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### Synthesis, Characterization and Chromogenic properties of Lead (II) Complexes containing Hydrazonic Ligands

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methoxybenzaldehyde.

#### ABSTRACT

The hydrazine and hydrazide compounds were subjected to condensation reaction with ketone and different aldehyde derivatives affording the corresponding expected hydrazones. Two hydrazone ligands, namely, 4-hydroxy-(2-hydroxy-3-methoxybenzylidene)benzohydrazide (L1) and 4-hydroxy-(2-hydroxy-4-methoxybenzylidene) benzohydrazide (L2) were synthesized and characterized. The complexation of these ligands with  $Pb^{2+}$  was also investigated and characterized. The chemical structures were found to be consistent with both analytical and spectroscopic data (CHN, FTIR, UV/Vis, TGA,  $^1H$  NMR and  $^{13}C$  NMR). The stoichiometric ratio of their complexes with  $Pb^{2+}$  was found to be 1:1 for (L1- $Pb^{2+}$ ) and (L2- $Pb^{2+}$ ). The chromogenic properties of the ligands upon their complexation with  $Pb^{2+}$  was carried out in different solvents including methanol, ethanol, acetone, acetonitrile, dimethylsulphoxide, and tetrahydrofuran. DMSO was found to be the best solvent for the complexation.

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#### INTRODUCTION

Hydrazine compounds or derivatives are the main starting material in the synthesis and preparation of hydrazone derivatives. Hydrazine, having the formula  $H_2N-NH_2$  or  $N_2H_4$ , can be considered as a nitrogen analog of hydrogen peroxide. It has an ammonia-like odour and is derived from ammonia but its physical properties are similar to water. Hydrazine has an endothermic enthalpy of formation; therefore it is an unstable compound (Brady, 1990). It has been used as rocket fuels because the combustion of hydrazine is very exothermic (Gillepie et al., 1989). Hydrazones have been intensively investigated and their chemical properties were studied. In inorganic chemistry (mainly due to their facile synthesis), tuneable electronic and steric properties and good chelating (Carcelli et al., 1995 and Das pal, 2005) were reported.

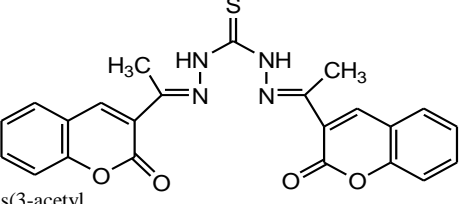
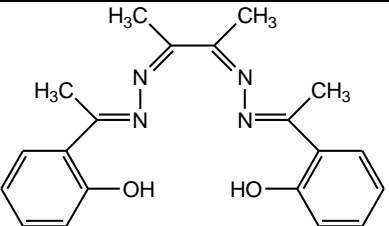
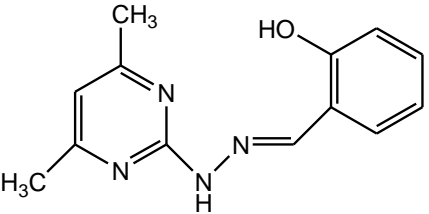
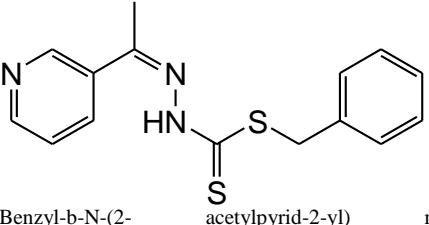
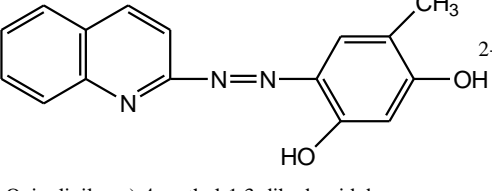
Hydrazone compounds are also found to versatile coordinating abilities towards different metal ions giving well-characterized metal complexes (Raj and Kurup, 2007). They act as multidentate ligands with metal ions (e.g., transition metals) forming coloured chelates which are then used in the selective and sensitive determination of

metal ions (Vasilikiotis and Stratis, 1975). They are also used to determine airborne aldehydes and ketones in air samples by using 2,4-dinitrophenylhydrazine (DNPH) method in which the analytes were analyzed by passing a stream of air through DNPH coated silica gel test tubes which are immediately eluted with acetonitrile and injected into HPLC system (Vogel et al., 2000). In addition they were used for the detection of formaldehyde in libraries (Hanoune et al., 2006). Hydrazone ligands and their complexes with different transition metal ions have been thoroughly investigated due to their biological activity. The arylhydrazones contain in their structure the  $(-CO-NH-N=C<$  group) that imparts on these chelating agents fungicidal. Table 1 shows some examples of hydrazone complexes with metal ions and their applications.

The stability of metal complexes is an important factor determining and predicting speciation, mobility and bioavailability of heavy metals in the environment. A comparative investigation of the complexation of  $Pb^{2+}$  with ligands, the complexes with ligands was investigated. It was found that  $Pb^{2+}$  form mononuclear complexes with ligands such as hydrazone compounds.

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**Table 1:** Some examples of hydrazone complexes with metal ions and their applications

	Ligand ( structure and name )	Metal ions	Application	Reference
1	 <p>Bis(3-acetyl coumarin)thiocarbohydrazone</p>	Co <sup>2+</sup> , Ni <sup>2+</sup> , Cu <sup>2+</sup>	Preliminary anti bacterial and anti fungal.	Sathisha, <i>et. al.</i> , (2008)
2	 <p>2Bis(2-hydroxyacetophenone)butane 2, 3- dihydrazone</p>	Cu <sup>2+</sup>	Excellent ion carrier in the construction of Cu <sup>2+</sup> membrane sensor.	Gholivand, <i>et. al.</i> , (2007)
3	 <p>2,5 Methyl-6-methyl-4-formyl pyrimidine-N(4)-ethyl theosemicarbazone</p>	Cu <sup>2+</sup>	Shows strongly ferromagnetic nature.	Gupta, <i>et. al.</i> , (2008)
4	 <p>S-Benzyl-b-N-(2-dinitrocarbazate methylene acetylpyrid-2-yl)</p>	Cu <sup>2+</sup>	Exhibit marked anti cancer activity.	Thahira, <i>et. al.</i> , (2007)
5	 <p>(2-Quinolinil-azo)-4-methyl-1,3-dihydroxidobenzene</p>	Ag <sup>+</sup> Cr <sup>3+</sup> Ni <sup>2+</sup> Cd <sup>2+</sup> Cu <sup>2+</sup>	Spectrophotometric reagent for determination of the heavy metal ions	Rollas, <i>et. al.</i> , (2007)

## 2. Experimental

### 2.1. Materials and Instrumentations:

The chemicals and solvents considered were of analytical grade, and were used without further purification. Table 2 depicted the chemicals and solvents used. Elemental (CHN) analysis of the prepared hydrazone compounds and their Pb<sup>2+</sup> complexes analysis were carried out using Perkin – Elmer Series II, 2400 elemental analysis. The infrared spectra (IR) were recorded by using KBr system on a Perkin - Elmer 2000 FT-IR spectroscopy unit in the region of 400 – 4000 cm<sup>-1</sup>

<sup>1</sup>. The <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded using a Bruker 300 MHz spectrometer. The structures of the compounds L1 and L2 were solved using direct methods and refined using the full-matrix least-squares method on F2 abs using the using the SHELXTL (Shelrick, 1997) software package. Thermogravimetric analysis (TGA) were carried out using a Perkin – Elmer Thermogravimetric analyzer TGA 7 under nitrogen gas from 0-1000 °C. A scanning rate of 20 °C min and 5.0 – 10.0 mg of the samples were

used. A Perkin- Elmer lambda 35 (dual beam) spectrophotometer was used to obtain UV spectra

for all over the 600-200 nm range with a quartz cell of 1.0 cm path length.

**Table 2:**Chemicals and solvents used in the study

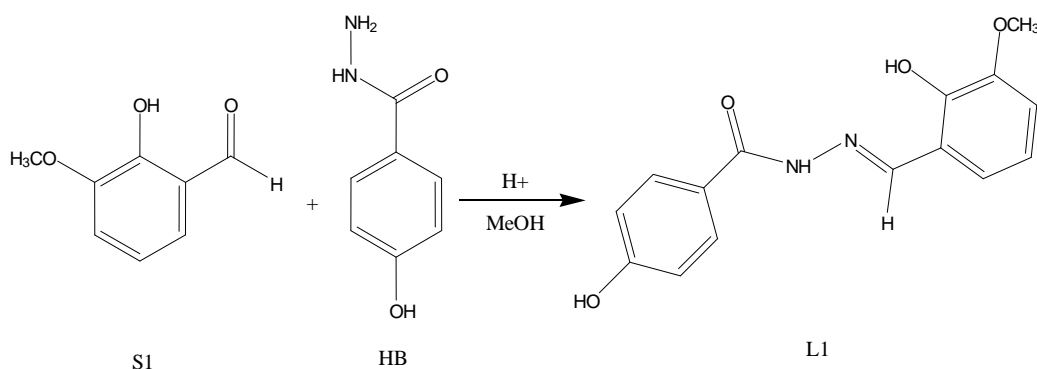
Chemical name	Formula	Purity%	Symbol	Source
4-Hydroxybenzhydrazide	C <sub>7</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	96	HB	MERCK
2-Hdroxy-3-methoxybenzaldehyde	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	98	S1	MERCK
2-Hydroxy-4-methoxybenzaldehyde	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	98	S2	MERCK
Methanol	CH <sub>3</sub> OH	99.8	MeOH	QR&C
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	99.7	EtOH	QR&C
Acetonitrile	C <sub>2</sub> H <sub>3</sub> NO <sub>4</sub>	99.5	MeCN	QR&C
Acetone	C <sub>3</sub> H <sub>6</sub> O	99.5	—	QR&C
Tetrahydrofuran	C <sub>4</sub> H <sub>8</sub> O	99.8	THF	SYSTEM
Dimethylsulphoxide	(CH <sub>3</sub> ) <sub>2</sub> SO	99.9	DMSO	QR&C
Lead acetate	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> Pb	99.5	—	MERCK

## 2.2. Synthesis of the Ligands:

### 2.2.1 Synthesis of 4-hydroxy-(2-hydroxy-3-methoxybenzylidene) benzohydrazide, L1:

A solution of 2-hydroxy-3-methoxybenzaldehyde (S1) (0.152 gm, 1 mmol) in methanol (10 mL) was added dropwise to a methanol solution (10 mL) of HB (0.152 gm, 1 mmol) and the mixture was refluxed for 2 h. The

resulting solution was condensed on a steam bath to 5 mL and cooled to room temperature. Yellow crystals suitable for X-ray diffraction were separated out, filtered off, and then washed with 5 mL of cooled methanol and dried in air (yield 95%). Figure 1 shows the schematic diagram of the reaction.

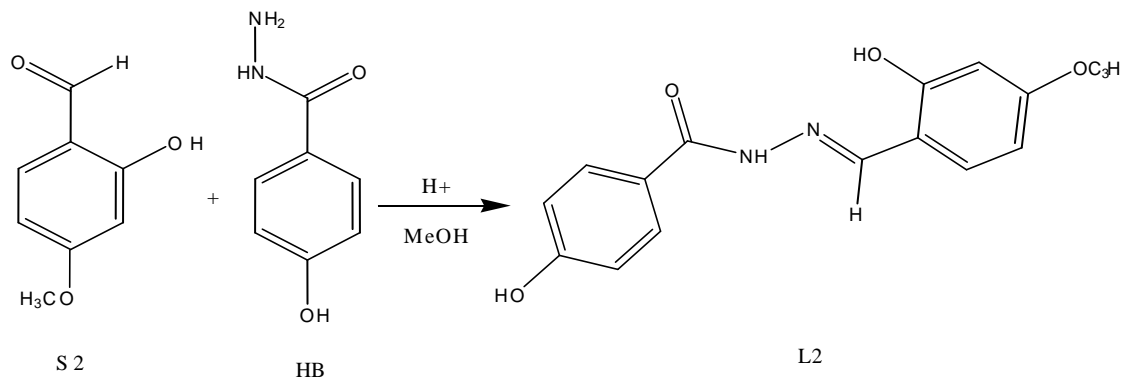


**Fig. 1:**Synthesis of 4-hydroxy-(2-hydroxy-3-methoxybenzylidene)benzohydrazide, L1

### 2.2.2 Synthesis of 4-hydroxy-(2-hydroxy-4-methoxybenzylidene) benzohydrazide, L2:

This ligand was prepared in a similar way as previous ligand [L1]. A solution of 2-hydroxy-4-methoxybenzaldehyde (S2) (0.152 gm, 1 mmol) in methanol (10 mL) was added dropwise to a methanol solution (10 mL) of HB (0.152 gm, 1 mmol) and the mixture was refluxed for 2 h. The resulting

solution was condensed on a steam bath to 5 mL and cooled to room temperature. Yellow crystals suitable for X-ray diffraction were separated out, filtered off, and then washed with 5 mL of cooled methanol and dried in air (yield 85%). Figure 2 shows the schematic diagram of the reaction.



**Fig. 2:**Synthesis of 4-hydroxy-(2-hydroxy-4-methoxybenzylidene) benzohydrazide, L2

### 2.3 Synthesis of the $Pb^{2+}$ complexes:

#### 2.3.1 Synthesis of the $L1-Pb^{2+}$ complex [Pb (L1)]:

To a hot solution of the L1 (2.863 gm, 10 mmol) in 20 mL of ethanol, the lead(II) acetate (1.210 gm, 5 mmol) in 10 mL of ethanol were added. The reaction mixture was heated under reflux for 2 h. The separated precipitate (yellow) was filtered off, washed with water, methanol and finally diethyl ether and then dried in air at room temperature.

#### 2.3.2 Synthesis of the $L2-Pb^{2+}$ complex [Pb (L2) ]:

To a hot solution of the L2 (2.863 gm, 10 mmol) in 20 mL of ethanol, the lead(II) acetate (1.210 gm, 5 mmol) in 10 mL of ethanol were added. The reaction mixture was heated under reflux for 2 h. The separated precipitate (yellow) was

filtered off, washed with water, methanol and finally diethyl ether and then dried in air at room temperature.

## RESULTS AND DISCUSSION

### 3.1 Characterization of ligands:

The hydrazones ligands were synthesized from the interaction of 2-hydroxy-3-methoxybenzaldehyde (S1) and 2-hydroxy-4-methoxybenzaldehyde (S2) with 4-hydroxybenzhydrazide (HB). Two hydrazone ligands namely, L1 and L2 were prepared in good yield via condensation of HB with the above mentioned aldehyde compounds. The ligands were easily purified by recrystallization. Table 3 shows the chemical formula and some of the physical properties of the synthesized ligands.

**Table 3:** Physical some properties of the prepared ligands

Ligands	Chemical formula	Molecular weight (g mol <sup>-1</sup> )	Color
L1	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	286.28	Yellow
L2	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	286.28	Yellow

#### 3.1.1 Elemental analysis (CHN):

The microanalysis of the elements of carbon, hydrogen and nitrogen are comparable with those

calculated from the suggested formula. The CHN analysis for the studied ligands are depicted in Table 4.

**Table 4:** The elemental analysis (CHN) of the synthesized ligands and their complexes

Compound/ Complex	%					
	C		H		N	
	Calculated	Found	Calculated	Found	Calculated	Found
L1	62.93	59.29	4.93	4.84	9.79	9.16
L2	62.93	59.20	4.93	4.91	9.79	9.13
Pb (L1)	36.51	39.85	2.86	2.88	5.68	5.24
Pb (L2)	36.51	37.44	2.86	2.14	5.68	5.11

#### 3.1.2 FT-IR analysis:

##### 3.1.2.1 Ligands:

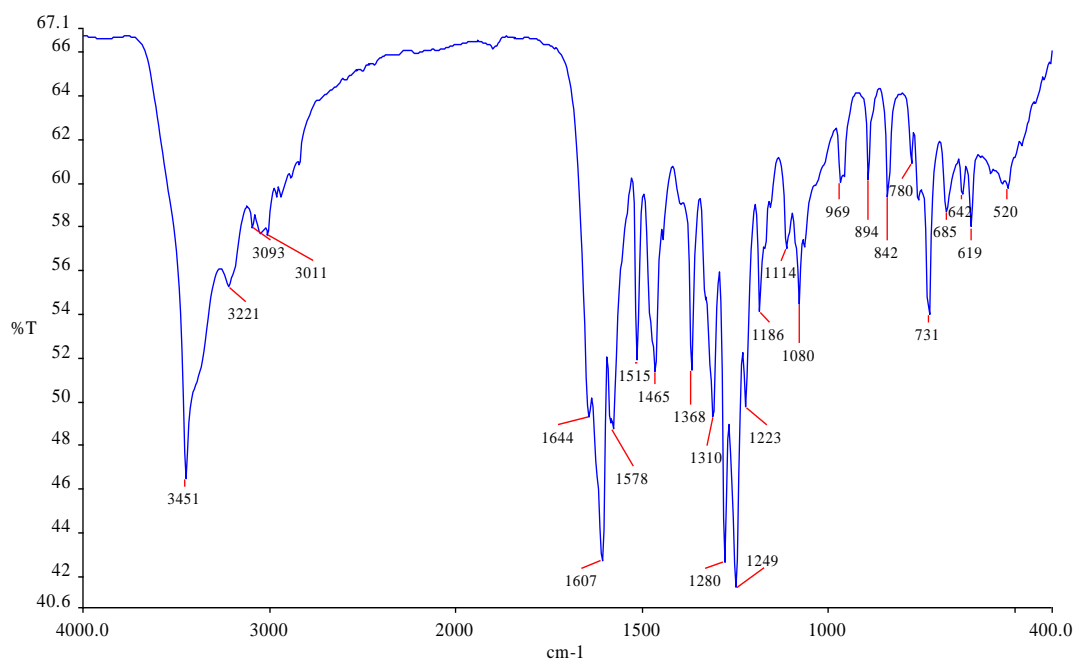
The FTIR data of the ligands (L1 & L2) are given in Table 5 and shown figure 3 and figure 4. The results showed that the O-H functional group in L1 and L2 were assigned at 3451 and 3444 cm<sup>-1</sup>, respectively (Kemp, 1996). The azomethine stretching at vibration for the ligands are observed at 1531-1578 cm<sup>-1</sup> (Stamatouiet al., 2008). Moreover, a strong bond at the frequency range of 1431-1494 cm<sup>-1</sup> can be assigned to the C=C stretching (Yeapet al., 2003).

##### 3.1.2.2 Ligands – $Pb^{2+}$ complexes:

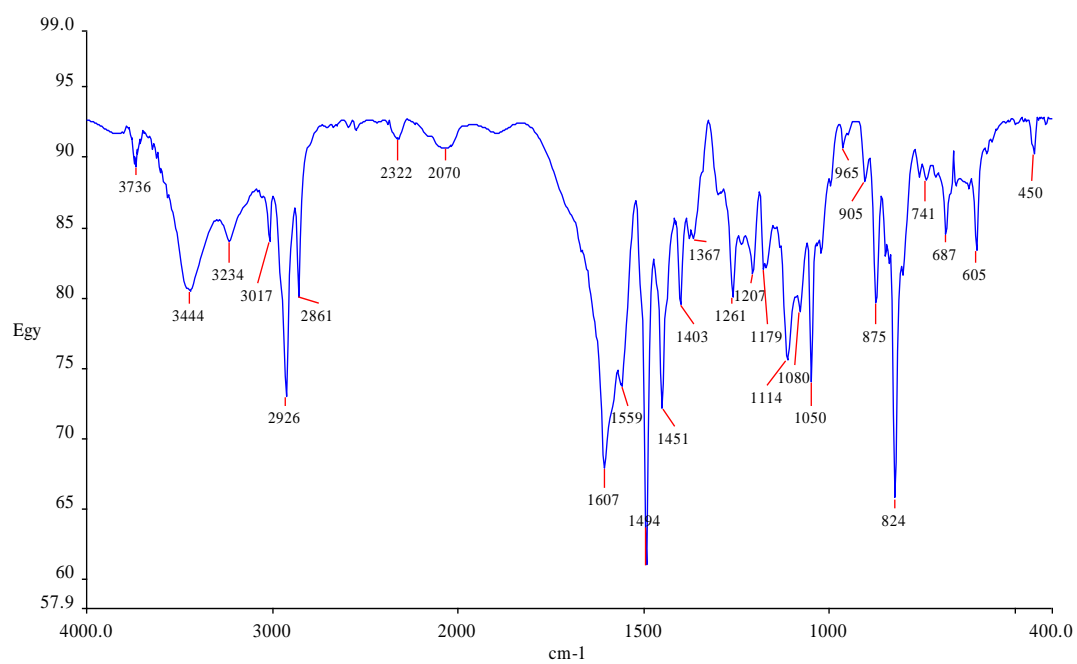
The comparison between the FT-IR spectra of ligands and ligands –  $Pb^{2+}$  complexes (Figure 5 and Figure 6) indicated that the ligands are principally coordinated to the metal ions in two ways; the band appearing at 1578 and 1559 cm<sup>-1</sup> (respectively) due to the C=N group is shifted to 1570 and 1531 cm<sup>-1</sup> in the complexes, indicating the participation of the azomethine nitrogen in the interaction with the metal ion. A broad band appearing at 3451 and 3444 cm<sup>-1</sup> assigned to the OH function group is also shifted to 3201 and 3097 cm<sup>-1</sup>. These confirm the participation of the O and N atoms in the coordination. Table 5 summarizes the IR data for the studied ligands and their complexes with  $Pb^{2+}$ .

**Table 5:** Summary of FT-IR spectral data for L1 and L2 and their complexes with lead, L1- $Pb^{2+}$  and L2 –  $Pb^{2+}$ .

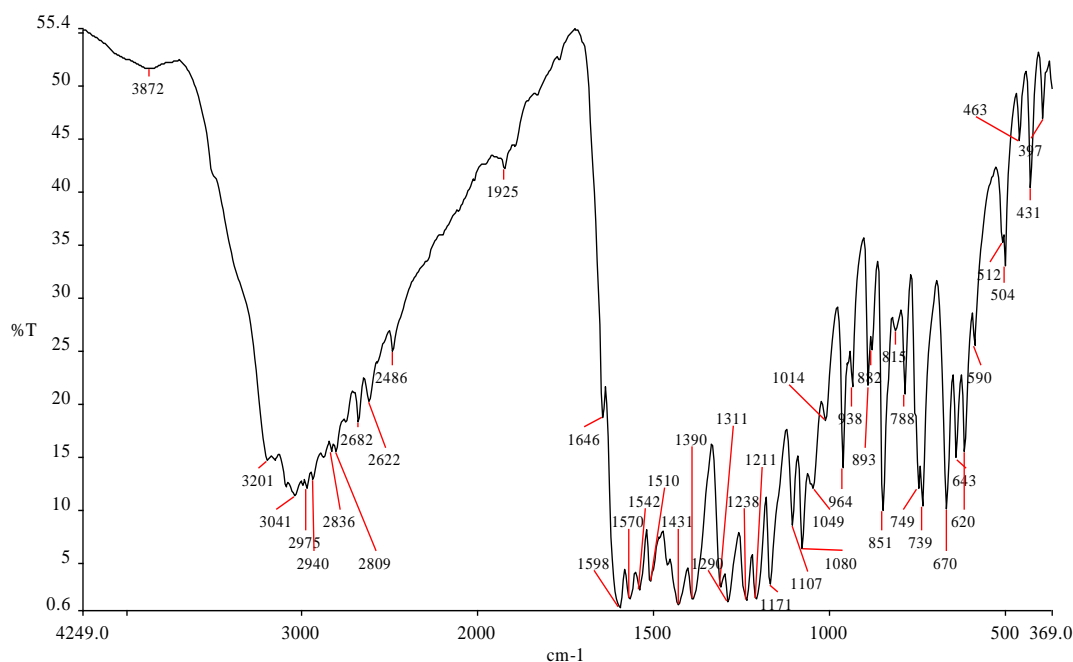
Absorption band	Vibration assignment (v) (cm <sup>-1</sup> )					
	O-H	C-H	C=O	C=C	C=N	C-O
L1	3451	3093	1644	1465	1578	1080
Pb(L1)	3201	3041	1598	1431	1570	1080
L2	3444	3017	1607	1494	1559	1050
Pb(L2)	3097	3010	1598	1461	1531	1020



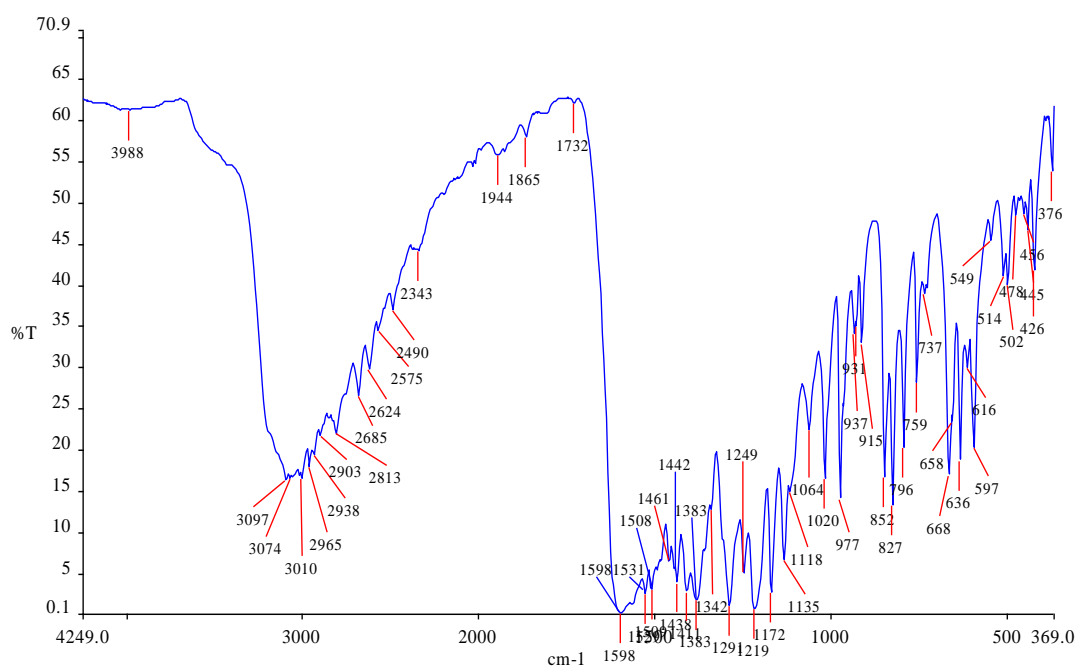
**Fig.3:** FT-IR spectrum of ligand1 (L1)



**Fig. 4:** FT-IR spectrum of ligand2 (L2)



**Fig.5:** FT-IR spectrum of ligand 1 – Pb<sup>2+</sup> complex [Pb (L1) ]



**Fig.6:** FT-IR spectrum of ligand2 – Pb<sup>2+</sup> complex [Pb (L2) ]

### 3.1.3 NMR spectroscopy analysis:

#### 3.1.3.1 <sup>1</sup>H NMR analysis:

The <sup>1</sup>H NMR spectra of the studied ligands compounds (L1 and L2) were measured in dimethylsulfoxide solutions (DMSO-*d*<sub>6</sub>). The solvent was chosen for the following reasons: firstly, insufficient solubility of the studied compounds in solvents such as chloroform or acetone. Secondly, electron-conducting properties of DMSO minimize the possibility of the formation of hydrogen-bonded association between the active groups of the

substituent of the compounds studied (Quellette *et al.*, 1965; Tumkevičius *et al.*, 2005).

#### 3.1.3.1.1 Ligand 1 (L1) & Pb<sup>2+</sup>– (L1):

The spectrum of L1 (Figure 7) shows ten groups of resonance (3.82, 6.86, 6.90, 7.01, 7.11, 7.84, 8.62, 10.22, 11.17 and 11.91 ppm). The signal at 3.46 ppm is due to solvent peak (DMSO-*d*<sub>6</sub>). Additionally, the N-H proton in L1 (H<sub>j</sub>) is observed at 11.91 ppm. The <sup>1</sup>H NMR spectrum also displayed the O-H protons of the phenolic groups and azomethine protons (H-C=N), which appear at

10.22, 11.17 ppm and 8.62 ppm, as singlets, respectively. The data of the L1 spectrum is summarized in condensed format as:

Ha :  $\delta$  3.82 ppm (3H, s), Hb  $\delta$  6.86 ppm (1H, t,  $^3J_{\text{HH}} = 4.7$  Hz), Hc  $\delta$  6.90 ppm (2H, d,  $^3J_{\text{HH}} = 5.2$  Hz), Hd  $\delta$  7.01 ppm (1H, d,  $^3J_{\text{HH}} = 4.8$  Hz), Hf  $\delta$  7.11 ppm (1H, d,  $^3J_{\text{HH}} = 4.1$  Hz), He  $\delta$  7.84 ppm (2H, d,  $^3J_{\text{HH}} = 5.4$  Hz), Hg  $\delta$  8.62 ppm (1H, s), Hh  $\delta$  10.22 ppm (1H, s), Hi  $\delta$  11.17 ppm (1H, s) and Hj  $\delta$  11.91 ppm (1H, s).

The difference between the  $^1\text{H}$  NMR spectra of L3, and its complex with  $\text{Pb}^{2+}$  can be noticed from the signals at 10.22 and 11.17 ppm (due to the OH group) at the free L1 being shifted downfield to 7.59 ppm (Figure 8) upon complexation. Additionally, the signal at 11.91 ppm (due to azomethine group) has also shifted downfield to 8.54 ppm, thus indicating the coordination of the hydroxyl oxygen to the metal atom. This confirms the participation of the O and N atom in the coordination.

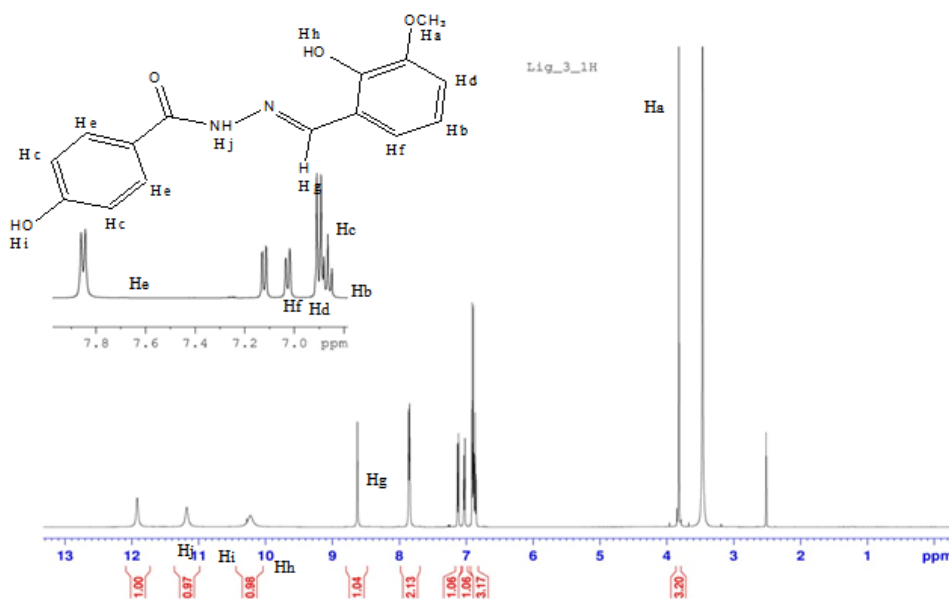


Fig. 7: The  $^1\text{H}$  NMR spectrum of the ligand L1 in  $\text{DMSO-}d_6$

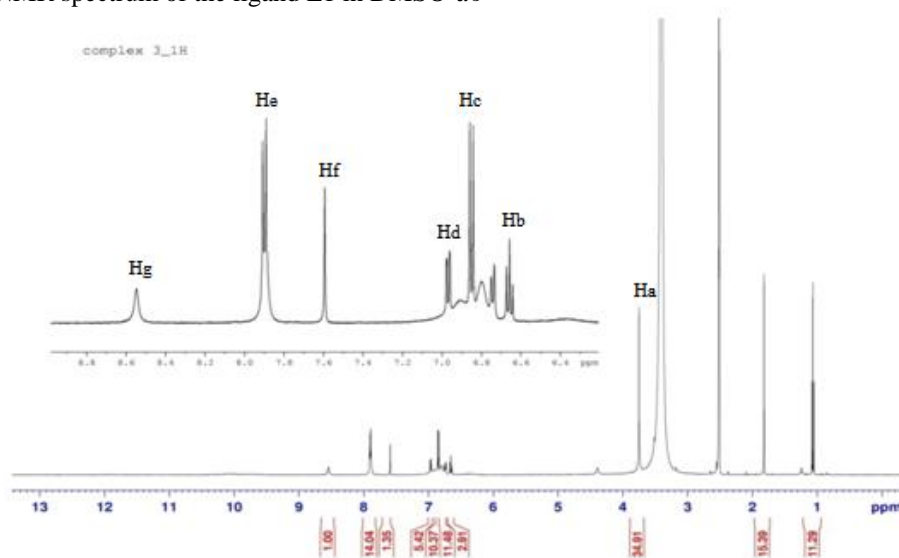


Fig. 8: The  $^1\text{H}$  NMR spectrum of the ligand L1- $\text{Pb}^{2+}$  complex in  $\text{DMSO-}d_6$

### 3.1.3.1.2 Ligand2 (L2) & $\text{Pb}^{2+}$ - (L2):

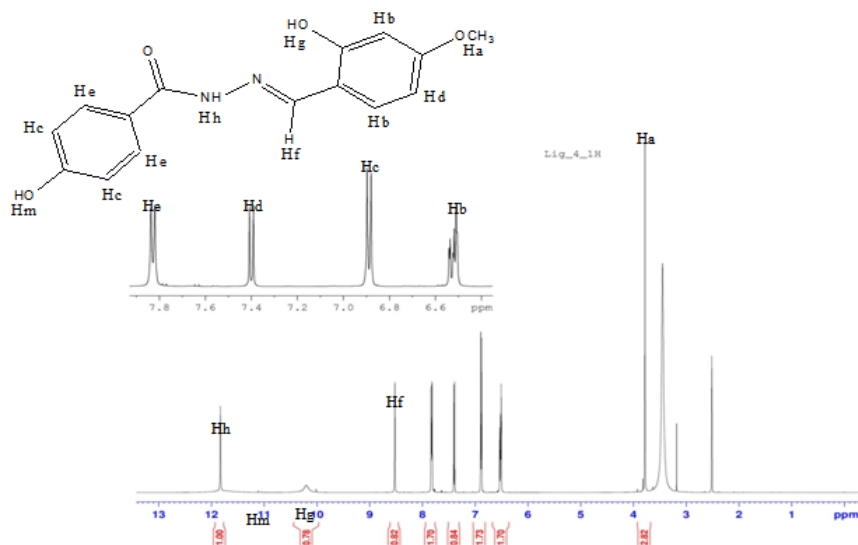
The spectrum of L2 (Figure 9) shows eight groups of resonance (3.78, 6.50, 6.89, 7.40, 7.81,

8.52, 10.20 and 11.83 ppm). The signal at 3.44 ppm is due to solvent peak ( $\text{DMSO-}d_6$ ). Additionally, the N-H proton in L2 (Hh) is observed at 11.83 ppm. The

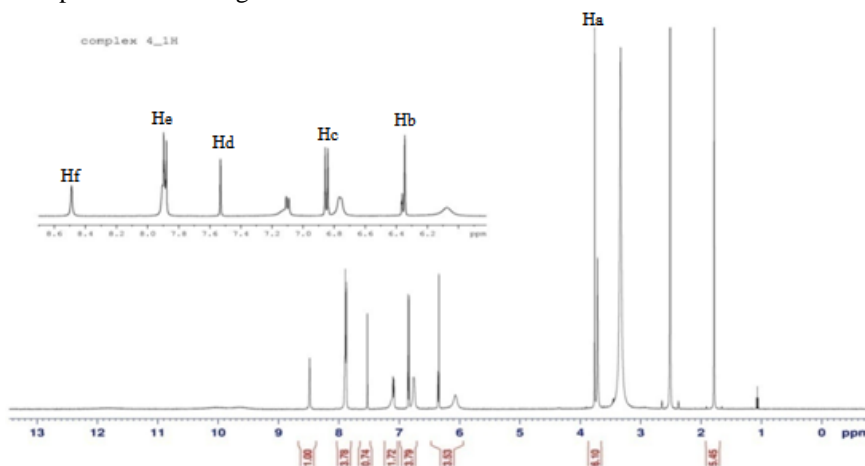
$^1\text{H}$  NMR spectrum also displayed the O-H protons of the phenolic groups and azomethine protons (H-C=N), which appear at 10.20 ppm, 11.11 ppm and 8.52 ppm, as singlets, respectively. The data of the L2 spectrum is summarized in condensed format as:

Ha :  $\delta$  3.78 ppm (3H, s), Hb  $\delta$  6.50 ppm (2H, d,  $^3J_{\text{HH}} = 2.7$  Hz), Hc  $\delta$  6.89 ppm (2H, d,  $^3J_{\text{HH}} = 5.2$  Hz), Hd  $\delta$  7.40 ppm (1H, d,  $^3J_{\text{HH}} = 5.1$  Hz), He  $\delta$  7.81 ppm (2H, d,  $^3J_{\text{HH}} = 5.1$  Hz), Hf  $\delta$  8.52 ppm (1H, s), Hg  $\delta$  10.20 ppm (1H, s), Hm  $\delta$  11.11 ppm (1H, s) and Hh  $\delta$  11.83 ppm (1H, s).

The difference between the  $^1\text{H}$  NMR spectra of L2, and its complex with  $\text{Pb}^{2+}$  can be noticed from the signal at 10.20 ppm and 11.11 ppm (due to the OH group) at the free L2 being shifted downfield to 7.53 ppm (Figure 10) upon complexation. Additionally, the signals at 11.83 ppm (due to azomethine group) has also shifted downfield to 8.48 ppm, thus indicating the coordination of the hydroxyl oxygen to the metal atom. This confirms the participation of the O and N atom in the coordination.



**Fig.9:**The  $^1\text{H}$ NMR spectrum of the ligand L2 in  $\text{DMSO}-d_6$



**Fig. 10:**The  $^1\text{H}$ NMR spectrum of the ligand L2- $\text{Pb}^{2+}$  complex in  $\text{DMSO}-d_6$

### 3.1.3.2 $^{13}\text{C}$ NMR analysis:

#### 3.1.3.2.1 Ligand 1 (L1) & $\text{Pb}^{2+}$ - (L1):

The  $^{13}\text{C}$  NMR spectrum for L1, gives rise to twelve signals (56.1, 113.8, 115.1, 119.0, 121.1, 123.2, 129.7, 147.2, 147.6, 147.9, 160.9 and 162.5 ppm). The signal at 39.6 ppm is due to solvent peak ( $\text{DMSO}-d_6$ ). The difference between the  $^{13}\text{C}$  NMR spectra of L1, and its complex with  $\text{Pb}^{2+}$  can be noticed from the signals at 115.1, 116.4, 129.7, 131.1 and 147.7 ppm being shifted downfield to

56.0, 112.0, 113.1, 115.5, 120.5, 121.6, 127.4, 142.0, 145.0, 147.1, 165.1 and 169.8 ppm upon complexation. The assignment of signals falling in the L1 and its complex with  $\text{Pb}^{2+}$  is summarized in Table 6.

#### 3.1.3.2.2 Ligand2 (L2) & $\text{Pb}^{2+}$ - (L2):

The  $^{13}\text{C}$  NMR spectrum for L2, gives rise to thirteen signals (155.3, 101.2, 106.6, 111.8, 115.2, 123.3, 129.6, 131.2, 148.6, 159.4, 160.8, 161.9 and



162.3 ppm). The signal at 39.7 ppm is due to solvent peak (DMSO-*d*<sub>6</sub>). The difference between the <sup>13</sup>C NMR spectra of L2, and its complex with Pb<sup>2+</sup> can be notice from the signals at 155.3, 101.2, 106.6, 111.8, 115.2, 123.3, 129.6, 131.2, 148.6, 159.4, 160.8, 161.9 and 162.3 ppm

being shifted downfield to 55.1, 105.5, 108.0, 115.2, 118.1, 125.5, 129.4, 136.2, 150.5, 164.7, 168.0, 168.9 and 171.1 ppm upon complexation. The assignment of signals falling in the L2 and its complex with Pb<sup>2+</sup> is summarized in Table 6.

**Table 6:** The assignment of chemical shift to the studies ligands their complexes with Pb<sup>2+</sup>

Compounds	Chemical shift, ppm												
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
L1	56.1	113.8	115.1	119.0	121.1	123.2	129.7	147.2	147.6	147.9	160.9	162.5	-
Pb(L1)	56.0	112.0	113.1	115.5	120.5	121.6	127.4	142.0	145.0	147.1	165.1	169.8	-
L2	155.3	101.2	106.6	111.8	115.2	123.3	129.6	131.2	148.6	159.4	160.8	161.9	162.3
Pb(L2)	55.1	105.5	108.0	115.2	118.1	125.5	129.4	136.2	150.5	164.7	168.0	168.9	171.1

### 3.1.4 Thermal analysis:

Thermogravimetric analysis (TGA) of the ligands (L1 and L2) shows that the free ligands and complexes exhibited high thermal stabilities. Tables 7 and 8, present the TGA data of these ligands (L1 and L2) and their complexes (L1-Pb<sup>2+</sup> and L2-

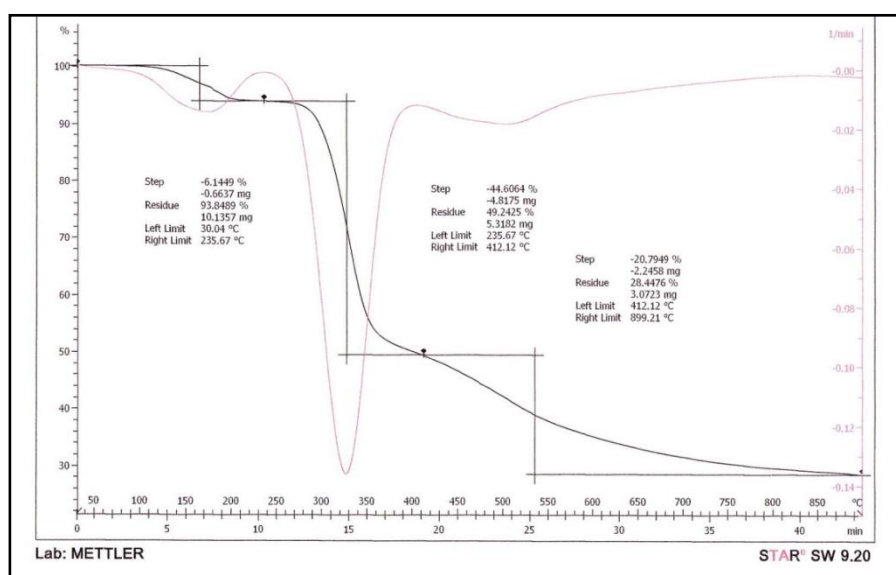
Pb<sup>2+</sup>). The decomposition of these ligands and their complexes began around 200 °C (Heating rate; 20°C/min in the range from 0 – 1000°C, under nitrogen atmosphere) and took place in three steps for L1 and four for L2, three for L1-Pb<sup>2+</sup> and L2-Pb<sup>2+</sup> (see the Figure 11 -Figure 14).

**Table 7:** Thermal data for the decomposition processes of ligands, L1 and L2

Compounds	M. wt	Temperature °C	Wt. Loss %	Residue %
L1	286.28	30.04 – 235.67	6.14	93.84
		235.67 – 412.12	44.60	49.24
		412.12 – 899.21	20.79	28.44
L2	286.28	30.05 – 191.45	5.79	94.24
		191.45 – 419.80	51.49	42.74
		419.80 – 589.40	6.99	35.75
		589.40 – 897.95	7.52	28.22

**Table 8:** Thermal data for the decomposition processes of complexes L1- Pb<sup>2+</sup> and L2-Pb<sup>2+</sup>

Compounds	M. wt	Temperature °C	Wt. Loss %	Residue %
Pb(L1)	809.83	30.61 – 216.62	2.80	97.17
		216.62 – 435.01	28.91	68.26
		435.01 – 896.66	13.51	54.74
Pb(L2)	809.83	29.77 – 304.20	10.74	89.26
		304.20 – 456.11	23.80	65.45
		456.11 – 895.98	13.93	51.51



**Fig. 11:** The Thermogravimetric analysis (TGA) of the ligand L1

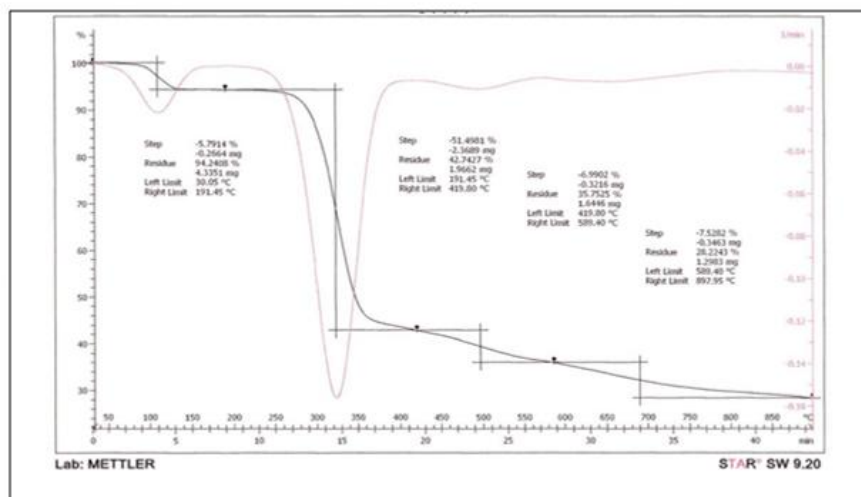


Fig. 12: The Thermogravimetric analysis (TGA) of the ligand L2

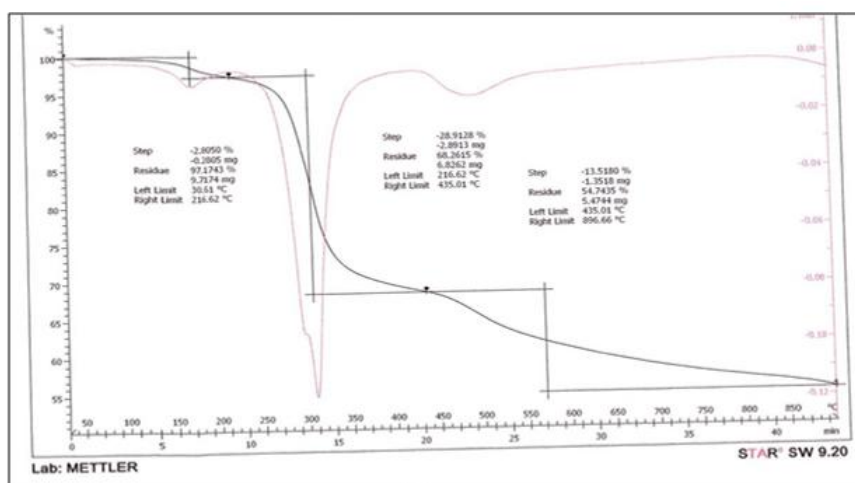


Fig. 13: The Thermogravimetric analysis (TGA) of the complex L1-Pb<sup>2+</sup>

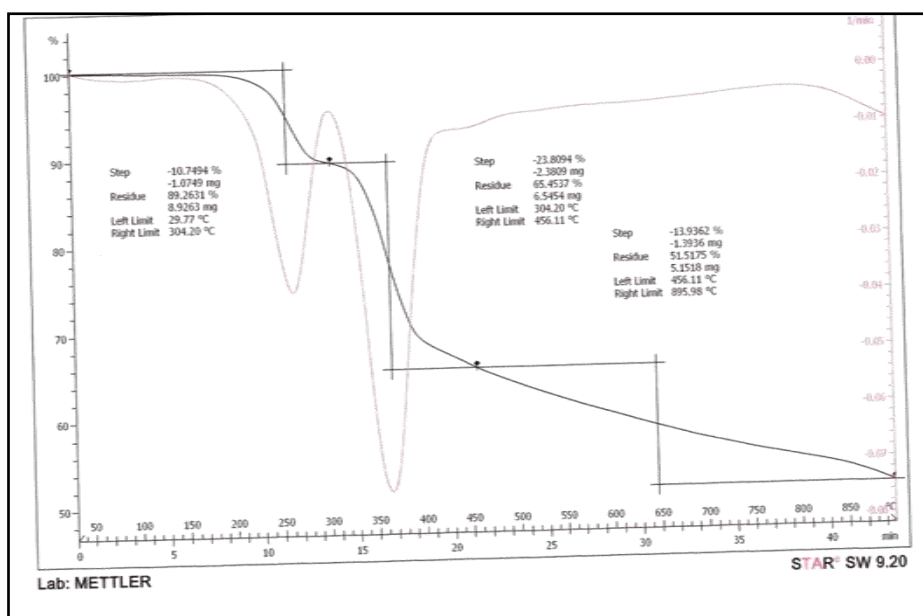


Fig. 14: The Thermogravimetric analysis (TGA) of the complex L2-Pb<sup>2+</sup>

### 3.2 Chromogenic properties of the ligands and their complexes:

#### 3.2.1 Solvent effects on the absorption spectra for the ligands and their complexes with lead:

The effect of solvent on the chromogenic properties of the ligands and their complexes was investigated. The absorption spectra of ligands (L1 and L2) and complexes (L1-Pb<sup>2+</sup> and L2-Pb<sup>2+</sup>) were recorded in various solvents at a concentration of  $1 \times 10^{-5}$  M for the five ligands and their complexes with lead (Figures 15 and 16). Their corresponding wavelength ( $\lambda_{\max}$ ) and their absorption

are given in Table 9. The main absorption band is located in the visible region within a range from 200 - 600 nm, which could be assigned to  $\pi$ - $\pi^*$  transition in the large conjugated system. Among the studied solvents, DMSO shows the best complexation medium for the complexation of the studied ligands with lead. Figure 16 shows a comparison between L1 and L2 where both ligands contained both -OH and -OCH<sub>3</sub> groups at different positions (2,3- and 2,4-positions, respectively). The ligand (L2) showed a better complexation with lead in all solvents except DMSO comparing with L1.

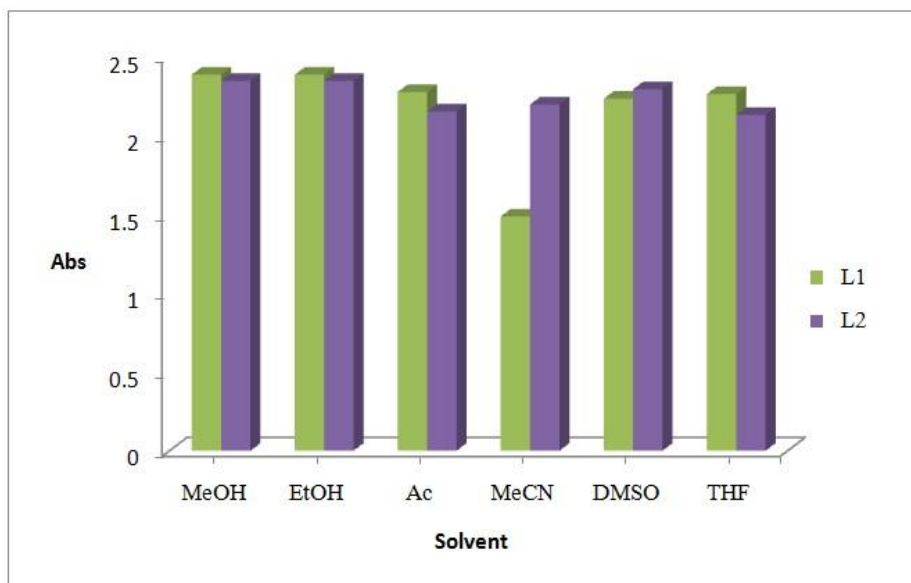


Fig. 15: Comparison of chromogenic properties the ligands

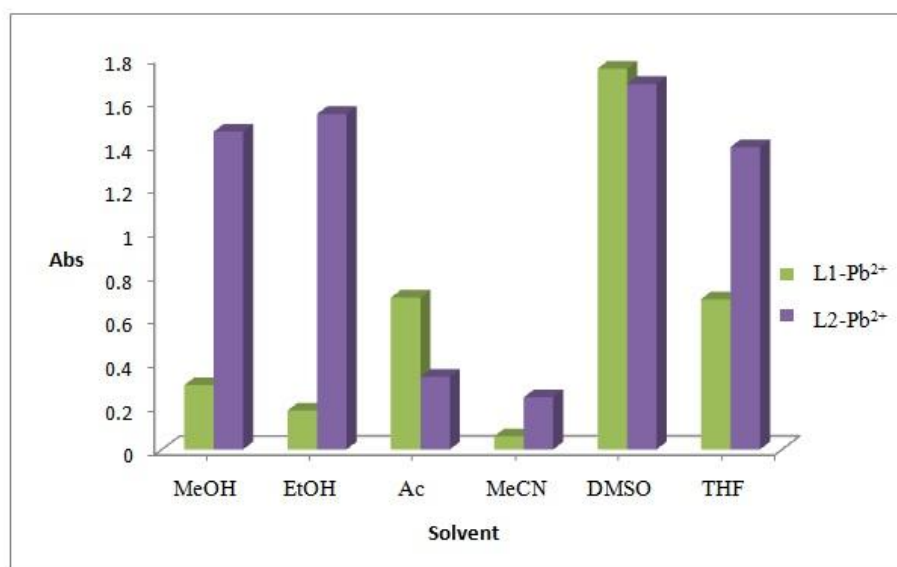


Fig. 16: Comparison of chromogenic properties the ligands complexes with Pb<sup>2+</sup>

**Table9:** The  $\lambda_{\text{max}}$  for ligands and their complex with lead ion in different solvent

Comp.	MeOH		EtOH		Acetone		MeCN		DMSO		THF	
	$\lambda_{\text{max}}$ (nm)	Abs.	$\lambda_{\text{max}}$ (nm)	Abs.	$\lambda_{\text{max}}$ (nm)	Abs.	$\lambda_{\text{max}}$ (nm)	Abs.	$\lambda_{\text{max}}$ (nm)	Abs.	$\lambda_{\text{max}}$ (nm)	Abs.
L1	354	2.3888	354	2.3888	351	2.2790	350	1.4882	350	2.2363	350	2.2655
L2	355	2.3491	355	2.3491	353	2.1558	354	2.1997	355	2.2963	351	2.1326
Pb(L1)	392	.2948	390	0.1788	390	0.6974	390	0.0604	453	1.7491	401	0.6897
Pb(L2)	418	1.4599	423	1.5407	390	0.3336	390	0.2395	443	1.6786	420	1.3890

### Conclusions

Two hydrazone ligands, L1 and L2 and their complexes with  $\text{Pb}^{2+}$ ,  $\text{L1-Pb}^{2+}$  and  $\text{L2-Pb}^{2+}$  were synthesized. Their structures were characterized and confirmed by using CHN, FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, TGA and UV-Vis spectroscopy.

Both synthesized ligands and complexes are insoluble in water, but soluble in other common organic solvents studied, such as acetone, acetonitrile, tetrahydrofuran and dimethylsulfoxide. The stoichiometric ratio of their complexes with  $\text{Pb}^{2+}$  was equal to 1:1 for ( $\text{L1-Pb}^{2+}$ ) and ( $\text{L2-Pb}^{2+}$ ). The chromogenic properties of the ligands upon complexation with  $\text{Pb}^{2+}$  was carried out in indifferent solvents including methanol, ethanol, acetone, acetonitrile, dimethylsulphoxide, and tetrahydrofuran. DMSO was the best solvent for the complexation. Among the studied ligands, L2 was the best ligand for complexation with  $\text{Pb}^{2+}$  in DMSO.

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