# *Mercury Complexes Derived From Some Acetone Derivatives Ligands*

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*Complejos de Mercurio Derivados de algunos ligandos de derivados de acetona.*

*Complexos de Mercuri derivats d'alguns lligands de derivats d'acetona.*

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## RESUMEN

Se prepararon complejos de $Hg_2$(II) y Hg(II) con 1,3-difenil-1-etanolimina-propiylidin-3-ona ($HB^1$), 4-phenyl-2-ethanolimino-2-butylidine-4-ona ($HB^2$), 2-ethanolimino-2-pentylidin-4-ona ($HB^3$), y 2-(2-hydroxy-anilidino)-2-pentylidine-4-ona ($H_2B^4$) como ligandos, los cuales se caracterizaron mediante análisis elemental, mediciones de conductividad eléctrica, determinación de susceptibilidad magnética, detección de contenido del agua, espectroscopia de masas, ir, uv/vis espectroscopia, y termo-gravimetría. Los complejos formados pueden ser formulados como $[Hg_2(B^n)_2(H_2O)_m]$ y $[Hg(B^n)(H_2O)_m]$. $NO_3$ (donde n = 1, 2, 3 o 4) con dos excepciones, uno de ellas se refiere al $Hg_2$(II)-$H_2B^4$, que tiene por fórmula $[Hg_2(HB^4)_2(H_2O)_m]$, y el otro para Hg(II)-$H_2B^4$, que tiene la fórmula $[Hg(B^4)(H_2O)_m]$. La conductividad de la solución 0,001M de los complejos en DMSO revela la naturaleza ionizable de un grupo nitrato para los complejos de mercurio(II), mientras que los complejos de Hg(I)-$B^4$ y mercurio (I), actúan como una solución no electrolítica. Los estudios termogravimétricos así como el balance de contenido de agua revelan la naturaleza coordinada de las moléculas de agua más que la naturaleza cristalina. La determinación de la susceptibilidad magnética muestra el comportamiento ferromagnético de los complejos formados. Los cálculos de mecánica molecular (MM2) y la modelización molecular se llevaron a cabo en la esfera de coordinación de los complejos sintetizados.

***Palabras clave:*** complejos sólidos, espectro de masas, estabilidad térmica, cálculo MM2.

## RESUM

Es van preparar complexos d'$Hg_2$(II) i Hg(II) amb 1,3-difenil-1-etanolimina-propiylidin-3-ona ($HB^1$), 4-phenyl-2-ethanolimino-2-butylidine-4-ona ($HB^2$), 2-ethanolimino-2-pentylidin-4-ona ($HB^3$), i 2-(2-hydroxy-anilidino)-2-pentylidine-4-ona ($H_2B^4$) com lligands, els quals es van caracteritzar mitjançant anàlisi elemental, mesuraments de conductivitat elèctrica, determinació de susceptibilitat magnètica, detecció de contingut d'aigua, espectroscòpia de masses, ir, uv/vis espectroscòpia, i termo-gravimetria. Els complexos formats poden ser formulats com $[Hg_2(B^n)_2(H_2O)_m]$ i $[Hg(B^n)(H_2O)_m].NO_3$ (on n = 1, 2, 3 o 4) amb dues excepcions, un d'elles per el $Hg_2$(II)-$H_2B^4$, que té per fórmula $[Hg_2(HB^4)_2(H_2O)_m]$, i l'altre per el Hg(II)-$H_2B^4$, que té per fórmula $[Hg(B^4)(H_2O)_m]$. La conductivitat de la solució 0,001M dels complexos en DMSO revela la naturalesa ionitzable d'un grup nitrat per als complexos de mercuri(II), mentre que els complexos d'Hg(I)-$B^4$ i mercuri (I), actuen com una solució no electrolítica. Els estudis termogravimètrics i també el balanç de contingut d'aigua revelen la naturalesa coordinada de les molècules d'aigua més que la naturalesa cristal·lina. La determinació de la susceptibilitat magnètica mostra el comportament ferromagnètic dels complexos formats. Els càlculs de mecànica molecular (MM2) i la modelització molecular es van dur a terme en l'esfera de coordinació dels complexos sintetitzats.

***Paraules clau:*** complexos sòlids, espectre de masses, estabilitat tèrmica, càlcul MM2, modelització molecular.

## SUMMARY

$Hg_2$(II) and Hg(II) complexes with 1,3-diphenyl-1-ethanolimine-propylidin-3-one ($HB^1$), 4-phenyl-2-ethanolimino-2-butylidine-4-one ($HB^2$), 2-ethanolimino-2-pentylidin-4-one ($HB^3$), and 2-(2-hydroxy-anilidino)-2-pentylidine-4-one ($H_2B^4$) as ligands were prepared and characterized by elemental analysis, electrical conductivity measurements, magnetic susceptibility determination, water content detection, mass, ir, uv/vis spectroscopy, and thermogravimetry. The formed complexes can be formulated as $[Hg_2(B^n)_2(H_2O)_m]$ and $[Hg(B^n)(H_2O)_m].NO_3$ (where n = 1, 2, 3 or 4) with two exception, one of them for $Hg_2$(II)-$H_2B^4$, has $[Hg_2(HB^4)_2(H_2O)_m]$ formula and the other for Hg(II)-$H_2B^4$, has $[Hg(B^4)(H_2O)_m]$ formula. The conductivity of 0.001M of the complexes in DMSO reveal of the ionizable nature of one nitrate group for mercury(II) complexes meanwhile Hg(II)-$B^4$ and mercury(I) complexes act as non-electrolyte solution. The thermalgravimetric studies and also the water content accounting reveal the coordinated nature of the water molecules rather than the crystalline nature. The magnetic susceptibility determination shows the ferromagnetic behavior of the formed complexes. Molecular mechanical calculation (MM2) and molecular modeling were carried out on the coordination sphere of the synthesized complexes

***Keywords:*** solid complexes, mass spectra, thermal stability, MM2 calculation, molecular modeling

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## 1. INTRODUCTION

*Schiff* bases derived from acetone derivatives have gained much attention because of their biological,[1, 2] industrial,[3-8] and analytical applications.[9-13] Of further interest, mercury(II) ion was used as a probe in bioinorganic studies. For example, the native zinc ion in carboxypeptidase's has been replaced by mercury(II) and other metal ions.[14], [15] Sulfur atom in position 4 of the uridine of the nucleic acid RNA has been shown to be a good metal binding site for Hg(II) and Pt(II) ions.[16] Also, the toxicological effects of mercury on human bodies have received wide concern and extensive study in recent years and it can accumulate in human issues that may induce biological diseases.[17-19] Therefore, determination of trace mercury in biological samples is very important. Moreover, mercury(II) ion was used by x-ray crystallographers and in electron microscopy to facilitate the elucidation of the structure of the macromolecules.[16] A careful survey of the literature has shown that no systematic work has been don on $Hg_2$(II) and Hg(II) complexes with the title compounds. We thought it to be interesting to prepare some $Hg_2$(II) and Hg(II) nitrate complexes with these ligands. The structure of the formed complexes was studied by different physicochemical methods. The molecular mechanical calculations (MM2) and the molecular modeling were carried out to evaluate the total energy of the formed complexes and compared it with the experimental results.

## 2. EXPERIMENTAL

### 2.1. Reagents

$Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ were purchased from BDH and used without extra purification. All organic solvents were of analytical grade and purified by standard methods. The *Schiff* base ligands *1,3-diphenyl-1-ethanolimine-propylidin-3-one ($HB^1$), 4-phenyl-2-ethanolimino-2-butylidine-4-one ($HB^2$), 2-ethanolimino-2-pentylidin-4-one ($HB^3$), and 2-(2-hydroxy-anilidino)-2-pentylidine-4-one ($H_2B^4$)* were prepared as described previously[20]

### 2.2. Syntheses

0.01*M* $Hg_2(NO_3)_2$ or $Hg(NO_3)_2$ (in ethanol-water mixture) and 0.02*M* of ethanolic Schiff base solution were mixed and refluxed for 4 h. Yellow, gray or black complexes were obtained after recrystallization from hot ethanol. The crystals were dried in *vacuo* for a few hours. The purities of the complexes were checked by measurement of their melting points and TLC (silica gel GF254 type 60, mesh size 50-250, eluted with ethanol-chloroform).

### 2.3. Equipments

Infrared spectra were recorded in the range of 4000-200 $cm^{-1}$ (KBr discs) on a Perkin-Elmer 883 spectrophotometer. Elemental analysis were carried out using a Heraeus CHN Rapid Analyzer. The water content of the complexes were carried out using Abimed Vaporizer VA-06 and Abimed Moisturemeter CA-06. Thermal analysis of the complexes under investigation were carried out on a STA 409 Netzsch Simultaneous thermoanalyzer. Uv/vis spectra were measured at room temperature on a Beckman model 5260 spectrophotometer (KBr discs). The conductance measurements of 0.001M solutions of the complexes in DMSO solvent were performed using a WTW model LF-42 conductivity bridge fitted with an LTA-100 conductivity cell. The MM2 calculations and the molecular modeling were carried out using chemoffice program. Mass spectra of the complexes were obtained with a mass spectrometer Varian MAT 711. Magnetic susceptibilities of the complexes were measured on a Bruker Magnet B-E 15 instrument.

## 3. RESULTS AND DISCUSSION

The reactions of $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ with the ligands $HB^1$, $HB^2$, $HB^3$ and $H_2B^4$ in ethanol-water medium resulted in the formation of 1:1 (metal:ligand) complexes with the molecular formula $[Hg_2(B^n)_2(H_2O)_m]$ and $[Hg(B^n)(H_2O)_m].NO_3$ (where n = 1, 2, 3 or 4) with two exception, one of them for $Hg_2$(II)-$H_2B^4$, has $[Hg_2(HB^4)_2(H_2O)_m]$ formula and the other for Hg(II)-$H_2B^4$, has $[Hg(B^4)(H_2O)_m]$ formula. The complexes were found to be yellow, gray, and black colored non-hygroscopic powders, stable at normal conditions. The el-

***Table 1.*** *Elemental analysis and physical properties of the synthesized complexes*

| Compounds | Molecular weight | Color | Melting point | Elemental analysis | | | | | | | | Cond. X10$^6$ | $\mu$eff |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C% | | H% | | N% | | M% | | | |
| | | | | Calculate | Found | Calculate | Found | Calculate | Found | Calculate | Found | | |
| $HB^1$ ligand | 267.33 | Yellow | 125 | 76.38 | 76.30 | 6.41 | 6.70 | 5.24 | 5.30 | -------- | ------- | ------- | ------ |
| $Hg_2$(II) | 1005.88 | Yellow | 240 | 40.60 | 40.84 | 4.01 | 3.72 | 2.79 | 2.50 | 39.88 | 39.61 | 12 | 0.732 |
| Hg(II) | 564.94 | Yellow | 185 | 36.14 | 36.58 | 3.57 | 3.18 | 4.96 | 5.02 | 35.51 | 35.88 | 58 | 0.459 |
| $HB^2$ ligand | 205.26 | Yellow | 170 | 70.22 | 70.60 | 7.37 | 7.43 | 6.82 | 6.96 | -------- | ------- | ------- | ------ |
| $Hg_2$(II) | 917.76 | Yellow | 120 | 31.41 | 31.27 | 4.39 | 4.11 | 3.05 | 3.28 | 43.71 | 44.02 | 10 | 0.707 |
| Hg(II) | 502.87 | Yellow | 185 | 28.66 | 28.39 | 3.61 | 3.40 | 5.57 | 5.36 | 39.89 | 39.70 | 71 | 0.370 |
| $HB^3$ ligand | 143.19 | Yellow | 160 | 58.72 | 58.48 | 9.15 | 9.15 | 9.78 | 9.78 | -------- | ------- | ------- | ------ |
| $Hg_2$(II) | 721.56 | Gray | > 300 | 23.30 | 23.52 | 3.91 | 3.98 | 3.88 | 3.50 | 55.60 | 55.72 | 15 | 1.105 |
| Hg(II) | 422.79 | Yellow | > 300 | 19.89 | 19.69 | 3.34 | 3.68 | 6.63 | 6.93 | 47.44 | 47.06 | 75 | 0.340 |
| $H_2B^4$ ligand | 191.23 | Yellow | 184 | 69.09 | 69.13 | 6.85 | 6.81 | 7.32 | 7.65 | -------- | ------- | ------- | ------ |
| $Hg_2$(II) | 853.68 | Yellow | 160 | 30.95 | 31.06 | 3.78 | 3.95 | 3.28 | 3.61 | 46.99 | 46.85 | 8 | 0.152 |
| Hg(II) | 443.85 | Black | > 300 | 29.77 | 30.05 | 3.86 | 3.59 | 3.16 | 3.40 | 45.19 | 45.34 | 11 | 0.182 |

cond. = conductivity ($Ohm^{-1}.cm^2.mol^{-1}$)

emental analysis (CHNM%) confirmed the postulated formula. Also the water molecules counting using the Abimed Vaporizer and Moisturemeter, predicting the quantity of the $H_2O$ molecules in the synthesized complexes (Table 1).

### 3.1. Conductivity

The conductance of the complexes in DMSO (0.001M) (Table 1) indicates the varieties in the conductance behavior. Mercury(I) complexes act as non-electrolytes meanwhile Hg(II) act as 1:1 electrolytes with one exception for Hg(II)-$H_2B^4$ complex which act as non-electrolyte. The 1:1 electrolytic solutions reveal the ionic nature of the corresponding complexes which may be act as $A^+B^-$ system, where $A^+$ = coordination sphere, and $B^-$ = ionization sphere = $NO_3^-$ group.[21, 22]

### 3.2. Magnetic Susceptibility ($\mu_s$)

The most obvious feature of the magnetism of second and third row elements, when compared to the first row, is the much greater frequency with which diamagnetism occurs and the fact that paramagnetic moments are usually much lower. The value of $\mu_s$ for the mercury(I) complexes lower than the expected value ($Hg_2$(II) is diamagnetic in the simple ionic salt), could be the effect of antiferromagnetic interaction causes a lowering in $\mu_s$ and where the interaction is direct, is the phenomenon of covalent bonding.[23] The Hg(II) complexes gave some ferromagnetic properties, where the $\mu$s is somewhat greater than the diamagnetic value ($\mu_s = 0$) (Table 1). The ferromagnetism and antiferromagnetism effect indicate in some extent, there are some intermolecular and/or intramolecular magnetic interaction.[23]

### 3.3. Infrared Spectra

The significant ir data of the ligands as well as those of their mercury(I) and mercury(II) complexes are listed in Table 2. The band which centered nearly at 3400 $cm^{-1}$ which is present in all complexes as a weak or a medium broad band may be due to the coordinated water molecules.[24] The band which appeared at 3000-3350 $cm^{-1}$ for the free ligands could be assigned as $\upsilon$O-H and $\upsilon$N-H which reveals the keto $\longleftrightarrow$ enol structure. These bands exerted shifts to lower frequencies for $HB^1$ and $HB^2$ complexes meanwhile $HB^3$ and $H_2B^4$ complexes gave positive shifts (shift to higher frequencies). This behavior may be indicated that, the alcoholic oxygen in the ligands could be involved in the coordination process. The bands centered nearly at 1600 and 1550 $cm^{-1}$ were assigned to $\upsilon$C=N and $\upsilon$C=C; they displayed positive shift upon complexation. This result may be due to the summation of two effects, which could be summarized in the following equation:

Total shift in $\upsilon$C=N = [shift due to the coordination with the metal ion] + [shift due to the breaking of the hydrogen bond in the ligand].

The shift of the $\upsilon$C=N due to the coordination with the metal ion always negative, because C=N look like C=O group as it good $\pi$ donor and bad $\sigma$ acceptor. The shift of the $\upsilon$C=N due to the breaking of the hydrogen bond ( inter and/or intrahydrogen bond) usually positive. When the total shift has negative value, could be indicated that, the coordination of the C=N group by the metal ion lowering the wavenumber more than the hydrogen bonding and the vice versa is true.[25, 20] The band centered at 1305 $cm^{-1}$ for the ligand $H_2B^4$, could be due to the $\upsilon$C-O of the phenol, which gave positive shift for the complexes of mercury(I) and mercury(II), which could be indicated the sharing of this site as coordinated one, and from the value of the shifting indicating that, the mercury(II) > mercury(I) with respect to the coordination process. The $\upsilon$M-O band appeared at 529-583 $cm^{-1}$, meanwhile $\upsilon$M-N band appeared at 450-485 $cm^{-1}$ which supports the chelation process through the N and O atoms. Nitrate group appeared at 1305, 1308 and 1350 $cm^{-1}$ for Hg(II)-$B^1$, Hg(II)-$B^2$ and Hg(II)-$B^3$ complexes respectively, which could be indicated that, the presence of this group in the ionization sphere as free ion.[26] Unfortunately, the stretching of the Hg-Hg bond don't detected in the working wavenumber range.

***Table 2.*** *Significant ir frequencies and uv/vis spectra ($cm^{-1}$) for the synthesized complexes using KBr disc.*

| Compounds | $\upsilon(H_2O)$ | $\upsilon$ (OH, NH) | $\upsilon$ N=C | $\upsilon$ C-O phenol | $\upsilon$ ($NO_{3)}$ | $\upsilon$M-O | $\upsilon$M-N | Uv/vis |
|---|---|---|---|---|---|---|---|---|
| $HB^1$ ligand | --------- | 3310 m, br | 1590 s,<br>1550 s,<br>1530 m | ---------- | -------- | -------- | -------- | 42553 sh, 40000 s, 29412 s,br |
| $[Hg_2(B^1)_2.4H_2O]$ | 3460 m | 3050 m | 1661 s<br>1591 s | --------- | --------- | 530 w | 470 w | 32258 m, 26316 m, 24096 sh |
| $[Hg (B^1).2H_2O]NO_3$ | 3435 m | 3056 m | 1661<br>1591<br>1576 | --------- | 1305 m | 567 w | 483 w | 32051 sh, 20833 m, 24390 sh |
| $HB^2$ ligand | ---------- | 3350 s | 1600 s<br>1590 s<br>1520 m | ---------- | -------- | -------- | -------- | 41667 sh, 40000 sh, 33333 s |
| $[Hg_2(B^2)_2.6H_2O]$ | 3420 m | 3232 m | 1680 sh<br>1630 m<br>1580 m | --------- | --------- | 553 w | 480 w | 32258 m, 26316 m |
| $[Hg(B^2).2H_2O]NO_3$ | 3438 m | 3260 sh | 1680 sh<br>1641 s<br>1571 sh | --------- | 1308 m | 555 w | 485 w | 32258 m, 27778 m |
| $HB^3$ ligand | ---------- | 3270 s | 1600 s<br>1550 s | ---------- | -------- | -------- | -------- | 41667 m, 33333 s |
| $[Hg_2 (B^3)_2. 2H_2O]$ | 3425 m | 3280 sh | 1686 m<br>1636 s | --------- | --------- | 530 w | 450 w | 32258 m, 26316 sh |
| $[Hg(B^3). H_2O]NO_3$ | 3434 m | 3275 sh | 1688 s<br>1635 s | --------- | 1350 m | 529 m | 451 w | 31746 m, 26178 sh |
| $H_2B^4$ ligand | ---------- | 3000 m | 1600 s<br>1540 s | 1305 s | -------- | -------- | -------- | 37037 s, 31746 w |
| $[Hg_2(HB^4)_2.4H_2O]$ | 3300 w | 3072 m | 1606 s<br>1551 s | 1319 s | --------- | 532 w | 463 w | 31746 w, 25641 m,<br>22472 w, 18349 w |
| $[Hg(B^4).3H_2O]$ | 3440 m | --------- | 1600 sh<br>1572 m | 1383 s | --------- | 583 w | 450 w | 31746 w, 25641 m,<br>22472 w, 18519 m |

br = broad s = strong m = medium sh = shoulder w = weak

### 3.4. Electronic Spectra

All complexes gave new band with red shifts for the ligands bands. The complexes derived from $H_2B^4$ ligands gave the largest number of bands while $HB^3$ has the smallest number. Although $HB^2$ has one phenyl group in the side chain and $HB^1$ has two phenyl group, they gave the lower number of bands when comparing with the $H_2B^4$. This result could be indicated that, the presence of phenyl group closely present near the interact site with the metal ion through the oxygen atom was favorable for the $\pi \rightarrow \pi^*$, d$\pi$-p$\pi$ transition and also the CT type. The presence of new bands in the synthesized complexes in the range of the visible spectra could be facilitate the use of the ligands under consideration as analytical reagent for detection the mercury(I) and mercury(II) ions in different samples[24] (Table 2, Figure 1).

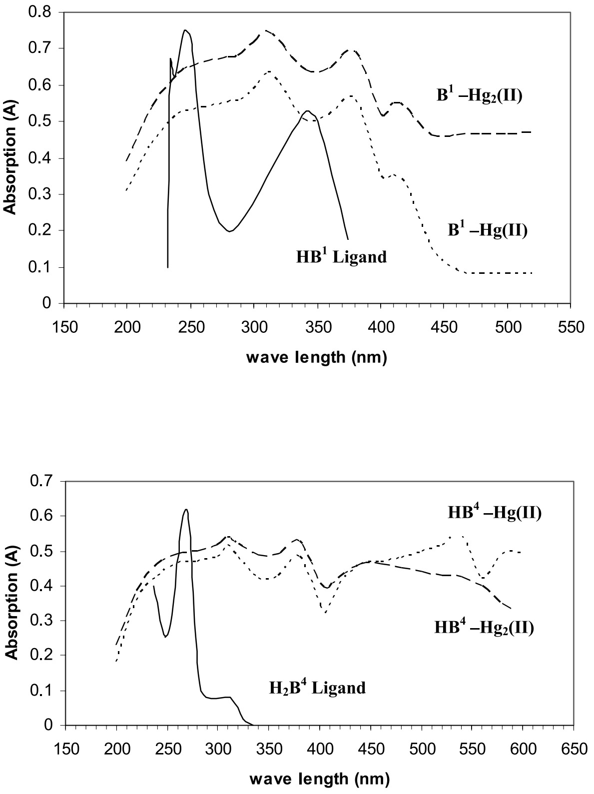


***Figure 1**: Uv/vis spectra of the $HB^1$ and $H_2B^4$ ligands and there complexes (as example).*

### 3.5. Thermal Analysis

The thermogravimetric studies of the synthesized complexes gave more insight on their molecular structure. The initial and final temperature peak indicate in some extent the high thermal stability of the decomposed components of the complexes. The liberation of water molecules from the complexes reveal the coordinating nature of these molecules. From the thermograms, the weight loss supports the formula listed in Table 2. The obtained results suggest the following thermal stability order of the different species (Table 3):

(1) thermal stability of the coordinated water:

$Hg_2$(II)-$B^1$ > Hg(II)-$B^4$ > Hg(II)-$B^1$ > $Hg_2$(II)-$B^3$ > Hg(II)-$B^3$ > $Hg_2$(II)-$HB^4$ > Hg(II)-$B^2$ > $Hg_2$(II)-$B^2$

(a) thermal stability of the coordinated water for mercury(I) complexes:

$Hg_2$(II)-$B^1$ > $Hg_2$(II)-$B^3$ > $Hg_2$(II)-$HB^4$ > $Hg_2$(II)-$B^2$

(b) thermal stability of the coordinated water for mercury(II) complexes:

Hg(II)-$B^4$ > Hg(II)-$B^1$ > Hg(II)-$B^3$ > Hg(II)-$B^2$

(2) thermal stability of the complexing agent:

Hg(II)-$B^4$ > $Hg_2$(II)-$HB^4$ ≈ $Hg_2$(II)-$B^2$ ≈ Hg(II)-$B^1$ > $Hg_2$(II)-$B^1$ > Hg(II)-$B^2$ > $Hg_2$(II)-$B^3$ ≈ Hg(II)-$B^3$

(a) thermal stability of the complexing agent for mercury(I) complexes:

$Hg_2$(II)-$HB^4$ ≈ $Hg_2$(II)-$B^2$ > $Hg_2$(II)-$B^1$ > $Hg_2$(II)-$B^3$

(b) thermal stability of the complexing agent for mercury(II) complexes:

Hg(II)-$B^4$ > Hg(II)-$B^1$ > Hg(II)-$B^2$ > Hg(II)-$B^3$

(3) the reaction interval ($T_F$-$T_I$) order for the coordinated water liberation:

$Hg_2$(II)-$B^1$ > Hg(II)-$B^4$ > Hg(II)-$B^1$ >$Hg_2$(II)-$B^3$ > $Hg_2$(II)-$HB^4$ > Hg(II)-$B^2$ > $Hg_2$(II)-$B^2$ > Hg(II)-$B^3$

(4) the reaction interval order for the liberation of the complexing agent:

$Hg_2$(II)-$B^2$ > $Hg_2$(II)-$HB^4$ > Hg(II)-$B^4$ > Hg(II)-$B^1$ > Hg(II)-$B^2$ > $Hg_2$(II)-$B^1$ > Hg(II)-$B^3$ > $Hg_2$(II)-$B^3$

From the thermograms and the data listed in Table 3, could be concluded the following concepts: (1) the most stable coordinated water belong the $Hg_2$(II)-$B^1$ complex, and the least one present in the complex $Hg_2$(II)-$B^2$. (2) the most stable ligand-metal bonds belong the complex Hg(II)-$B^4$, and the least one is Hg(II)-$B^3$. (3) the fastest thermal reaction (small reaction interval) for the liberation of the coordinated water belong the decomposition of the $Hg_2$(II)-$B^1$ and the lowest one cam from Hg(II)-$B^3$. (4) the smallest reaction interval for the decomposition of the complexing agent belong $Hg_2$(II)-$B^2$ and the largest one belong $Hg_2$(II)-$B^3$ complex. (5) the order of the thermal stability of the coordinated water go well with its thermal reaction interval with one exception for Hg(II)-$B^3$. The high stability of the complexing agent of the complexes derived from $H_2B^4$ might be due to the unsaturated orbitals of this ligand which nearly occurring beside the metal ion orbitals, which could be overlapped with the orbitals of the mercury(I) and mercury(II) through the d$\pi$-p$\pi$ interaction. This result go well with the data obtained from uv/vis spectroscopy. The final residue, which inspected at nearly 650 °C, nearly equal zero, which may be concluded that, the complete evaporation of the mercury(I) and mercury(II) after some thermal redox reaction which turn these ions to the metallic nature, which easily evaporate under this conditions.

### 3.6. Mass Spectra

The mass spectra of the synthesized complexes gave the molecular ion peak without the coordinated water, which could be due to the high temperature of the measuring conditions. The molecular ion peak for mercury(I) complexes derived from $HB^1$, $HB^2$, $HB^3$ and $H_2B^4$ are 467, 405, 343, and 391 respectively, which could be formed after the breaking of Hg-Hg bond, meanwhile mercury(II) complexes are 529, 467, 405, and 390 respectively. All mercury(I) complexes gave m/z = 202 reveal the presence of the mercury(I) while mercury(II) appeared at 101. Scheme 1 and figure 2 shows the fragmentation of the mercury(I)-$B^1$ complex (as an example). The complex undergo thermal loss of the coordinated water to form the fragment ($C_{14}H_{16}NO_2Hg$) which has m/z = 467 (I = 10), followed by sequence of fragmentations to give different m/z values, like 466(5), 465(6), 423(10), 422(12), 421(10), 349(15),

***Table 3.*** *The thermal analysis for the synthesized complexes.*

| Compound | T (°C) | | | Weight loss (%) | | Assignment |
|---|---|---|---|---|---|---|
| | $T_I$ | $T_F$ | RI | Found | Calculated | |
| $[Hg_2(B^1)_2.4H_2O]$ | 120 | 206 | 86 | 7.50 | 7.16 | Liberation of 4 $H_2O$ |
| | 206 | 600 | 394 | 93.00 | 92.83 | Decomposition of $B^1$+ evaporate Hg |
| $[Hg\ (B^1).2H_2O]NO_3$ | 140 | 200 | 60 | 6.40 | 6.38 | Liberation of 2 $H_2O$ |
| | 200 | 620 | 420 | 94.01 | 93.63 | $B^1$+ evaporate Hg + liberation of $NO_3$ |
| $[Hg_2(B^2)_2.6H_2O]$ | 120 | 161 | 41 | 12.00 | 11.78 | Liberation of 6 $H_2O$ |
| | 161 | 620 | 459 | 88.50 | 88.22 | Decomposition of $B^2$+ evaporate Hg |
| $[Hg(B^2).2H_2O]NO_3$ | 120 | 162 | 42 | 7.42 | 7.16 | Liberation of 2 $H_2O$ |
| | 162 | 580 | 418 | 93.00 | 92.84 | $B^2$+ evaporate Hg + liberation of $NO_3$ |
| $[Hg_2\ (B^3)_2.\ 2H_2O]$ | 130 | 185 | 55 | 5.00 | 4.99 | Liberation of 2 $H_2O$ |
| | 185 | 560 | 375 | 94.80 | 95.01 | Decomposition of $B^3$+ evaporate Hg |
| $[Hg(B^3).\ H_2O]NO_3$ | 150 | 180 | 30 | 4.02 | 4.26 | Liberation of $H_2O$ |
| | 180 | 560 | 380 | 95.88 | 95.74 | $B^3$+ evaporate Hg + liberation of $NO_3$ |
| $[Hg_2(HB^4)_2.4H_2O]$ | 130 | 175 | 45 | 8.73 | 8.44 | Liberation of 4 $H_2O$ |
| | 175 | 620 | 445 | 91.30 | 91.55 | Decomposition of $B^4$+ evaporate Hg |
| $[Hg(B^4).3H_2O]$ | 140 | 205 | 65 | 12.00 | 12.18 | Liberation of 3 $H_2O$ |
| | 205 | 640 | 435 | 83.50 | 87.82 | Decomposition of $B^4$+ evaporate Hg |

$T_I$ = Initial temperature peak
$T_F$ = Final temperature peak
RI = Reaction interval

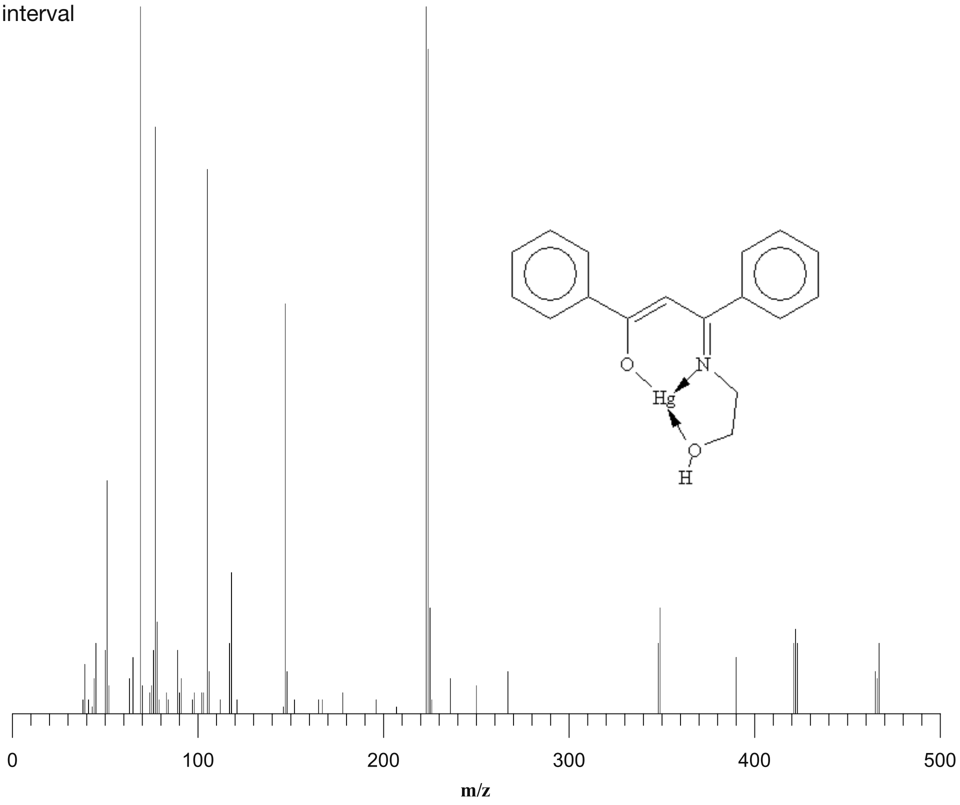
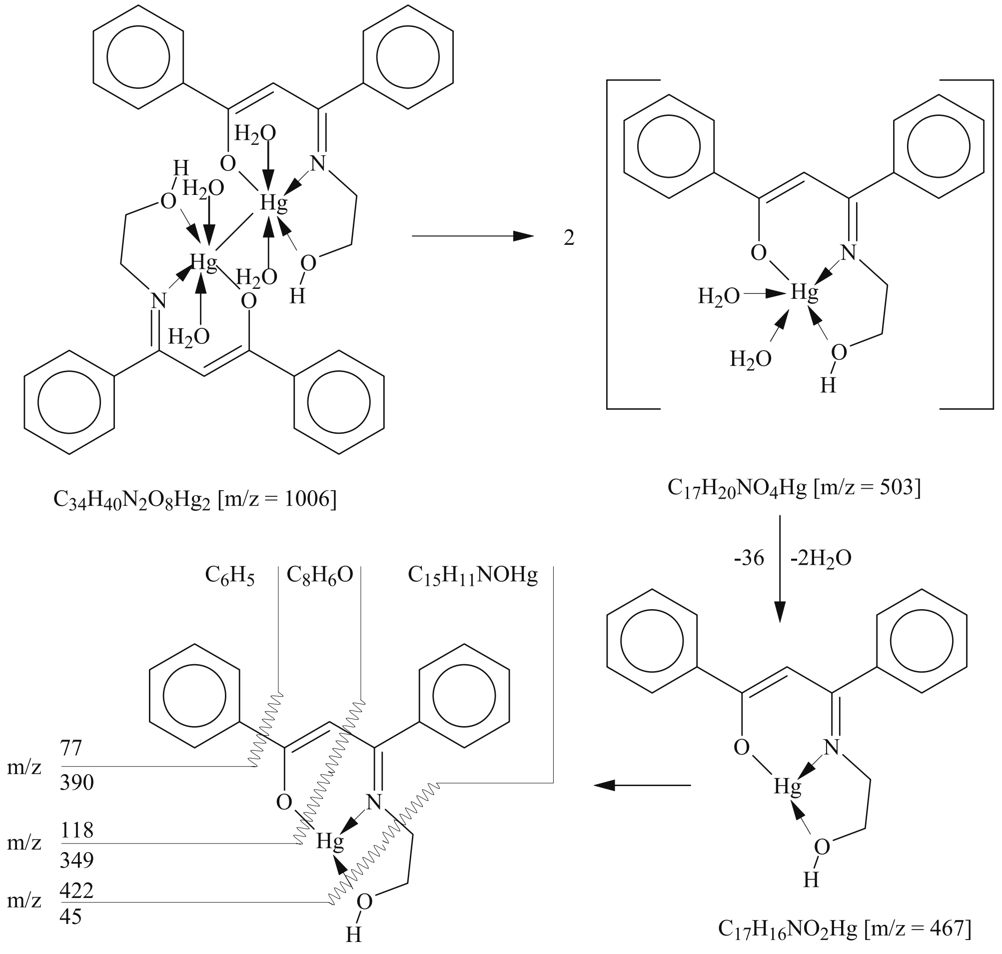


***Figure 2:*** *The Mass spectra of the $Hg_2$(II)-$B^1$ complex.*

sequence of fragmentations to give different m/z values, like 466(5), 465(6), 423(10), 422(12), 421(10), 349(15), 348(10), 340(8), 118(20), 117(10), 77(75), 45(10) Figure 2. The data obtained from the mass spectra go well with the other tools used in this work.

Finally, from the elemental analysis, conductance, magnetic susceptibility, ir, uv/vis, thermal analysis, mass spectra, the structure of the formed complexes could be postulated as shown in the Schemes 2 and 3.



***Scheme 1**: The main fragments of the [$Hg_2(B^1)_2$.$4H_2O$] complex.*

### 3.7. Molecular Mechanical Calculation (MM2) and Molecular Modeling

Molecular mechanics (using chem.-office program) describes the energy of a molecule in terms of a set of classically derived potential energy functions. The potential energy functions and the parameters used for their evaluation are known as a “force-field”. Molecular mechanics typically treats atoms as spheres, and bonds as springs. The mathematics of spring deformation (Hooke’s Law) is used to describe the ability of bonds to stretch, bend, and twist. Non-bonded atoms (greater than two bonds apart) interact through van der Waals attraction, steric repulsion, and electrostatic attraction/repulsion. These properties are easiest to describe mathematically when atoms are considered as spheres of characteristic radii. The total potential energy of a molecule can be described by the following summation of interactions.[27-29] Total Energy = Stretching Energy + Bending Energy + Torsion Energy + Non-Bonded Interaction Energy.

Table 4, shows the results which obtained from the MM2 calculations which carried out on the different spatial arrangement of the synthesized complexes to obtain the most stable structure which give the least total energy. The values of the total energy were found to be at 140.69-551.29 kcal/mol range for complexes derived from $Hg_2$(II) ions, meanwhile Hg(II) complexes has 138.10-158.60 kcal/mol range. The torsion parameter could be assigned as the predominate parameter with one exception for complex derived from $HB^3$ ligand and $Hg_2$(II) ion, where the 1.4VDW parameter was the predominant. The total steric energy order for the coordination sphere for the synthesized complexes could be arranged as the following:

(a) $Hg_2$(II) complexes > Hg(II) complexes

(b) $Hg_2$(II)-$B^2$ > $Hg_2$(II)-$HB^4$ > $Hg_2$(II)-$B^1$ > Hg(II)-$B^1$ > Hg(II)-$B^4$ ≥Hg(II)-$B^3$ > $Hg_2$(II)-$B^3$ ≥ Hg(II)-$B^2$

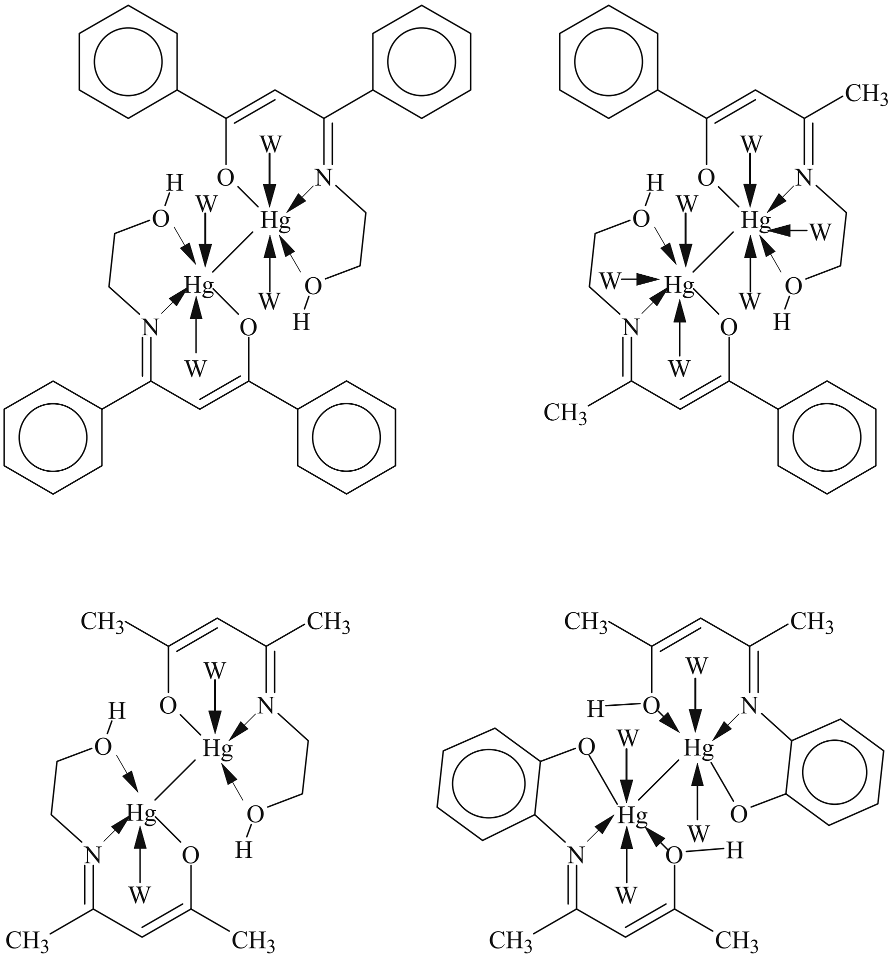
From the table 4, [$Hg_2(B^2)_2$.$6H_2O$] has the highest steric energy (551.29 kcal/mol), meanwhile, [Hg($B^2$).$2H_2O$] gave the lowest energy (138.10 kcal/mol).

The obtained order go well with some extent with the inverse order of the thermal stability of the decomposition of the complexing agent and the coordinated water, i.e, when the total decomposition temperature is high reveal

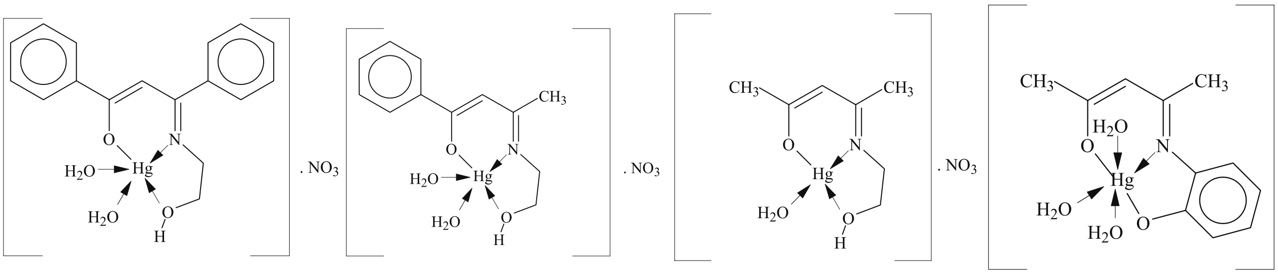
the stability of the complex, which consequently gave minimum total steric energy in the MM2 calculations.
(c) the contribution of the parameter in the total steric energy has the following order:
Torsion > 1.4VDW > bend > stretch > non 1.4VDW > dipole/dipole > stretch-bend.This order indicate the high energy for the through-space interaction of atoms separated by two atoms (more than two bonds).[27-31] From the MM2 and molecular modeling work, could be formulated the coordination sphere of the complexes under investigation as shown in the Scheme 4, which go well with the postulated structures which obtained previously from the experimental works (Scheme 2 and 3).

## 4. CONCLUSION

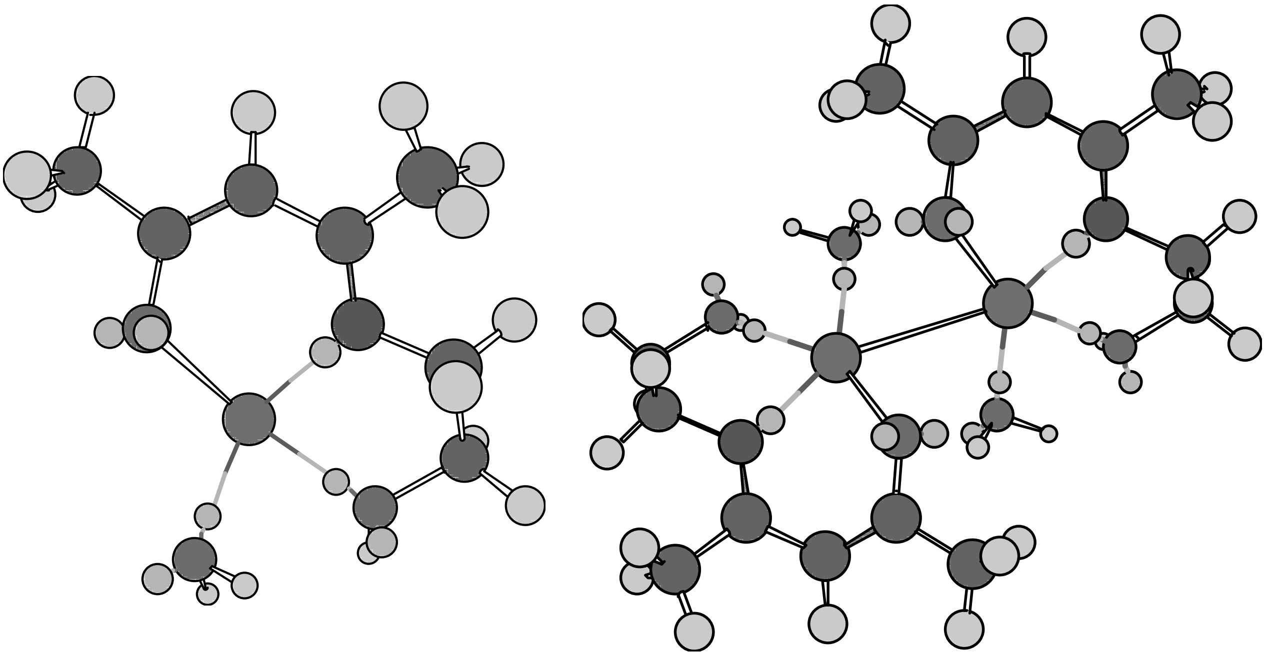
The ability of the preparation of the solid complexes of the Hg(II) ions with the Schiff bases under consideration could be give some promotion in the detection and/or extraction of this metal ions, which play very harmful role in the environmental as toxic element. The ligands, which able to interact with Hg(II) ion could be designed as efficient ligands and could be used as a part in the manufacturing of some sensors which could be able to detecting Hg(II) ions in soil, water and air. The molecular modeling and quantum mechanics calculations introduce some numerical parameters which gave some ability to select the best ligand accompanied with the best conformation to obtained the most stable complex.



***Scheme 2:*** *The postulated structures of the synthesized $Hg_2$(II)-ligand complexes (W = water molecule).*



***Scheme 3:*** *The postulated structures of the synthesized Hg(II)-ligand complexes.*



[a]

[b]

***Scheme 4:*** *The molecular modeling of the synthesized complexes [a]: $[Hg(B^3).H_2O]^+$, [b]: $[Hg_2(B^3)_2.2H_2O]$ as example.*

***Table 4.*** *The types of the energy which effect on the synthesized complexes inside the coordination sphere.*

| Complexes | Types of energy* | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|
| | Stretch | Bend | Stretch-bend | Torsion | Non-1.4VDW | 1.4VDW | Dipole/dipole | |
| $[Hg_2(B^1)_2.4H_2O]$ | 36.29 | 47.69 | -1.27 | 157.94 | -20.95 | 74.69 | 23.05 | 317.44 |
| $[Hg\ (B^1).2H_2O]NO_3$ | 21.27 | 24.43 | -0.10 | 82.08 | -5.51 | 31.02 | 5.40 | 158.60 |
| $[Hg_2(B^2)_2.6H_2O]$ | 78.70 | 65.34 | 0.91 | 306.57 | -4.20 | 90.21 | 13.75 | 551.29 |
| $[Hg(B^2).2H_2O]NO_3$ | 8.28 | 17.34 | 0.19 | 74.39 | -4.02 | 32.37 | 9.56 | 138.10 |
| $[Hg_2\ (B^3)_2.\ 2H_2O]$ | 14.67 | 28.68 | -0.30 | 48.57 | -8.86 | 54.82 | 3.11 | 140.69 |
| $[Hg(B^3).\ H_2O]NO_3$ | 4.48 | 65.84 | 0.09 | 51.49 | -1.69 | 25.62 | 2.72 | 148.55 |
| $[Hg_2(HB^4)_2.4H_2O]$ | 84.64 | 56.38 | 0.34 | 171.92 | -5.40 | 67.15 | 9.01 | 384.04 |
| $[Hg(B^4).3H_2O]$ | 10.14 | 17.78 | -0.08 | 97.97 | -5.36 | 31.91 | -3.31 | 149.05 |

** The units are kcal/mole for all terms. The values of the energy terms shown here are approximate and can vary slightly based on the type of processor used to calculate them*

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