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Synthesis and Characterization of Pd(II) And Pt(II) Complexes with Bis [Hg (2-Apt)] Compound.

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Abstract

The reaction of one mole of Hg(II) acetate with two mole of 2-amino thiophenol gave one mole of [Hg(2-apt)] compound. While the reaction of one mole of [Hg(2-apt)] with two moles of MCL2 salt. Produced new complexes in general formula [M2{Hg(2-apt)Cl4] where M=Pt(II) or Pd(II).All the prepared complexes were identified using FT-IR, 1H-NMR,13C-NMR,elemental analyses (CHNS) and molar conductivity. The results exhibited that metal bounded to the ligand via S and N in squar planer geometries.

Keywords: bis [Hg (2-apt)] compound, Pd(II) and Pt(II) complexes, Spectral data.

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تحضير و تشخيص معقدات Pt(II), Pd(II) مع مركب ثنائي [Hg (2-apt)].

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الملخص

تفاعل مول واحد من خلات Hg(II) مع مولين من 2-امينوثايوفينول اعطت مول واحد من مركب[Hg(2-apt) بينما تفاعل مول واحد من [Hg(2-apt)] مع مولين من ملح $[MCl_2]$ انتجت معقدات جديدة ذوات الصيغة $[M_2\{Hg(2\text{-}apt)Cl_4]$. حيث M=Pd(II), Pt(II) تم تشخيص جميع المعقدات باستخدام ^{1}H-NMR, ^{13}C-NMR FT-IR وقياسات تحليل الدقيق للعناصر(CHNS) و المولارية. وقد اظهرت النتائج بان الفلز يتناسق مع الليكاند من خلال S, N مكونا شكل المربع المستوي.

الكلمات الدالة: مركبات[Hg(2-apt)، معقدات Pd(II)، Pt(II)، حقائق اطياف.

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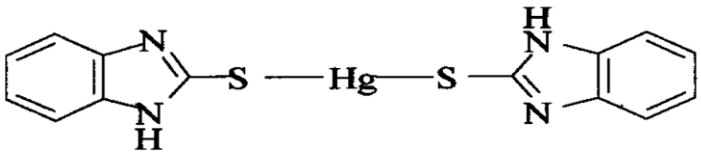
1. Introduction

[Hg(2-apt)] The metal complexes which containing mercury (II)-thiolate have been considerable interest, due to their wide biological application [1]. The complexes of Pd (II) and Pt(II) ions with (N, S, O) donor ligands have attracted a great attention because of their, anticancer, and catalytic biological abilities [2]. The investigation of Pd(II) and Pt(II) complexes with 2-mercaptobenzimidazole have been reported in recent years [3]. The compound of $Hg(bzimtH)_2$. (where; $bzimtH_2$= benzo-1, 3-imidazole-2-thione) has been obtained by reaction of the mercury (II) acetate with benzo-1, 3-imidazole-2-thione in the appropriate molar ratio (1:2) [4]. as it shown in the following structure :



In this present work we reported synthesize of new ligand of bis (2-amino phenylthio) mercury and their complexes with Pd(II) and Pt(II). Our interest aim is synthesize of compound which binding with the central metal though sulpher and nitrogen atoms which plays importance role in biological and medical fields.

2. Experimental

2.1 Materials and instrumentation:

All chemical were used in the present work are in reagent grade. They were used as supplied (Fluka), (merk), (Alpha), or (B.D.H). Infrared spectra were recorded on Shimadzu FT-IR. 8400 spectrometer in the (400-4000) cm^{-1} range. Melting point were measured using Melting Point-MPD-100Pixel Technology CO., Limited. Elemental analysis were carried out on Perkin Elmer-2400. The elemental analyses for carbon, hydrogen, sulfur and nitrogen were performed by Innoventon at the Nelson Mandela Metropolitan University. CHNS analysis in (Al-ALBayt) University Central Labs (Jordon). ^{1}H-NMR,^{13}C-NMR spectra of complexes were carried on Bruker ultra shield 300 MHz with TMS as internal reference, in (Al-ALBayt) University Central Labs (Jordon), using DMSO-d6 as a solvent. Conductivity measurements were carried out on a Jenway conductivity meter 4200 (093 cell constant) (UK.).

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2.2 Synthesis of bis-(2-amino phenyl thio) mercury [Hg(2-apt)]

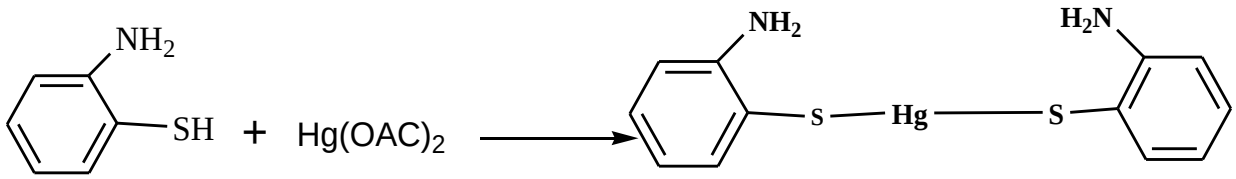
A solution of 2-aminothiophenol (40 mmole, 5g) was mixed with a solution of mercuric acetate (20mmole, 6g) in 25ml of methanol. The mixture was stirred for 5hr in room temperature until the green precipitate was formed. The resulted product was separated by filtration, dried in air and recrystallized from ethanol [1]. Yield 80%, analytical calculated% for $C_{12}H_{12}S_2N_2Hg$= Carbon, 43.1, Hydrogen, 2.67, Nitrogen, 6.26,. Sulfur, 14.2. Found %, Carbon,44.0, Hydrogen, 2.69, Nitrogen, 6.69,. Sulfur, 13.18 %. FT-IR (ν_{max}/cm^{-1}): ν (NH) 3238(b). ν (C-H)3012(w), ν (C-N) 1597(s) ν (C-S)750(s).

2.3 Synthesis of the Complexes

A clear solution of [Hg (2-apt)] compound (0.5mmole, 0.117g) in ethanol (10ml) was added to a suspended solution of MCl_2 (M= Pd(II), Pt(II)) (1mmole) in (10ml) ethanol, the reaction mixture was stirred at room temperature for 12hrs to produce the precipitate which was filtered off, washed with diethyl ether. Analytical calculated % for $C_{12}H_{12}S_2N_2Pd_2Cl_4$: Carbon, 23.90, Hydogen, 2.01, Nitrogen, 4, 65,. Sulfur, 11.63. Found, Carbon, 24.22, Hydrogen, 2.65, Nitrogen, 4.09, . Sulfur, 11.02 and analytical calculated.% for $C_{12}H_{12}S_2N_2Pt_2Cl_4$ Carbon,18,47, Hydrogen, 1,55, Nitrogen, 3.59,. Sulfur, 8.22. Found, Carbon, 18,95, Hydrogen, 1.95, Nitrogen, 4.11,. Sulfur, 9.11 .

3. Results and Discussion

3.1 Schemes of reaction:



2-aminothiophenol mercury acetate bis(2-aminophenylthio)mercury

(2 mole) **(1 mole)**

Scheme 1: Synthesis of bis-(2-amino phenyl thio) mercury [Hg(2-apt)].

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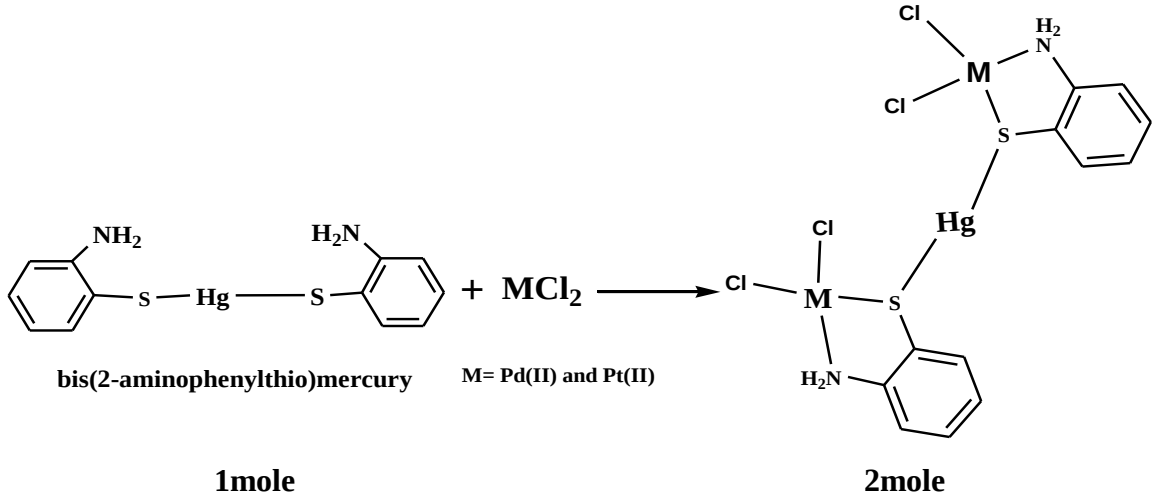

bis(2-aminophenylthio)mercury

1mole

2mole

Scheme 2: Synthesis of the Complexes.

3.2 ^{1}H-NMR, ^{13C}-NMR spectra:

The ^{1}H-NMR, ^{13}C-NMR spectra of compound [Hg (2-apt)] in DMSO-d6 solvent . All protons were seen according to the expected chemical shift, the ^{1}H-NMR which appeared at (δ= 6.4-7.4)ppm for (4H) proton of [Hg(2-apt)] compound [5]. singlet peak at (δ= 5.3)ppm due to the (NH) proton of amine group [6]. ^{13}C-NMR spectra for [Hg(2-apt)] compound was measured in DMSO-d6 the signals at (δ= 147.4, 115.01, 126.3, 120, 133.9, 119.1)ppm were appeared due to aromatic ring of carbon atoms [7].

3.3 FT-IR spectra:

The infrared spectrum of [Hg(2-apt)] compound showed new peaks in the range (3311-3238)cm^{-1} ,which are corresponding to ν(NH) of NH2 amine [8, 9]. Weak bands within the range (3012-3055)cm^{-1} ,assigned to ν(C-H) aromatic ring. A sharp band absorption at 1597 cm^{-1} in the spectrum of [Hg(2-apt)] compound assigned to ν (C-N) band [10]. The strong band at 750cm^{-1} was attributed to ν(C-S) [11]. The negative shift of ν(N-H) amine at (3151-3107)cm^{-1} for complexes due to the coordination of nitrogen with metal ions. The bands of (C-N) and (C-S) shifted to 1543 and 758cm^{-1} respectively, these shifting to a lower and higher frequency from the compound indicated coordination of nitrogen and sulfur to metal ions of Pd(II) and Pt(II) [12]. The new bands at 570-420cm^{-1} which are supported the coordination of metal ions with N and S atoms (M-N), (M-S)[13], Table 2. The UV-Vis spectrum in 10^{-3} M DMSO shows three transitions of Pd(II) complex ,at 21739 cm^{-1}, 27027 cm^{-1}, and 29411 cm^{-1} which are due to to the $^{1}A_{1}g \rightarrow {}^{1}A_{2}g$, $^{1}A_{1}g \rightarrow {}^{1}Eg$ and charge transfer respectively, these

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transitions are indicated to square planner geometry [14]. The Pt(II) complex exhibits three peaks at 23753 cm^{-1}, 26667 cm^{-1}, and 27700 cm^{-1} which are assigned to the $^1A_1g \rightarrow {}^1A_2g$, $^1A_1g \rightarrow {}^1Eg$ and charge transfer transition respectively, These transitions values are indicated to square planner geometry [14]. The molar conductivity of complexes in dimethyl sulfoxide (DMSO) are 10.2 and 8. 6 ($cm^2.ohm^{-1}. mol^{-1}$) suggesting that they are non electrolytes complexes.

4. Conclusion

The present work includes synthesis of new ligand and their complexes of Pd(II)and Pt(II), we concluded that the complexes of Pd(II) and Pt(II) most probably to have square planner geometry the ligand chelated with the ionic metal through S and N atoms .

Table 1: Physical properties of synthesized compound and complexe.

Abb.	Formula	Yield%	d.p (°C)	Color
Hg(2-apt)	$C_{12}H_{12}S_2N_2Hg$	80	140	**Light green**
[Pd_2 Hg(2-apt)Cl_4]	$C_{12}H_{12}S_2N_2Pd_2Cl_4$	62	280	**Brown**
[Pt_2 Hg(2-apt)Cl_4]	$C_{12}H_{12}S_2N_2Pt_2Cl_4$	58	258	**Black**

Table 2: Infrared spectral and analysis found (calc.) % data ligand and their complexes.

Cmpound No.	IR spectra (cm^{-1})						Analysis calc. (found.)%			
	N-H	C-H	C-N	C-S	M-N	M-S	C	H	N	S
Hg(2-apt)	3311	3055	1597	750	-	-	43.1 (44.0)	2.67 (2.69)	6.26 (6.69)	14.2 (13.18)
[Pd_2 Hg(2-apt)Cl_4]	3151	3057	1543	758	-	420	23.9 (24.22)	2.01 (2.65)	4.65 (4.09)	1163 (11.02)
[Pt_2 Hg(2-apt)Cl_4]	3157	3049	1550	758	570	-	18.47 (18.95)	1.55 (1.95)	3.59 (4.11)	8.22 (9.11)

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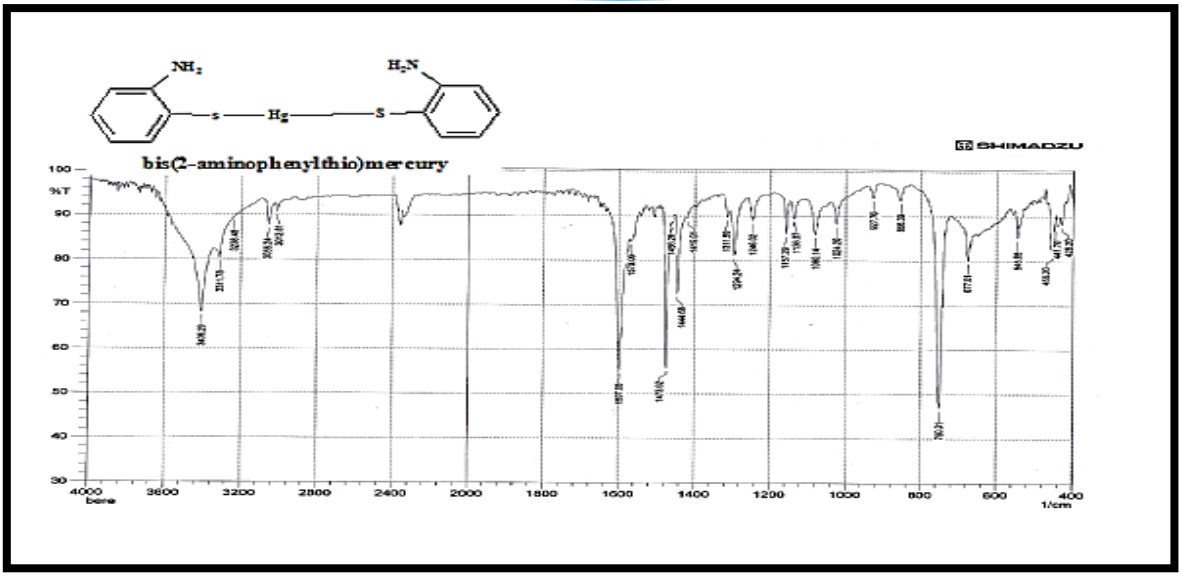

Fig. 1: The IR spectrum of [Hg(2-apt)] compound.

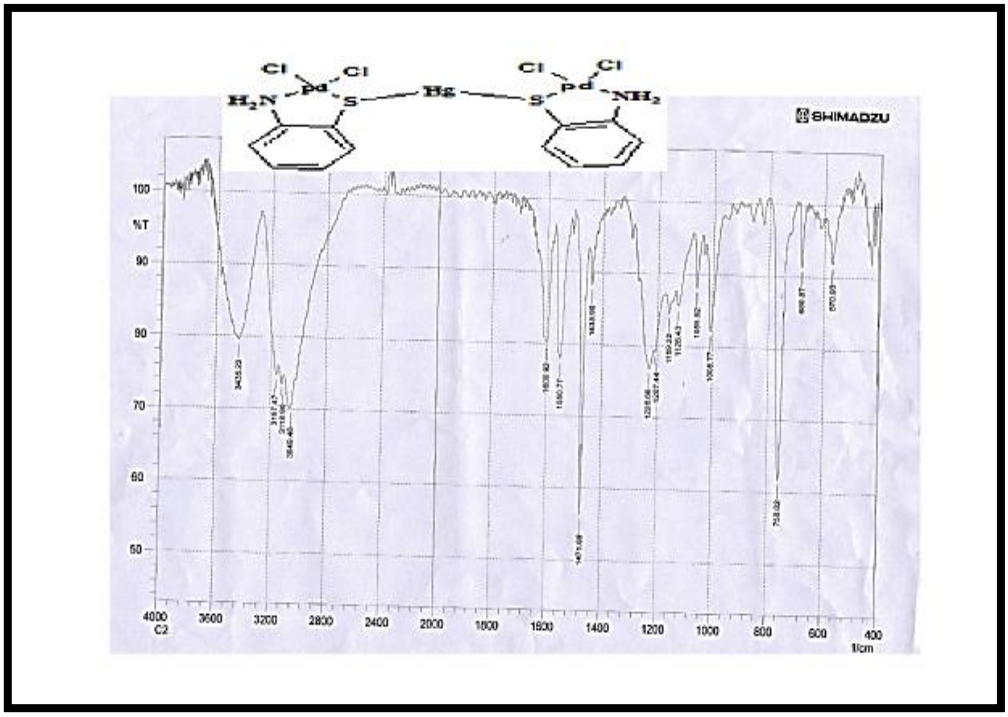

Fig. 2: the IR spectrum of [Pd_2 Hg(2-apt)Cl_4] complex.

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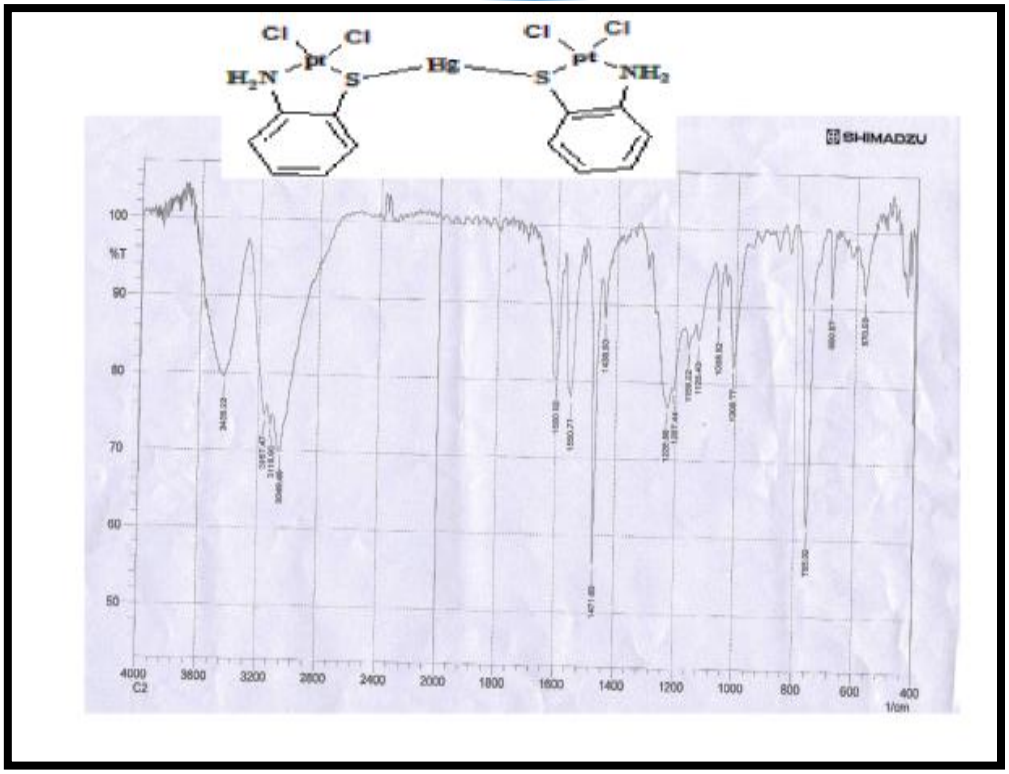

Fig. 3: the IR spectrum of [Pt_2 Hg(2-apt)Cl_4] complex.

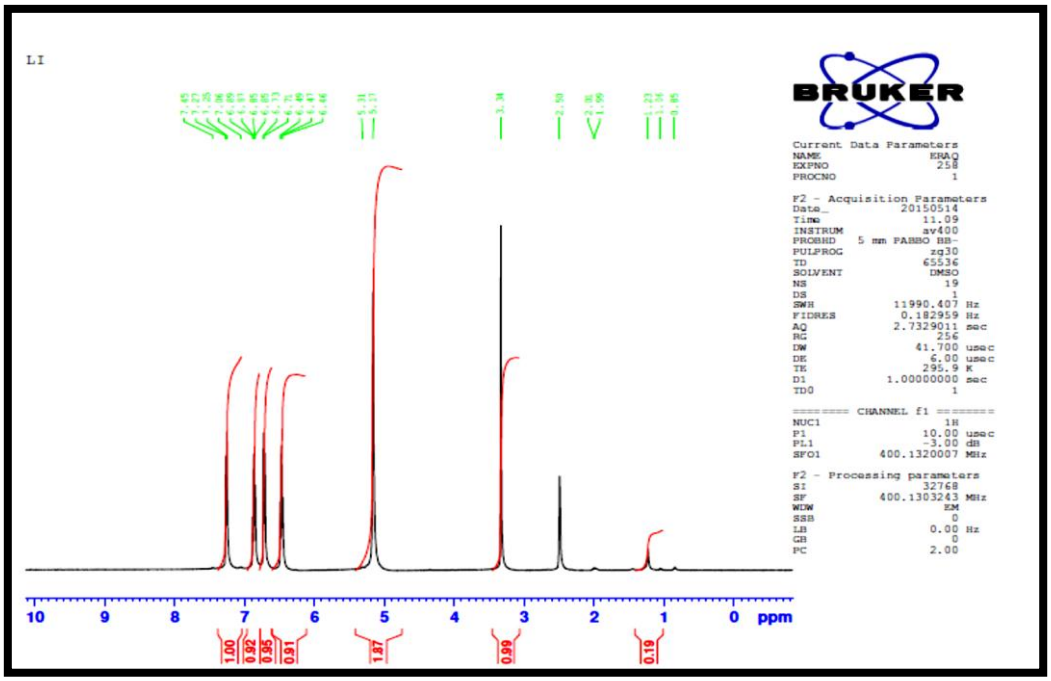

Fig. 4: the ^{1}H-NMR of [Hg(2-apt)] compound.

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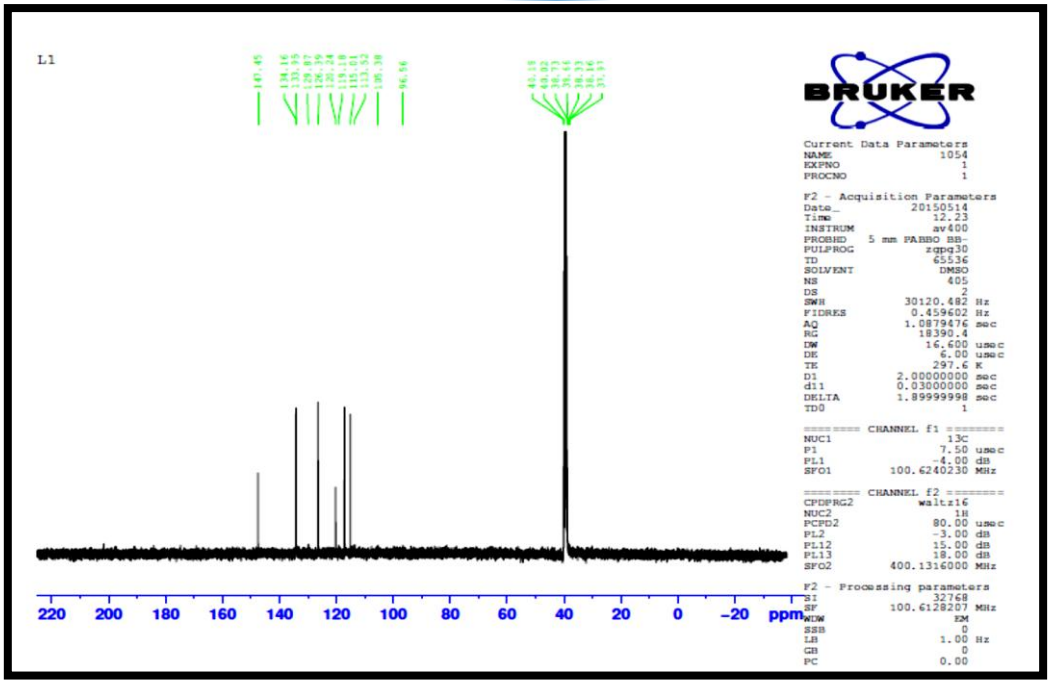

Fig. 5: the ^{13}C-NMR of [Hg(2-apt)] compound.

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