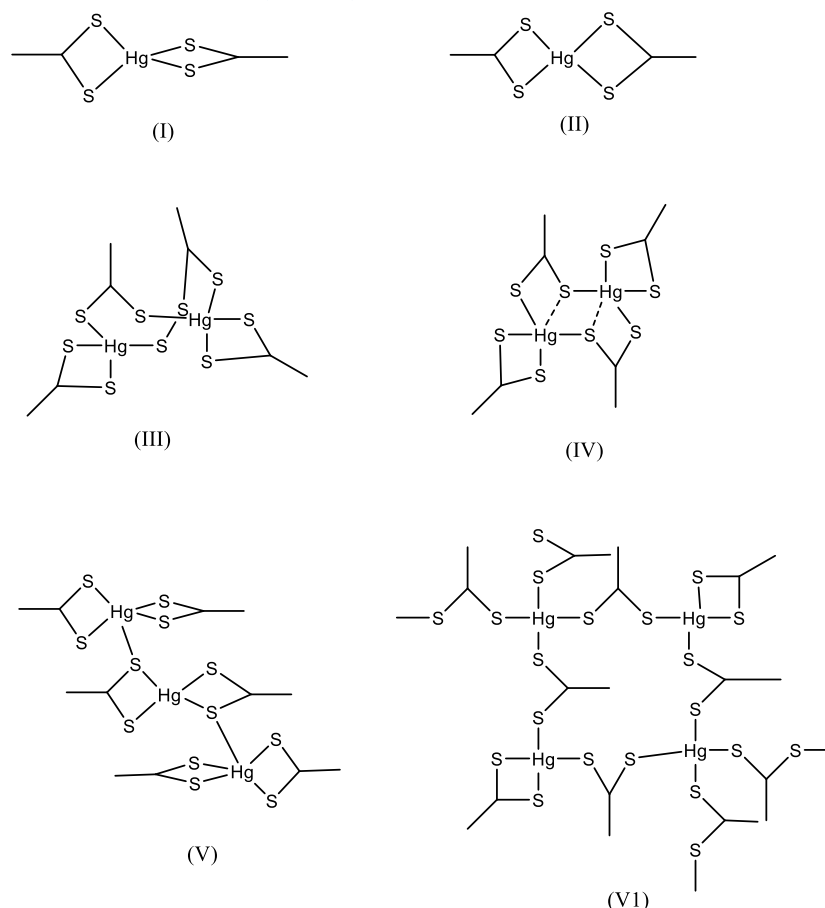


Fig. 1: Different coordination modes of dithiocarbamate mercury complexes

Dithiocarbamates have been extremely utilized to form stable metal complexes especially with those of high oxidation states [12-14]. Sulfur atoms of the dithiocarbamate moiety can accommodate π electrons through the unoccupied $d\pi$ orbitals of sulfur atom. In addition to the π electrons, the (N-CSS⁻) group can possess additional π bonds through the delocalization of the π -electron system from nitrogen to sulfur, resulting of a rich electron donor ligand (Fig.2). Dithiocarbamate complexes with different transition metal ions have been continuously reported in the literature [15]. However, complexes incorporating mixed ligands compounds have been poorly represented in literature. To prepare mixed ligand complexes of 1,1-dithiolate moiety, ligands with comparable ligating ability must be added, especially chelating ligands such as diimine or diphosphine.

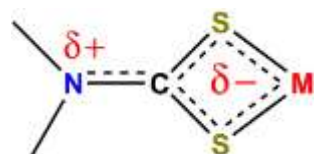


Fig. 2: The delocalization of the π -electron system through N-CSS group

In this work, we designate the preparation of eight Hg(II) mixed ligand complexes of piperidine dithiocarbamate (PipDT⁻) with monodentate ligands {triphenyl phosphine (Ph₃P), triphenyl phosphine

oxide (Ph₃PO), triphenyl phosphine sulfide (Ph₃PS), 2-aminopyridine (2Apy), 3-aminopyridine (3Apy), 2-aminopyrimidine (2Apmy) and Pyridine (Py)}. Different methods were used to identify the prepared complexes including IR, CHN analysis, molar conductivity and NMR.

2. Experimental

2.1. Materials and Methods

All chemical components, reagents, and solvents are supplied and used in the manner intended. A Shimadzu model FTIR-8400S apparatus and a Varian Unity spectrometer (400 MHz) are used, respectively, to obtain NMR and IR spectra. On the Euro-vector model EA 3000, digital conductivity meter model CD-2005, and Stuart model SMP10, respectively, melting point, elemental analysis (CHN), and molar electric conductivity are measured.

2.2 Preparation of [Hg(κ^2 -PipDT)₂] (1)

To a hot ethanolic solution of mercuric acetate (0.247 g, 0.64 mmol) (10 mL) was added an aqueous solution of sodium piperidine dithiocarbamate (NaPipDT) (0.100 g, 1.28 mmol) (10 mL). The reaction resulted in a direct precipitate of an off white solid. The reaction was left to stir further at room temp. for 3h. Then, it was filtered, washed with ethanol and dried under vacuum (Yield: 93%, m.p(°C): 312-315 (decompose)).

2.2 Preparation of $[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{PPh}_3)_2]$ (2)

Triphenyl phosphine (Ph_3P) (0.100 g, 0.64 mmol) dissolved in CH_2Cl_2 (10 mL) was added to a hot solution of $[\text{Hg}(\kappa^2\text{-PipDT})_2]$ (0.247 g, 0.64 mmol) in dichloromethane (10 mL), a colorless solution was formed. Next, the reaction was left to stir at room temp. for 6h., then filtered and left aside for slow evaporation. The formed white solid was filtered, washed with cold ethanol and dried under vacuum to give a white powder as $[\text{Zn}(\kappa^1\text{-PipDT})_2(\text{PPh}_3)_2]$ (2).

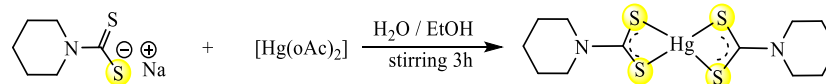
Closely related triphenyl phosphine oxide (Ph_3PO) (3), triphenyl phosphine sulfide (Ph_3PS) (4), 2-

aminopyridine (2Apy) (5), 3-aminopyridine (3Apy) (6), 2-aminopyrimidine (2Apy) (7) and Pyridine (Py) (8) complexes were prepared and isolated using similar methods.

3. Results and Discussion

3.1 Synthesis of complexes

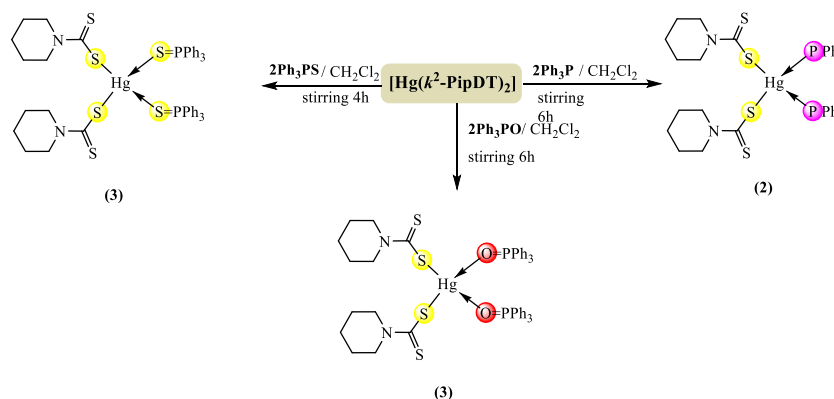
The reactions of sodium piperidine dithiocarbamate (NaPipDT) with $\text{Hg}(\text{oAc})_2$ in (1:2) molar ratio, afforded complex of the formula $[\text{Hg}(\kappa^2\text{-PipDT})_2]$ (Scheme 1) in high yield (93%). The PipDT^- was joined as bidentate mode via the S atoms.



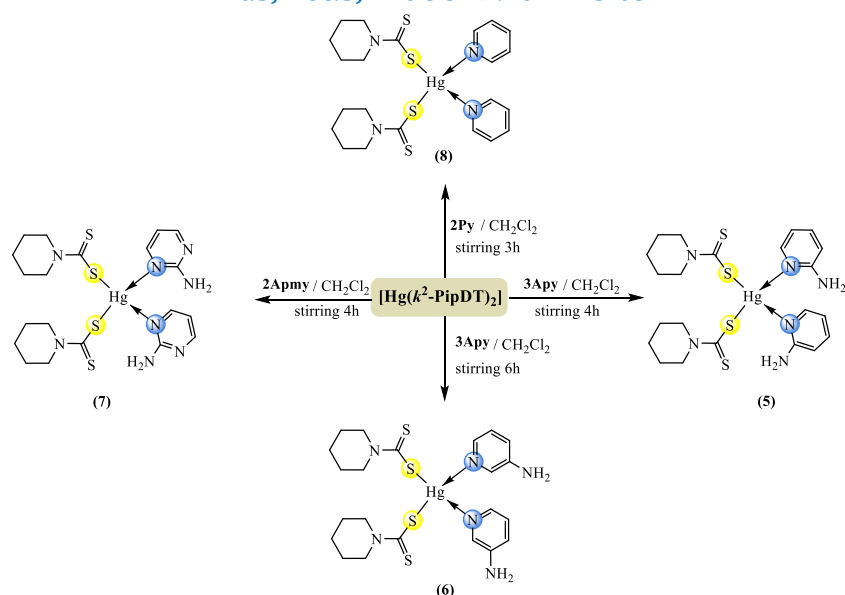
Scheme 1: The synthesis of complex (1).

The reaction of $[\text{Hg}(\kappa^2\text{-PipDT})_2]$ complex with two moles of monophosphine (phos) {triphenyl phosphine (Ph_3P), triphenyl phosphine oxide (Ph_3PO), triphenyl phosphine sulfide (Ph_3PS)} or mono amine ligands (amine){ 2-aminopyridine (2Apy), 3-aminopyridine (3Apy), 2-aminopyrimidine (2Apy) and Pyridine (Py)} gave complexes of the type $[\text{Hg}(\kappa^1\text{-PipDT})(\text{phos})_2]$ (2-4) (Scheme 2) or $[\text{Hg}(\kappa^1\text{-PipDT})(\text{amine})_2]$ (5-8) (Scheme 3) in good yields

(74-89%). The PipDT^- was joined via the S atoms as monodentate fashion. The mixed ligand complexes are quite soluble in heated CHCl_3 or CH_2Cl_2 , soluble in DMSO, and DMF. Through the use of molar conductivity, $^1\text{H-NMR}$, IR, and CHN methods, the complexes were analyzed Table 1-3. No crystals appropriate for X-ray diffraction research could be obtained despite all attempts.



Scheme 2: The synthesis of complexes (2-4)



Scheme 3: The synthesis of complexes (5-8)

Table 1: Physical properties of complexes (1-8)

Seq.	Complexes	Yield (%)	m.p. (°C)	$\Lambda_M(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ $1 \times 10^{-3} \text{ M / DMSO}$	Elemental analysis		
					Calc.(Found)%		
					C	H	N
1	$[\text{Hg}(\kappa^2\text{-PipDT})_2]$	93	312-315D	7.1	27.66 (27.89)	3.87 (3.93)	5.38 (5.71)
2	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{PPh}_3)_2]$	83	291-295	8.2	55.13 (55.41)	3.82 (4.02)	2.68 (2.81)
3	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{OPPh}_3)_2]$	81	>300	5.7	53.50 (53.36)	4.68 (4.79)	2.60 (2.73)
4	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{SPPH}_3)_2]$	89	257-258	4.1	51.95 (52.28)	4.54 (4.73)	2.52 (2.73)
5	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-2Apy})_2]$	74	278-281	5.6	37.25 (37.57)	4.55 (4.39)	11.85 (12.08)
6	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-3Apy})_2]$	79	>300	7.3	37.25 (37.11)	4.55 (4.42)	11.85 (11.92)
7	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-2Apmy})_2]$	80	198-201D	5.0	37.77 (37.92)	4.25 (4.50)	15.75 (16.03)
8	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-Py})_2]$	77	263-265	10.8	38.90 (38.67)	4.45 (4.73)	8.25 (8.40)

D= Decomposition

3.2 Characterization of complexes

3.2.1 NMR spectra

The ^1H NMR spectrum of complex (1) (Fig. 3) showed the ligand's protons of PipDT⁻ as three

separated peaks at δH 1.92 ppm, 2.76 ppm and 3.52 ppm, which is attributed to CH₂ alkyl backbone, represented as 2 protons, 4 protons and 4 protons, respectively.

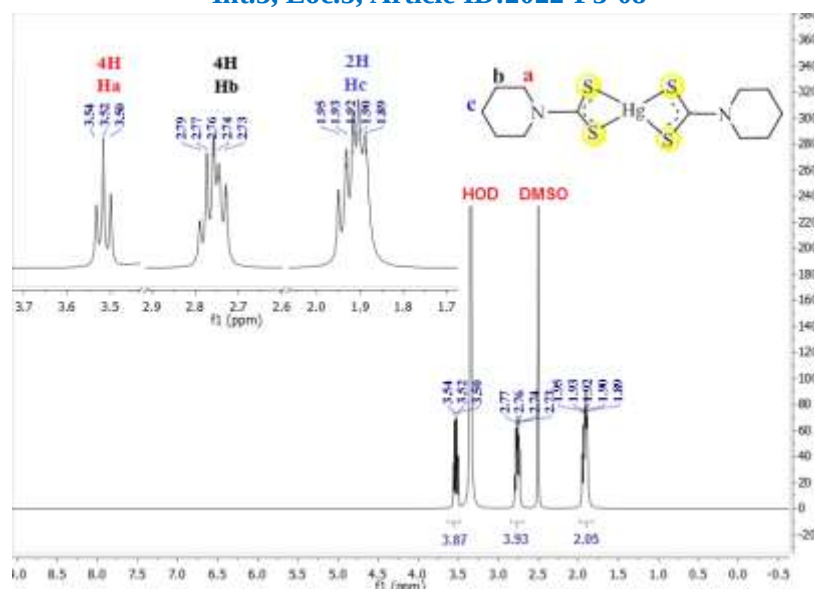


Fig. 3: ^1H NMR spectrum of complex (1)

The $^1\text{H}\{-^{31}\text{P}\}$ NMR spectra of (2-4) unmistakably revealed the PipDT $^-$ protons and phosphine ligand in aliphatic and aromatic region as three separated peaks. Each of the produced compounds contains two-piperidine dithiocarbamate and two phosphine, according to the integration values under each signal. The Table 2 lists each of these peaks.

^1H -NMR spectra of $[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-amine})_2]$ (5-8) complexes, show the amine and PipDT $^-$ ligands' protons in an apparent manner. The ^1H NMR spectra

presented the protons of PipDT $^-$ ligand as three separated signals in the range of (1.62-1.81) ppm, (2.24-2.80) ppm and (3.63-4.08) ppm. Benzene rings protons combined with amine protons appeared as broad peaks in the range of 6-8 ppm. Also the protons of the NH_2 group are shown in each spectrum in complexes (5-7) as a singlet peak at $\delta\text{H}=6.23$ ppm, 5.65 ppm and 4.97 ppm respectively (Fig. 4).

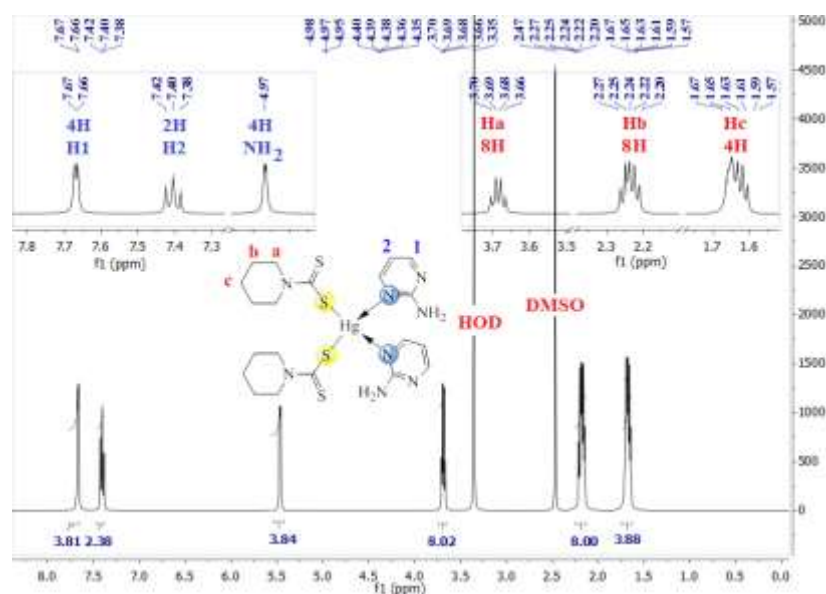


Fig. 4: ^1H nmr spectrum of $[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-2Apm})_2]$ (7)

The $^{31}\text{P}\{-^1\text{H}\}$ nmr spectra of (2-4) displayed a singlet peak at $\delta\text{P}=23.68$ ppm, 37.22 ppm and 25.48 ppm

respectively (Fig. 5), refereeing to a major product with no side products.

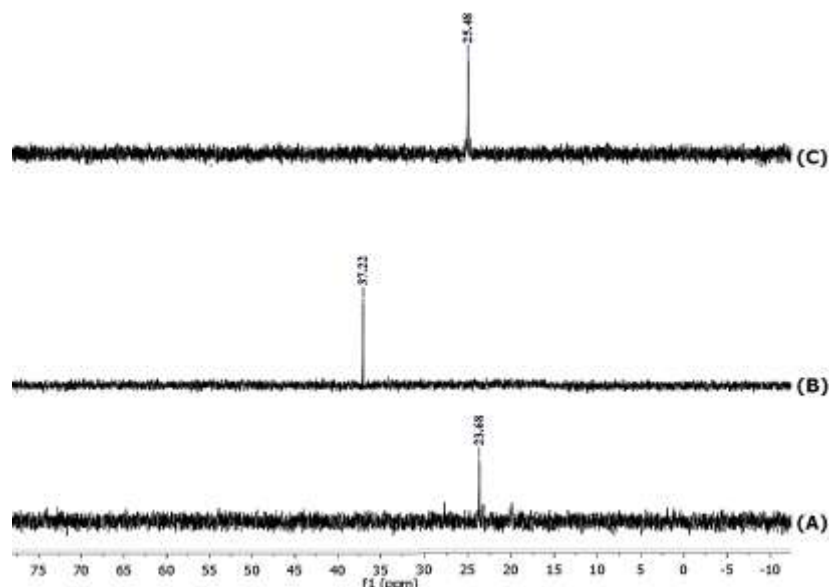


Fig.5: The $^{31}\text{P}\{-^1\text{H}\}$ nmr spectra of the (A) complex (2), (B) complex (3) and (C) complex (4)

Table 2: ^1H and ^{31}P NMR data, chemical shifts (δ ppm) and coupling constant (Hz) for some of the prepared complexes measured in DMSO-d^6

Seq.	Complex	Chemical shift (ppm)	
		δP	δH^*
1	$[\text{Hg}(\kappa^2\text{-PipDT})_2]$	---	1.92(m, 4H, 2CH ₂ -PipDT); 2.79(m, 8H, 4CH ₂ -PipDT); 3.52(t, 8H, $J_{\text{HH}} = 7.86\text{Hz}$, 4CH ₂ -PipDT);
2	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{PPh}_3)_2]$	23.68	1.81(m, 4H, 2CH ₂ -PipDT); 2.63(m, 8H, 4CH ₂ -PipDT); 3.89(t, 8H, $J_{\text{HH}} = 8.06\text{Hz}$, 4CH ₂ -PipDT); 7.23(m, 30H, H-phenyl)
3	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{OPPh}_3)_2]$	37.22	1.67(m, 4H, 2CH ₂ -PipDT); 2.80(m, 8H, 4CH ₂ -PipDT); 3.91(t, 8H, $J_{\text{HH}} = 7.86\text{Hz}$, 4CH ₂ -PipDT); 7.47(m, 30H, H-phenyl)
4	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{SPPH}_3)_2]$	25.48	1.78(m, 4H, 2CH ₂ -PipDT); 2.66(m, 8H, 4CH ₂ -PipDT); 4.01(t, 8H, $J_{\text{HH}} = 7.86\text{Hz}$, 4CH ₂ -PipDT); 7.37(m, 30H, H-phenyl)
5	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-2Apy})_2]$	---	1.72(m, 4H, 2CH ₂ -PipDT); 2.62(m, 8H, 4CH ₂ -PipDT); 3.92(t, 8H, $J_{\text{HH}} = 7.92\text{Hz}$, 4CH ₂ -PipDT); 6.23(bs, 4H, NH ₂); 6.93(m, 4H, H-2Apy); 7.65(d, 2H, $J_{\text{HH}} = 7.32\text{Hz}$, H-2Apy); 7.92(d, 2H, $J_{\text{HH}} = 7.60\text{Hz}$, H-2Apy)
6	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-3Apy})_2]$	---	1.67(m, 4H, 2CH ₂ -PipDT); 2.35(m, 8H, 4CH ₂ -PipDT); 4.08(t, 8H, $J_{\text{HH}} = 8.00\text{Hz}$, 4CH ₂ -PipDT); 5.65(bs, 4H, NH ₂); 6.90(s, 2H, H-3Apy); 7.46(dd, 2H, $J_{\text{HH}} = 7.8\text{Hz}$, H-3Apy); 7.74(d, 2H, $J_{\text{HH}} = 7.8\text{Hz}$, H-3Apy); 7.92(d, 2H, $J_{\text{HH}} = 7.2\text{Hz}$, H-3Apy)
7	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-2Apmy})_2]$	---	1.62(m, 4H, 2CH ₂ -PipDT); 2.24(m, 8H, 4CH ₂ -PipDT); 3.69(t, 8H, $J_{\text{HH}} = 7.80\text{Hz}$, 4CH ₂ -PipDT); 4.97(s, 4H, NH ₂); 7.40(t, 2H, $J_{\text{HH}} = 6.8\text{Hz}$, H-2Apmy); 7.66(d, 2H, $J_{\text{HH}} = 6.8\text{Hz}$, H-2Apmy)
8	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-Py})_2]$	---	1.80(m, 4H, 2CH ₂ -PipDT); 2.39(m, 8H, 4CH ₂ -PipDT); 3.77(t, 8H, $J_{\text{HH}} = 7.70\text{Hz}$, 4CH ₂ -PipDT); 7.34(m, 6H, H-Py); 7.82(d, 4H, $J_{\text{HH}} = 7.4\text{Hz}$, H-Py)

3.2.2 IR spectra

Table 3 lists IR absorption bands of the complexes (1-8). In IR spectrum $[\text{Hg}(\kappa^2\text{-PipDT})_2]$ (1) displayed the frequency of $\nu(\text{CSS})$ group as one distinguishing band at 1023cm^{-1} which confirms the chelating mode of dithiocarbamate ligand [6]. The complexes (2-4) displayed two distinguishing bands in the range of $(1431\text{-}1437)\text{cm}^{-1}$ and $(498\text{-}503)\text{cm}^{-1}$ due to the $\nu(\text{P-Ph})$ and $\nu(\text{P-C})$ of the phosphine ligands, indicating that are participated in the coordination to metal ions [16-18]. In IR spectra of complexes (5-8), clearly

displayed the $\nu(\text{C=N})$ of amine ligand within $(1579\text{-}1592)\text{cm}^{-1}$. The little shift in the absorbed bands indicates that the coordination to metal ions was happened via the N atom of the amine ligand [19, 20]. The spectra of complexes (5-7), displayed the stretching of the two N-H group within $(3356\text{-}3398)\text{cm}^{-1}$ and $(3147\text{-}3175)\text{cm}^{-1}$, respectively. The ligand displayed two peaks within the $(934\text{-}981)\text{cm}^{-1}$ and $(1023\text{-}1087)\text{cm}^{-1}$ which were marked to ν CS group, indicates that the PipDT^- ligand bonded as monodentate fashion [6].

Table 3: The IR absorption bands in (cm⁻¹) of the complexes (1-7)

Seq.	Complex	$\nu(\text{NH}_2)$ asy/sy	$\nu(\text{C-H})$		$\nu(\text{C=N})$	$\nu(\text{CSS})$	$\nu(\text{Ph-P})$ $\nu(\text{P-C})$
			Ar.	Alph.			
1	$[\text{Hg}(\kappa^2\text{-PipDT})_2]$	----		2873w	1463s	979s	----
2	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{PPh}_3)_2]$	----	3058w	2854w	1471s	981m 1018m	1431s 503m
3	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{OPPh}_3)_2]$	----	3058w	2835w	1483m	965m 1066m	1434s 498m
4	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\text{SPPH}_3)_2]$	----	3083w	2875w 2818w	1497m	973m 1052m	1437s 501m
5	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-2Apy})_2]$	3398s 3175s	3088w	2854w 2802w		973m 1079m	----
6	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-3Apy})_2]$	3356m 3169s	3099w	2875w 2791w	1472s 1573s	969m 1055m	----
7	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-2Apmy})_2]$	3379s 3147s	3023w	2882w 2821w	1495m 1571m	980m 1067m	----
8	$[\text{Hg}(\kappa^1\text{-PipDT})_2(\kappa^1\text{-Py})_2]$	----	3056w	2821w 2789m	1492m 1545s	980m 1023m	----

Conclusion

Sodium piperidine dithiocarbamate (NaPipDT) reacts with $[\text{Hg}(\text{oAc})_2]$ to afford $[\text{Hg}(\kappa^2\text{-PipDT})](1)$, in which two PipDT ligands are bonded as bidentate chelating ligand. Reaction of $[\text{Hg}(\kappa^2\text{-PipDT})](1)$ with monodentate ligand (L) {L= triphenyl phosphine (Ph_3P), triphenyl phosphine oxide (Ph_3PO), triphenyl phosphine sulfide (Ph_3PS), 2-

aminopyridine (2Apy), 3-aminopyridine (3Apy), 2-aminopyrimidine (2Apmy) and Pyridine (Py)}. afforded $[\text{Hg}(\kappa^1\text{-PipDT})(\text{L})_2]$ (2-8). The PipDT is coordinated as a mono-dentate via the sulfur atom of the CSS moiety to give the Hg as a tetrahedral shape. Additionally, CHN analysis and spectroscopic techniques were employed to characterize the complexes.

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