

## Synthesis, spectral characterization and theoretical investigation of some new mercury four coordinated complexes

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Some new mercury complexes of a bidentate Schiff base ligand with two nitrogen atoms as donor sites have been prepared and characterized by spectroscopic and analytical studies such as IR, UV-Vis, <sup>1</sup>H NMR and <sup>13</sup>C NMR, elemental analysis and molar conductivity. The IR spectrum of ligand showed the characteristic asymmetric and symmetric vibrations of iminic groups at 1624 and 1620 cm<sup>-1</sup> respectively that were unified and shifted by 6-8 cm<sup>-1</sup> to lower energies. The iminic proton signals of ligand were appeared as two doublets at 7.87 and 7.77 ppm that were downfielded to 7.92-8.91 ppm after coordination to mercury ion in the complexes. The analytical data confirmed 1:1 ratio for ligand to metal salt in all complexes. The structural optimization of ligand and complexes was performed at the UB3LYP/LANL2MB/ level of theory and then some important structural (Bond length(Å), Bond angle(°) and Torsion angle(°)) and theoretical energetic(HF-Energy, ZPE, ΔE, ΔG, ΔE<sub>electronic</sub> and ΔH) data were derived. The bond lengths(Å) of Hg-N(1) and Hg-N(2) were decreased from mercury chloride to mercury thiocyanate complex and then decreased in mercury azide complex. The bond angle (°) of N(1)-Hg-N(2) in the complexes was smoothly increased from mercury chloride to mercury thiocyanate complex and then decreased in mercury azide complex. The opposite of this trend was evaluated for X(1)-Hg-X(2). Accordingly pseudo-tetrahedral geometry was suggested for all complexes. Therefore the general formula for Hg(II) complexes is MLX<sub>2</sub> that in which X= Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup> and N<sub>3</sub><sup>-</sup>.

**Key-words:** Schiff base; Theoretical; Optimization; Spectroscopic; Mercury.

### INTRODUCTION

Schiff bases as an important class of chelating ligands have played an important role in the development of coordination chemistry because of formation of various stable complexes with the most transition metal ions [1–7]. Synthesis of new Schiff bases and their metal complexes are still the aim of many recent investigations due to the wide applications of Schiff bases ligands and their complexes in the biological and chemical fields [6–10]. DNA cleavage activity [11], biomimetic enzyme models [12–14], tumor growth inhibitors, as antiviral, antifungal and antibacterial agents in biological fields [15–18] and ability to reversibly binding oxygen [19], their usage as catalysis [20–23], liquid crystal [24, 25], pigments and dyes and polymer stabilizers [26] in chemical fields are the most important applications of Schiff bases. Also, Schiff-bases with donors (N, O, S and etc.) have structural similarities with neutral biological systems and due to the presence of imine groups are

utilized in explanation of the mechanism of transformation and racemization reaction in biological system [27–29].

In the course of our studies on transition metal Schiff base complexes [30–35], we report synthesis and characterization a series of HgLX<sub>2</sub> in which X= Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup> and N<sub>3</sub><sup>-</sup> with N, N'-bis((E)3-phenylallylidene)-4-methyl-1,2-phenyldiamine (L) as a new bidentate ligand. The structural features of the Schiff base and their metal complexes have been studied by various spectral and analytical. Furthermore, the structural optimization of ligand and complexes was performed at the UB3LYP/LANL2MB/ level of theory and then some important structural and theoretical energetic data were derived.

### EXPERIMENTAL

#### Materials and methods

Cinnamaldehyde, 4-methyl-1,2-phenyldiamine, mercury(II) halides and other chemicals were purchased from either Aldrich, Merck or BDH Chemicals. All of the chemicals used were analytical grade. Solvents such as methanol and dichloromethane were purified and dried before the

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use according to the standard methods. FT-IR spectra as KBr pellets were recorded on a JASCO FT/IR-680 spectrometer in the 4000–400  $\text{cm}^{-1}$  range. Electronic spectra were recorded in DMSO and chloroform solutions on a JASCO-V570 model spectrometer with quartz cells of 0.5 cm path length.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker DPX FT-NMR spectrometer at 500 MHz with the samples dissolved in DMSO- $d_6$  mixture using TMS as internal standard. Carbon, hydrogen and nitrogen of dried samples were performed using elemental analyzer. The melting points ( $^{\circ}\text{C}$ ) of the complexes were recorded on BI Barnstead melting point instrument. Conductivity measurements of the ligand and their complexes were made on freshly prepared  $10^{-3}$  M solutions in DMSO and/or chloroform at room temperature with a Metrohm 712 conductometer with a dip-type conductivity cell made of platinum black. Theoretical optimization of the Schiff-base ligand and its complexes were carried out at the UB3LYP/LANL2MB/level of theory.

*Preparation of N, N'-bis((E)3-phenylallylidene)-4-methyl-1,2-phenyldiamin (L)*

N, N'-bis((E)3-phenylallylidene)-4-methyl-1,2-phenyldiamin (L) as a bidentate Schiff base was synthesized by condensation reaction between 4-methyl-1,2-phenyldiamine (5 mmol, 0.611 g) and trans-cinnamaldehyde (10 mmol, 1.321 g) in 40 mL diethyl ether as solvent under ice bath with rigorous stirring for 5-6 h. After completion of the reaction, the solvent was reduced under vacuum to give the Schiff base as very viscous oil. For more purification, the oil was washed twice with n-hexane and dried under vacuum.

IR(KBr,  $\text{cm}^{-1}$ ): 3376(m), 3051(w), 3024(w), 2916(w), 2848(w), 1624(s), 1600(s), 1582(s), 1507(s), 1448(s), 1382(w), 1302(m), 1150(w), 998(m), 848(w), 802(m), 751(s), 690(s). UV-Vis [(CHCl<sub>3</sub>),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 296(37173) and 376(13002).  $^1\text{H}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 7.87(d, 1H, J= 7.15 Hz), 7.77(d, 1H, J= 6.52 Hz), 7.66-7.42(m, 6H), 7.24(m, 5H), 7.04(d, 2H, J= 8.30 Hz), 7.00(bd, 2H, J= 8.20 Hz), 6.91(d, 2H, J= 8.45 Hz), 2.43(s, 3H).

*Preparation of mercury complexes*

A solution of ligand (1 mmol, 0.350 g) in 10 mL methanol was added drop wise to a methanolic solution (20 mL) of  $\text{HgX}_2$  salts, in which X= chloride, bromide, iodide, thiocyanate and azide (mercury thiocyanate and azide were prepared similar to previous report[31]), under severe stirring

under room temperature conditions. The complexes were obtained after 2-3 h as colored precipitates that were filtered and washed with ethanol for more purification. Then complexes were dried at 80-100  $^{\circ}\text{C}$  under vacuum and were kept in a desiccator over silica-gel.

*HgLCl<sub>2</sub>:*

IR(KBr),  $\text{cm}^{-1}$ : 3434(m), 3055(w), 3026(w), 2919(w), 2854(w), 1618(vs), 1575(vs), 1564(vs), 1492(m), 1448(m), 1368(m), 1168(s), 992(m), 857(w), 807(m), 748(s), 686(s), 458(w). UV-Vis[(CHCl<sub>3</sub>),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 326(44496) and 376(33708).  $^1\text{H}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 8.77(bs, 2H), 7.68(bs, 4H), 7.58(bs, 3H), 7.42(bs, 6H), 7.24(m, 4H), 2.35(s, 3H).  $^{13}\text{C}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 164.30, 163.56, 148.52, 148.12, 140.98, 138.75, 138.52, 134.88, 134.82, 130.68, 130.63, 129.20, 129.08, 129.00, 128.04, 127.99, 126.70, 119.72, 119.08, 20.73.

*HgLBr<sub>2</sub>:*

IR(KBr),  $\text{cm}^{-1}$ : 3445(m), 3054(w), 3026(w), 2919(w), 2852(w), 1618(vs), 1575(vs), 1562(vs), 1492(m), 1348(m), 1366(w), 1167(s), 990(m), 856(w), 748(s), 686(s), 458(w). UV-Vis[(CHCl<sub>3</sub>),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 327(39674) and 377(29963).  $^1\text{H}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 8.85(s, 1H), 8.84(s, 1H), 7.67(d, 4H), 7.62(m, 4H), 7.43(m, 6H), 7.34(d, 1H, J= 7.90 Hz), 7.14(d, 2H, J= 14.10 Hz), 2.36(s, 3H).  $^{13}\text{C}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 164.46, 163.68, 149.02, 148.60, 140.84, 138.80, 138.62, 134.77, 134.72, 130.83, 130.77, 129.45, 129.14, 128.99, 128.91, 128.64, 126.36, 119.74, 119.12, 20.76.

*HgLI<sub>2</sub>:*

IR(KBr),  $\text{cm}^{-1}$ : 3466(m), 3053(w), 3024(w), 2920(w), 2856(w), 1616(vs), 1575(vs), 1561(vs), 1491(m), 1448(m), 1364(w), 1168(s), 985(s), 861(w), 806(m), 748(vs), 686(s), 458(w). UV-Vis[(CHCl<sub>3</sub>),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 326(32623) and 376(23042).  $^1\text{H}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 7.92(d, 1H, J= 16.50 Hz), 7.89(d, 1H, J= 19.60 Hz), 7.73(bs, 6H), 7.51(m, 4H), 7.29(m, 5H), 7.27(d, 2H, J= 16.05 Hz), 3.17(s, 3H).

*HgL(SCN)<sub>2</sub>:*

IR(KBr),  $\text{cm}^{-1}$ : 3481(m), 3056(w), 3025(w), 2922(w), 2853(w), 2118(vs), 1617(vs), 1575(vs), 1562(vs), 1493(m), 1448(m), 1368(m), 1169(s), 993(m), 853(w), 750(s), 685(m), 462(w). UV-Vis[(DMSO),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 333(41070) and 379(32160).  $^1\text{H}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 8.91(bs, 2H), 7.63(m, 6H), 7.44(m, 5H), 7.19(m, 4H), 6.75(m, 1H), 6.53(m, 1H), 2.37(s, 3H).  $^{13}\text{C}$ -NMR spectra (in DMSO- $d_6$ )(ppm): 164.72, 163.96, 149.30, 148.91, 141.00, 138.80, 138.71, 134.77,

134.72, 130.76, 130.70, 129.38, 129.02, 128.24, 128.20, 127.86, 127.44, 126.39, 119.86, 119.24, 20.68.

*HgL(N<sub>3</sub>)<sub>2</sub>*:

IR(KBr), cm<sup>-1</sup>: 3453(m), 3055(w), 2926(w), 2853(w), 2035(vs), 1616(m), 1575(m), 1490(w), 1448(m), 1367(w), 1166(m), 995(m), 858(w), 752(m), 685(m), 458(w). UV-Vis[(CHCl<sub>3</sub>), λ(nm) (ε, M<sup>-1</sup>cm<sup>-1</sup>): 323(33768) and 377(24461). <sup>1</sup>H-NMR spectra (in DMSO-d<sub>6</sub>)(ppm): 8.55(bs, 2H), 7.78(m, 2H), 7.66(m, 4H), 7.41(m, 8H), 7.20(m, 2H), 6.99(s, 1H), 2.33(s, 3H).

## RESULTS AND DISCUSSION

### *Physical data*

The Schiff base ligand, N, N'-bis((E)3-phenylallylidene)-4-methyl-1,2-phenylenediamin (L) was prepared by condensation of trans-cinnamaldehyde and 4-methyl-1,2-phenylenediamine in a 2:1 molar ratio. Some Schiff base complexes of mercury(II) were synthesized successfully with this ligand and the structure of ligand and its complexes was confirmed by the data obtained from elemental analysis, IR, UV-Vis and <sup>1</sup>H and <sup>13</sup>C NMR spectra. Elemental analyses and other physical properties of the ligand and its complexes are summarized in table 1. The results of the elemental analyses are in a good agreement with the proposed formula. The molar conductivity of ligand and all mercury complexes have been recorded in the solutions of chloroform (10<sup>-3</sup> M) except for HgL(N<sub>3</sub>)<sub>2</sub> that measured in DMSO at room temperature. The range of molar conductivity (0.44-15.840 cm<sup>2</sup> Ω<sup>-1</sup>M<sup>-1</sup>) exhibit all complexes are naturally non-electrolytes [36].

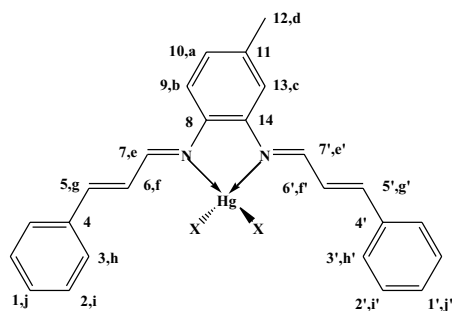
### *IR spectra*

The most important infra-red frequencies of the Schiff base ligand (L) and its complexes are listed in table 2. In the spectrum of ligand, appearance of the strong bands at 1624 and 1620 cm<sup>-1</sup> that are assigned to the asymmetric and symmetric stretching modes of the azomethine groups, ν(C=N), indicating that the condensation has been occurred successfully. In the spectra of all complexes this peak shifted about 6-8 cm<sup>-1</sup> to the lower energies [37, 38]. The lowering in frequency of vibration of the azomethine (C=N) bond in the complexes spectra is an evidence that the Schiff base has been bonded to the mercury ion. In the

spectrum of ligand, the absorption bands assigned to aromatic, aliphatic and iminic CH were appeared at 3051 and 3024, 2916 and 2848 cm<sup>-1</sup>, respectively. For all complexes, these bands have smoothly shifted to the higher frequencies. The stretching frequency in the spectrum of ligand at 1582 cm<sup>-1</sup> is assigned to the olefinic moieties [39], ν(C=C), that shifted to the lower frequency after coordination of ligand to the metal ion. The most important absorption bands in the spectra of complexes that are observed as weak peaks at the region 446-474 cm<sup>-1</sup> maybe assigned to stretching frequency of M-N [40]. In the IR spectrum of HgL(SCN)<sub>2</sub>, the strong absorption peak at 2118 cm<sup>-1</sup> is assigned to coordination of -SCN(S-coordinated) to the mercury ion while the peak at 2035 cm<sup>-1</sup> in the spectrum of HgL(N<sub>3</sub>)<sub>2</sub> is attributed to coordination of the N<sub>3</sub><sup>-</sup> to metal ion [41, 42].

### *Electronic Spectra*

The spectral data including the λ<sub>max</sub> are shown in table 2. Electronic spectra of the ligand and its complexes were measured in CHCl<sub>3</sub> except for HgL(N<sub>3</sub>)<sub>2</sub> that was recorded in DMSO at room temperature. In the spectrum of ligand two absorption bands are appeared. One of them is due to π-π\* electron transfer of aromatic rings that is appeared at 296 nm and the other one at 376 nm is attributed to π-π\* transition of the azomethine group which is mainly localized within the imine chromophore. In the electronic spectra of the complexes, the absorption band of aromatic rings shifted to the higher wavelengths. Observation of electronic spectra of complexes exhibited that the iminic band for entries 3, 5 and 6 shifted a few nanometers to higher wavelengths and for entries 2 and 4, this band had not shift. Each two transition bands are found to have more intensity after coordination of ligand to metal ion. For the complexes of IIB transition metals, the d-d transition bands are not expected due to d<sup>10</sup> electron configuration. In these types of complexes, the most important bands are charge transfer (L-M) transition. In the electronic spectra of titled complexes, the bands of charge transfer (L-M) transition were not observed that may be because of overlapping of it with π-π\* transition of the ligand [43]. According to our previous report on this type of ligands, the suggested structure for the complexes is pseudo-tetrahedral [30, 31, 44] as drawn in fig. 1.



**Fig. 1.** Suggested structure for the complexes with general formula  $Hg LX_2$  wherein  $X = Cl^-, Br^-, I^-, SCN^-, N_3^-$ .

**Table 1.** Synthetic, analytical and conductivity data for the ligand and its complexes.

Compound	Color	M.p.(°C)	Yield (%)	Found (Calcd.) (%)			$\Delta M$ ( $cm^2 \Omega^{-1} M^{-1}$ )	
				C	N	H		
1	Ligand	Light yellow	Viscose oil	81	85.38 (85.68)	8.19(7.99)	6.13(6.33)	0.313
2	Hg $LC l_2$	Brown	183(dec.)	71	48.48(48.28)	4.38(4.50)	3.46(3.57)	0.440
3	Hg $LB r_2$	Orange	172(dec.)	70	42.34(42.24)	4.04(4.94)	3.22(3.12)	3.297
4	Hg $LL_2$	Brown	172(dec.)	88	37.52(37.31)	3.39(3.48)	2.86(2.76)	1.399
5	Hg $L(SCN)_2$	Brown	161(dec.)	70	-	-	-	0.912
6	Hg $L(N_3)_2$	Brown	169(dec.)	72	-	-	-	15.840

**Table 2.** Infra-red ( $cm^{-1}$ ) and UV-Vis (nm) spectral data of the Schiff-base ligand and its complexes.

Compounds	$\nu CH_{arom.}$	$\nu CH_{aliph.}$	$\nu CH_{i, min}$	$\nu C=N$	$\nu C=C$	$\nu CH_{arom(oop)}$	$\nu C-C_{arom(oop)}$	$\nu M-N$	$-SCN/ -N_3$	$\lambda_{max}$	
1	Ligand	3051, 3024	2916	2848	1624	1582	751	690	-	-	296, 376
2	Hg $LC l_2$	3055, 3026	2919	2854	1618	1575	748	686	458	-	326, 376
3	Hg $LB r_2$	3054, 3026	2919	2852	1618	1575	748	686	458	-	327, 379
4	Hg $LL_2$	3053, 3024	2920	2856	1616	1575	748	686	458	-	326, 376
5	Hg $L(SCN)_2$	3056, 3025	2922	2853	1617	1575	750	685	462	2118	333, 379
6	Hg $L(N_3)_2$	3055	2926	2853	1616	1575	752	685	458	2035	323, 379

### $^1H$ and $^{13}C$ NMR spectra

The  $^1H$  and  $^{13}C$  NMR spectra of ligand and its complexes were recorded in deuterated dimethylsulfoxide (DMSO- $d_6$ ) at 500 MHz. The results obtained from the studies of  $^1H$  and  $^{13}C$  NMR spectra exhibit that the data are in agreement with pseudo-tetrahedral structure that is proposed for complexes (fig 1.). According to  $^1H$  NMR spectrum of ligand, the signal of methylene protons ( $3H_d$ ) appeared at 2.43 ppm as a singlet. This signal shifted to up fields after coordination of ligand to mercury ion except in entry 4 that shifted to 3.17 ppm. Because of unsymmetrical structure of ligand, the signals of iminic protons have different chemical shifts and showed as individual doublet signal at 7.87 ppm for  $1H_e$  and 7.77 ppm for  $1H_{e'}$  due to coupling with  $1H_f$  and  $1H_{f'}$  respectively that shifted to weaker fields in the  $^1H$  NMR spectra of all complexes in relative to free ligand. After

coordination of ligand to metal ion, the shapes of the iminic protons peaks have been changed in some cases. For example, these signals in the entries 2, 5 and 6 overlapped together and were shown as broad singlet. The changes in the locations and shapes of iminic protons resonance signals are other evidences to confirm the synthesis of Schiff base complexes. In the spectrum of ligand, the signals of  $4H_{h, h', j}$  and  $j'$  and  $3H_{i, i'}$  and  $c$  are appeared as multiplet signals at 7.42-7.66 and 7.24 ppm respectively. The resonance of  $1H_a$  and  $1H_b$  were observed at 7.04 ppm as a broad doublet signals that were shifted to down field after complexation in the complexes. In the spectrum of ligand, the signal of olefinic protons  $1H_f$  and  $1H_{f'}$  appeared at 7.00 ppm as a broad doublet that had a red shift in the spectra of all complexes.  $1H_g$  and  $1H_{g'}$  exhibited a doublet signal at 6.91 ppm due to coupling with  $1H_f$  and  $1H_{f'}$  respectively. In the spectra of all complexes, this signal shifted to down

fields except for complex of entry 5 that shifted to up fields as two individual multiplet signals. The  $^{13}\text{C}$  NMR spectra of the complexes showed two different signals for iminic carbons that appeared at 164.30-164.72 ppm for  $\text{C}_7$  and at 163.56-164.96 ppm for  $\text{C}_7$ . The signals of carbon atoms adjacent to the donor nitrogen atoms,  $\text{C}_{14}$  and  $\text{C}_8$  were appeared in weaker fields at the region 148.52-149.30 ppm and 148.12-148.91 ppm respectively. Also the resonances of methyl carbon atoms ( $\text{C}_{12}$ ) were observed at the range of 20.68-20.76 ppm. In the  $^{13}\text{C}$  NMR spectrum of  $\text{HgL}(\text{SCN})_2$ , the resonance at 129.38 ppm may be assigned to carbons of  $\text{SCN}^-$  moiety. The other signals are appeared as it has listed in the experimental section. FT-IR, UV-visible,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of  $\text{HgLCl}_2$  are depicted in figure 2 as typical spectra.

#### Optimization of structures

The structure of ligand and its mercury complexes was optimized theoretically at the level of UB3LYP/LANL2MB. The optimized structures of ligand,  $\text{HgLBr}_2$  and  $\text{HgL}(\text{N}_3)_2$  are shown in Figure 3. The results predict the pseudo-tetrahedral

geometry for all complexes. Some energetic and structural parameters are summarized at table 3 and 4. HF energy, zero point energy, total energy, Gibbs free energy, enthalpy, electronic energy and corrected ones were evaluated in the ranges of -1062.10 –(-1428.90), 0423-0.446, -1061.696-(-1428.461), -1061.739-(-1428.518), -1061.655-(-1428.410) respectively as seen in table 1. As shown in table 4, the imine bonds of free ligand are shortened after coordination to mercury ion due to probable  $\pi$ -back bonding from mercury ion to  $\pi^*$  of  $\text{C}=\text{N}$  bond of ligand. M-N(1) and M-N(2) bonds are shortened from mercury chloride to mercury thiocyanate complex and then lengthened at azide complex. The angle of N(2)-Hg-N(1) is increased from mercury chloride( $72.446^\circ$ ) to mercury thiocyanate complex( $73.598^\circ$ ) and then decreased at azide complex( $68.335^\circ$ ). The angle of X(1)-M-X(2) show a reverse trend with respect to N(2)-Hg-N(1) so that is decreased from mercury chloride( $129.603^\circ$ ) to mercury thiocyanate complex( $125.858^\circ$ ) and then increased at azide complex( $169.605^\circ$ ). The torsion angles around the

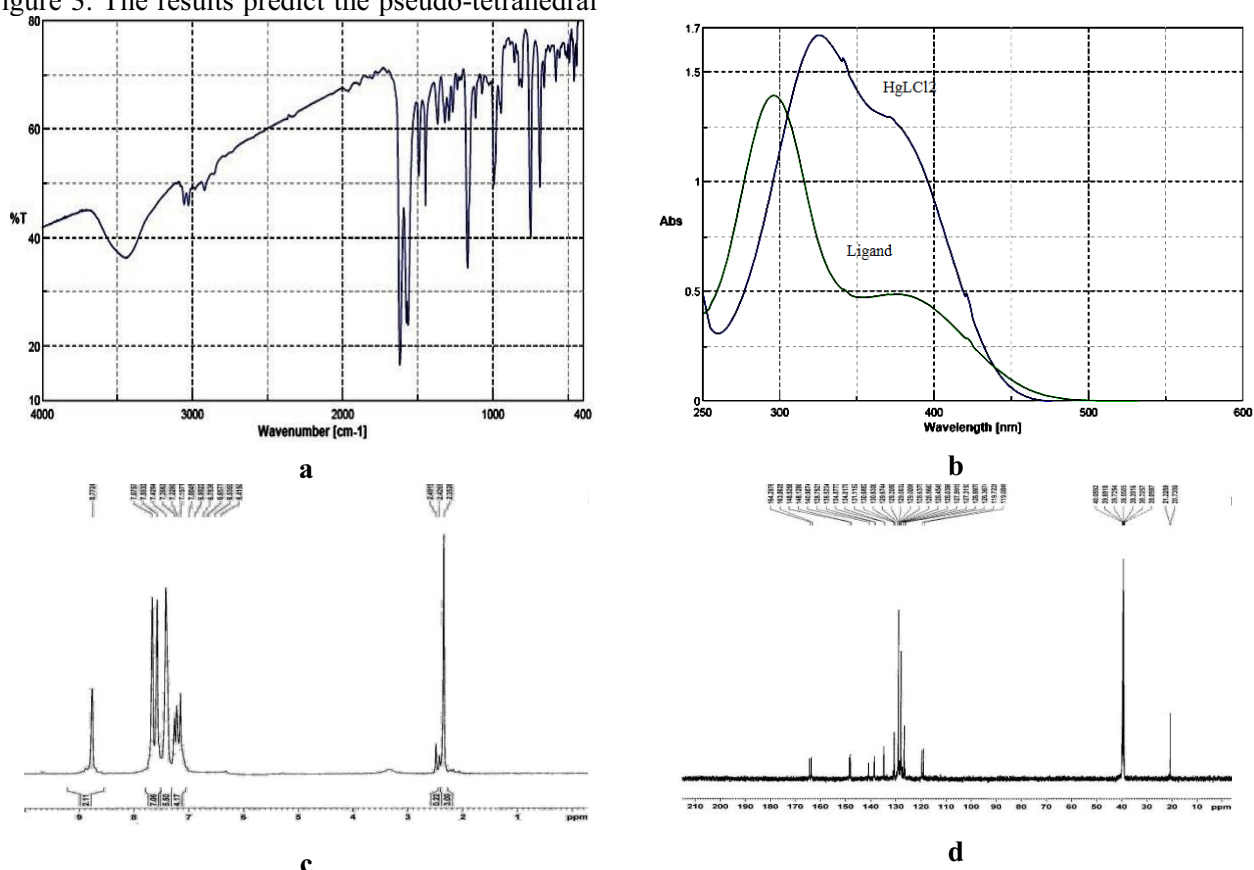
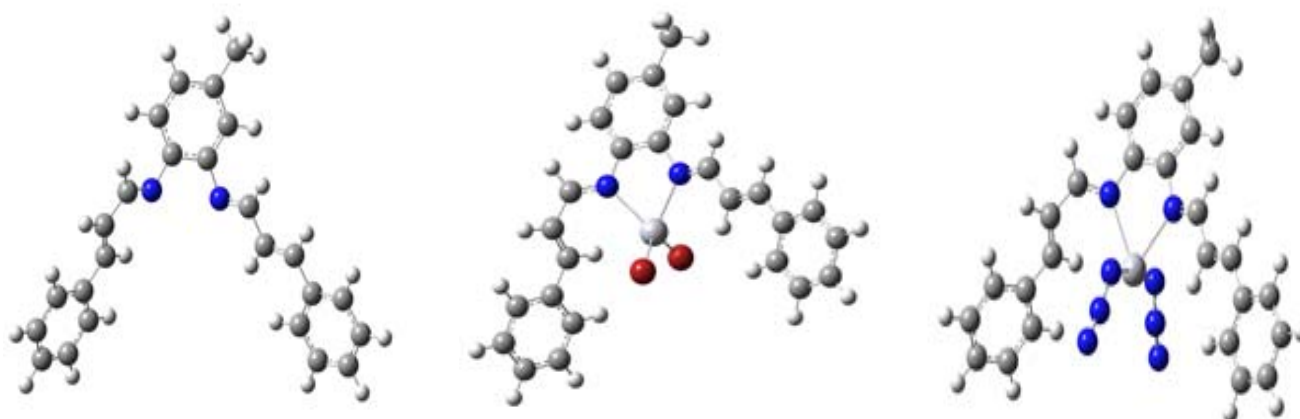


Fig. 2. The FT-IR(a) UV-visible(b),  $^1\text{H}$ -NMR(c) and  $^{13}\text{C}$ -NMR(d) spectra of  $\text{HgLCl}_2$



Ligand

HgLBr<sub>2</sub>

HgL(N<sub>3</sub>)<sub>2</sub>

Fig. 3. Optimized structure of ligand and two complexes

Table 3. Some energetic parameters derived for optimized structure of complexes.

Compound	HF Energy	ZPE	corrected ZPE	corrected total $\Delta E$	$\Delta G$	Corrected $\Delta G$	Total $\Delta E_{\text{elect.}}$	$\Delta H$	corrected $\Delta H$
ligand	-1062.10	0.423	0.406	-1061.696	-1061.739	-1061.755	-1061.656	-1061.655	-1061.671
HgCl <sub>2</sub>	-1134.90	0.426	0.409	-1134.490	-1134.545	-1134.561	-1134.443	-1134.442	-1134.458
HgLBr <sub>2</sub>	-1131.35	0.426	0.409	-1130.940	-1130.996	-1131.012	-1130.894	-1130.893	-1130.909
HgI <sub>2</sub>	-1127.80	0.425	0.409	-1127.388	-1127.443	-1127.459	-1127.342	-1127.341	-1127.357
HgL(SCN) <sub>2</sub>	-1308.40	0.444	0.426	-1307.969	-1308.026	-1308.042	-1307.919	-1307.918	-1307.935
HgL(N <sub>3</sub> ) <sub>2</sub>	-1428.90	0.446	0.429	-1428.461	-1428.518	-1428.535	-1428.410	-1428.410	-1428.427

Table 4. Selected bond distances, bond angles and torsion angles of optimized structures.

Selected data	L	HgCl <sub>2</sub>	HgLBr <sub>2</sub>	HgI <sub>2</sub>	HgL(SCN) <sub>2</sub>	HgL(N <sub>3</sub> ) <sub>2</sub>
<u>Bond length(Å)</u>						
Hg-N(1)	-	2.377	2.373	2.370	2.355	2.510
Hg-N(2)	-	2.375	2.373	2.368	2.369	2.504
Hg-X(1)	-	2.622	2.786	2.985	2.754	2.265
Hg- X(2)	-	2.620	2.787	2.987	2.759	2.262
C(7)=N(1)	1.331	1.339	1.339	1.340	1.340	1.336
C(7')=N(2)	1.330	1.338	1.338	1.340	1.342	1.336
<u>Bond angle(°)</u>						
N(2)-Hg-N(1)	-	72.446	72.695	72.989	73.598	68.335
N(2)-Hg-X	-	106.889	112.268	112.05	111.394	92.636
N(2)-Hg-Y	-	105.411	109.876	111.63	112.989	96.022
N(1)-Hg-X(1)	-	113.928	106.908	108.30	114.820	92.936
N(1)-Hg-X(2)	-	114.292	112.138	110.51	106.242	95.595
X(1)-M-X(2)	-	129.603	128.942	127.88	125.858	169.605
<u>Torsion angle(°)</u>						
N(1)-C(8)-C(14)-N(2)	0.089	-1.700	-1.281	-0.801	-2.079	-1.708
N(1)-C(7)-C(6)-C(5)	-1.015	-27.649	-26.509	-25.775	-26.838	25.321
N(2)-C(7')-C(6')-C(5')	-179.181	-179.625	-178.869	-2.423	177.861	179.032
C(6)-C(5)-C(4)-C(3)	179.63	-179.812	-179.422	-179.83	169.894	177.325
C(6')-C(5')-C(4')-C(3')	-0.429	174.951	-4.114	-2.948	-5.738	-1.431

C(8)-C(14), C(7)-C(6), C(7')-C(6'), C(5)-C(4) and C(5')-C(4') based on numbering in the figure 1, were extracted from optimized structures and tabulated in table 4. As seen in table 4, torsional angles suggest the non-planer structure of ligand in all compounds. Two azomethine nitrogens are not in a plane and have an angle in the range of  $0.089^\circ$ - $(-2.079)^\circ$  with respect to each other. The imine and olefin bonds have torsional angles of  $-27.649^\circ$  to  $-1.015^\circ$  and  $-178.869^\circ$  to  $179.032^\circ$  in both sides of ligand structure of complexes. The left and right phenyl rings of aldehyde section of ligand have torsional angles of  $-179.83^\circ$  to  $179.63^\circ$  and  $-5.738^\circ$  to  $174.951^\circ$  respectively with respect to the conjugated olefin bonds in the ligand and its complexes.

### CONCLUSION

In this work, we reported the synthesis of some new mercury complexes of a bidentate Schiff base ligand. These compounds were characterized by spectroscopic and analytical studies such as IR, UV-Vis,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, elemental analysis and molar conductivity. The general formula of  $\text{MLX}_2$  was proposed for Hg(II) complexes in which X is  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$  and  $\text{N}_3^-$ . Furthermore, the structural ligand and complexes were optimized at the UB3LYP/LANL2MB/ level of theory and then some important structural (Bond length(Å), Bond angle( $^\circ$ ) and Torsion angle( $^\circ$ )) and theoretical energetic(HF-Energy, ZPE,  $\Delta\text{E}$ ,  $\Delta\text{G}$ ,  $\Delta\text{E}_{\text{electronic}}$  and  $\Delta\text{H}$ ) data were derived. Consequently, the pseudo-tetrahedral geometry was suggested for all mercury complexes.

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## СИНТЕЗА, СПЕКТРАЛНО ОХАРАКТЕРИЗИРАНЕ И ТЕОРЕТИЧНО ИЗСЛЕДВАНЕ ЗА НЯКОИ ЖИВАЧНИ КОМПЛЕКСИ С КООРДИНАЦИОННО ЧИСЛО ЧЕТИРИ

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(Резюме)

Получени са нови комплекси на живака с лиганди от бидентатни Шифови бази с два азотни атома като донори охарактеризирани чрез спектроскопични и аналитични методи, като IR, UV-Vis, <sup>1</sup>H NMR и <sup>13</sup>C NMR, елементен анализ и моларна проводимост. IR-спектрите на лигандите показват характеристични на асиметрични и симетрични вибрации на имино-групите при съответно 1624 и 1620 cm<sup>-1</sup>, които се изравняват и отместват с 6-8 cm<sup>-1</sup> към по-ниски енергии. Иминните протонни сигнали на лигандите се появяват като два дублета при 7.87 и 7.77 ppm, които се понижават до 7.92-8.91 ppm след координиране към живачните йони в тези комплекси. Данните от анализите, потвърдени при отношение 1:1 за лигандите към металната сол във всички комплекси. Структурната оптимизация на лигандите и комплексите е представена при нивото UB3LYP/LANL2MB на теорията и са получени някои важни структурни данни (дължина на връзката (Å), ъгъл на връзката (°) and ъгъл на усукване (°)) и на енергетични характеристики (HF-енергия, ZPE, ΔE, ΔG, ΔE<sub>електронна</sub> и ΔH). Дължините на връзката (Å) Hg-N(1) и Hg-N(2) намаляват от комплексите меркури-хлорид към меркури-тиоцианат и до комплекса меркури-азид. Ъгълът на връзката (°) от N(1)-Hg-N(2) в комплексите плавно намалява от комплексите меркури-хлорид към меркури-тиоцианат и до комплекса меркури-азид. Обратната тенденция се забелязва за X(1)-Hg-X(2). Псевдо-тетраедрична геометрия се предлага за всички комплекси. Обща формула за Hg(II)-комплексите е MLX<sub>2</sub> където X= Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup> and N<sub>3</sub><sup>-</sup>.