

## Synthesis and Characterization of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Phenyl Amino Acetic Acid Ethyl Acetoacetate-2-ylmethylene Hydrazone

TAHANI I. KASHAR<sup>1,\*</sup>, AHMED M. EL-NAHAS<sup>1</sup> and ASMAA M. EL-MUGHAMSI<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, El-Menoufia University, Shebin El-kom, Egypt

<sup>2</sup>Department of Chemistry, Girls College, Madina Monawara, Saudi Arabia

\*Corresponding author: E-mail: tahanikashar@yahoo.com

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Phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone and its Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been synthesized and characterized by elemental analyses, IR, UV-vis, electrical conductivity, magnetic moment and thermal analyses (DTA, TGA). All the investigated complexes are mononuclear. The ligand behaves as di- or tridentates mono or dibasic acid in mononuclear complexes. Density functional theory (DFT) calculations indicated that the diketo forms are the most tautomers and the agreement between the calculated and experimental frequencies is very good.

**Key Words:** Complexes, Spectral studies, Conductivity, Thermal analyses, Synthesis, Density functional theory calculations.

### INTRODUCTION

The chemistry of hydrazones and their metal complexes have created great interest and enthusiasm among chemists because of their analytical, industrial and biological application<sup>1-3</sup>.  $\beta$ -Diketone hydrazone derivatives are known to act as good chelating agents<sup>4-7</sup> and show immense antitumor activity<sup>8-16</sup>. These compounds and their metal complexes are used as anti-tuberculosis agents<sup>17</sup>. Furthermore, some hydrazones are used as quantitative analytical reagents, especially in colorimetric and fluorimetric determination of metal ions<sup>18,19</sup>. Hydrazone complexes could be of mono-, di- or multinuclear nature. Continuous efforts to synthesize and characterize new hydrazones and relevant metal complexes for a variety of metal ions are devoted in attempts to find ligands and complexes of potential bioactivity. Our objective in this work is two folds. First to shed some light into the tautomeric equilibrium of the phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone (PAAEH) ligand both in the gas phase and in DMSO using quantum chemical calculations. Secondly to investigate the interaction of phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) so as to study their differential stoichiometric ratio. As the bioactivity study is beyond the scope of the current work, it is also our hope for biologists to find these targeted ligand and its metal complexes as promising active species.

### EXPERIMENTAL

Reagent grade chemicals were used. The elemental analyses were performed at the Micro analytical unit, Cairo University,

Egypt. Standard methods were used for determining the metal ions. IR and UV-vis spectra were recorded using a Perkin-Elmer 598 and a Lambda 4B-UV-vis spectrophotometers. <sup>1</sup>H NMR spectra in DMSO recorded using Varian EM-390, 90 MHz NMR spectrometer. Molar conductance was measured on a Bibby conductometer using 10<sup>-3</sup> M in DMF, DTA and TGA. Analyses were carried using Shimadzu TGA-50 instruments under nitrogen atmosphere.

A mixture of equimolar amount of (0.01 mol) aniline, ethyl chloro acetate and sodium acetate trihydrate in 20 mL of absolute ethanol was refluxed for 3 h. The solid so obtained was isolated and crystallized from ethanol to give ethyl anilino acetate. A mixture of equimolar amount of ethyl anilino acetate and hydrazine hydrate was stirred magnetically at 60 °C for 1 h. A white solid so obtained was isolated, dried and dissolved in ethanol (20 mL) and then treated with ethylacetoacetate (0.01 mol). The reaction mixture was refluxing for 2 h. The resulting product was filtered off and crystallized from ethanol and dried under vacuum P<sub>4</sub>O<sub>10</sub>. All complexes were prepared by mixing Ni(II), Co(II), Cu(II) Zn(II) and Fe(III) chloride and nitrate salts with the ligand in (1:1) (M:L) stoichiometries in ca. 50 mL EtOH and stirring for 5 h. The precipitated products were removed by filtration washed several times with EtOH and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

**Methods of quantum chemical calculations:** All electronic structure calculations were performed using the Gaussian98W suite of programs<sup>20</sup>. Geometry optimizations for seven tautomers of phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone have been performed using Density functional

theory (DFT) at the B3LYP level<sup>21-23</sup> using 3-21G(d) basis sets. Transition states between the most stable tautomers have been located. For each stationary point, we carried out vibrational frequency calculation to characterize their nature as minima or transition states. The vibrational modes were examined by using the ChemCraft program<sup>24</sup>. Vibrational analyses indicated that all tautomers are minima on the potential energy surface of phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone (all eigenvalues of the force-constant matrices are positive). For transition states, one negative eigenvalue has been found in the Hessian matrix. Zero-point vibrational energies (ZPE's) were evaluated and retrieved from frequency calculations. Theoretical energies refer to motionless state and correction for ZPE is needed to get 0 K energies.

Energies were further refined at the B3LYP/6-31+G(d) level using geometries optimized at B3LYP/3-21G(d). Solvation in DMSO has been modeled at the B3LYP/6-31+G(d)/B3LYP/3-21G(d) level using the polarized continuum model (PCM) of Tomasi and coworkers<sup>25</sup>.

## RESULTS AND DISCUSSION

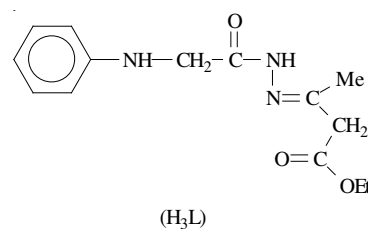
The analytical and spectral data of phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone and its complexes are given in Tables 1-3. The <sup>1</sup>H NMR spectrum of the ligand in DMSO at room temperature showed signals at 9.5<sup>26</sup> and 8.8 ppm for two NH groups. Also multiplet signals of aromatic protons appeared at 6.6-7.5 ppm<sup>27</sup>. The triplet and quartet signals appeared at 3.3 and 1.3 ppm are assigned to CH<sub>3</sub> and CH<sub>2</sub> of the ester group. The spectrum also showed signals at 1.8 ppm<sup>28</sup> and 4-4.5 ppm due to CH<sub>3</sub> and CH<sub>2</sub> groups.

The IR spectrum of the ligand (Table-2) showed a strong bands at 3393, 3180 and 3032 due to two ν(N-H) and ν(C-H) vibration, respectively. The band at 1736 and 1674 cm<sup>-1</sup> is

No.	Compound	λ <sub>max</sub> (nm)	Λ <sub>m</sub> (μs)	μ <sub>eff</sub> (BM)
C-1	[HLFeCl]Cl·4H <sub>2</sub> O	344, 310, 304, 290, 250	42.3	4.7
C-2	[HLCoCl·2H <sub>2</sub> O]·H <sub>2</sub> O	391, 350, 331, 310, 303, 274, 240	13.9	5.1
C-3	[HLNi·3H <sub>2</sub> O]Cl·3H <sub>2</sub> O	413, 350, 341, 310, 302, 275, 242	81.5	2.3
C-4	[HLCuCl]·H <sub>2</sub> O	351, 344, 310, 303, 289, 255	20.3	1.97
C-5	[(HL) <sub>2</sub> Zn·2H <sub>2</sub> O]·2H <sub>2</sub> O	369, 350, 303, 289, 243	5.0	dia
C-6	[H <sub>2</sub> LNi·3H <sub>2</sub> O](NO <sub>3</sub> )·2H <sub>2</sub> O	600, 410, 309, 302	168.3	2.4
C-7	[HLCuH <sub>2</sub> O]NO <sub>3</sub> ·H <sub>2</sub> O	530, 420, 308, 301, 251, 211	73.6	2.2

assigned to the two group of ν(C=O)<sup>29</sup>. A strong band observed at 1607 cm<sup>-1</sup> corresponds to ν(C=N) vibration<sup>30</sup>. The band appeared at 1032 cm<sup>-1</sup> is assigned to ν(N-N) vibration<sup>26,31</sup>.

Depending on these data the following structure of the ligand PAAEH (H<sub>3</sub>L) is suggest



Optimized structures of seven different phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone tautomers and related transition states are displayed in Figs. 1 and 2. The

TABLE-1  
ELEMENTAL ANALYSIS OF THE PAAEH AND ITS METAL COMPLEXES

No.	Compound	Colour	m.w.	Found/calcd. (%)					m.p. (°C)
				C	H	N	Cl	M	
	(H <sub>3</sub> L)	Pale yellow	277.0	61.1 (60.7)	7.5 (6.9)	16.2 (15.2)	–	–	235
C-1	[HLFeCl]Cl·H <sub>2</sub> O	Dark brown	476.0	35.9 (35.3)	4.8 (5.4)	8.7 (8.8)	15.2 (14.9)	10.4 (11.8)	>310
C-2	[HLCoCl·2H <sub>2</sub> O]·H <sub>2</sub> O	Gray	424.0	40.6 (39.6)	5.1 (5.7)	11.0 (10.0)	8.7 (8.4)	14.5 (13.9)	>310
C-3	[HLNiCl·3H <sub>2</sub> O]Cl·3H <sub>2</sub> O	Yellow	478.2	35.6 (35.1)	5.9 (6.2)	7.9 (8.8)	8.3 (7.4)	11.8 (12.3)	>310
C-4	[HLCuCl]·H <sub>2</sub> O	Brown	393.0	43.0 (42.7)	4.7 (5.1)	10.2 (11.2)	10.3 (10.6)	17.0 (16.1)	>310
C-5	[(HL) <sub>2</sub> Zn·2H <sub>2</sub> O]·2H <sub>2</sub> O	Pale yellow	689.5	49.5 (49.0)	5.2 (6.1)	12.3 (12.2)	–	10.2 (9.5)	>310
C-6	[H <sub>2</sub> LNi·3H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Green	531.7	31.7 (31.4)	4.9 (5.1)	12.9 (13.2)	–	10.8 (11.0)	>310
C-7	[HLCuH <sub>2</sub> O]NO <sub>3</sub> ·H <sub>2</sub> O	Brown	437.5	38.5 (38.4)	4.5 (5.0)	12.3 (12.8)	–	14.9 (14.5)	>310

TABLE-2  
IMPORTANT IR SPECTRAL BANDS OF PAAEH AND ITS METAL COMPLEXES

No	Compound	ν(O-H)	ν(NH, CH)	ν(C=O) diketone	ν(C=O) hydrazone	ν(C=N)	ν(N-N)	ν(M-O)	ν(M-N)
	(H <sub>3</sub> L)		3393 (s), 3180 (s), 3032 (s)	1736 (s)	1674 (s)	1607 (s)	1032 (s)	–	–
C-1	[HLFeCl]Cl·H <sub>2</sub> O	3000-3400 (br)	–	1720 (s)	–	1589 (s)	1100 (m)	521 (m)	430 (m)
C-2	[HLCoCl·2H <sub>2</sub> O]·H <sub>2</sub> O	3261 (br)	–	–	1605 (s)	1551 (s)	1115 (m)	512 (m)	430 (m)
C-3	[(HLNi·3H <sub>2</sub> O]·2H <sub>2</sub> O	3100-3400 (br)	–	–	1603 (s)	1560 (s)	1098 (m)	516 (m)	420 (m)
C-4	[HLCuCl]·H <sub>2</sub> O	3200-3300	3217 (m), 3000 (w)	1724 (s)	–	1600 (m)	1098 (m)	511 (m)	430 (m)
C-5	[(HL) <sub>2</sub> Zn·2H <sub>2</sub> O]·2H <sub>2</sub> O	3327 (s)	–	–	–	1552 (s)	1103 (s)	510 (w)	430 (m)
C-6	[H <sub>2</sub> LNi·3H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	3440 (br)	–	1710 (m)	1627 (m)	1590 (m)	1100 (m)	414 (m)	–
C-7	[HLCuH <sub>2</sub> O]NO <sub>3</sub> ·H <sub>2</sub> O	3214 (br)	–	–	1640 (m)	1600 (m)	1100 (m)	–	507 (m)

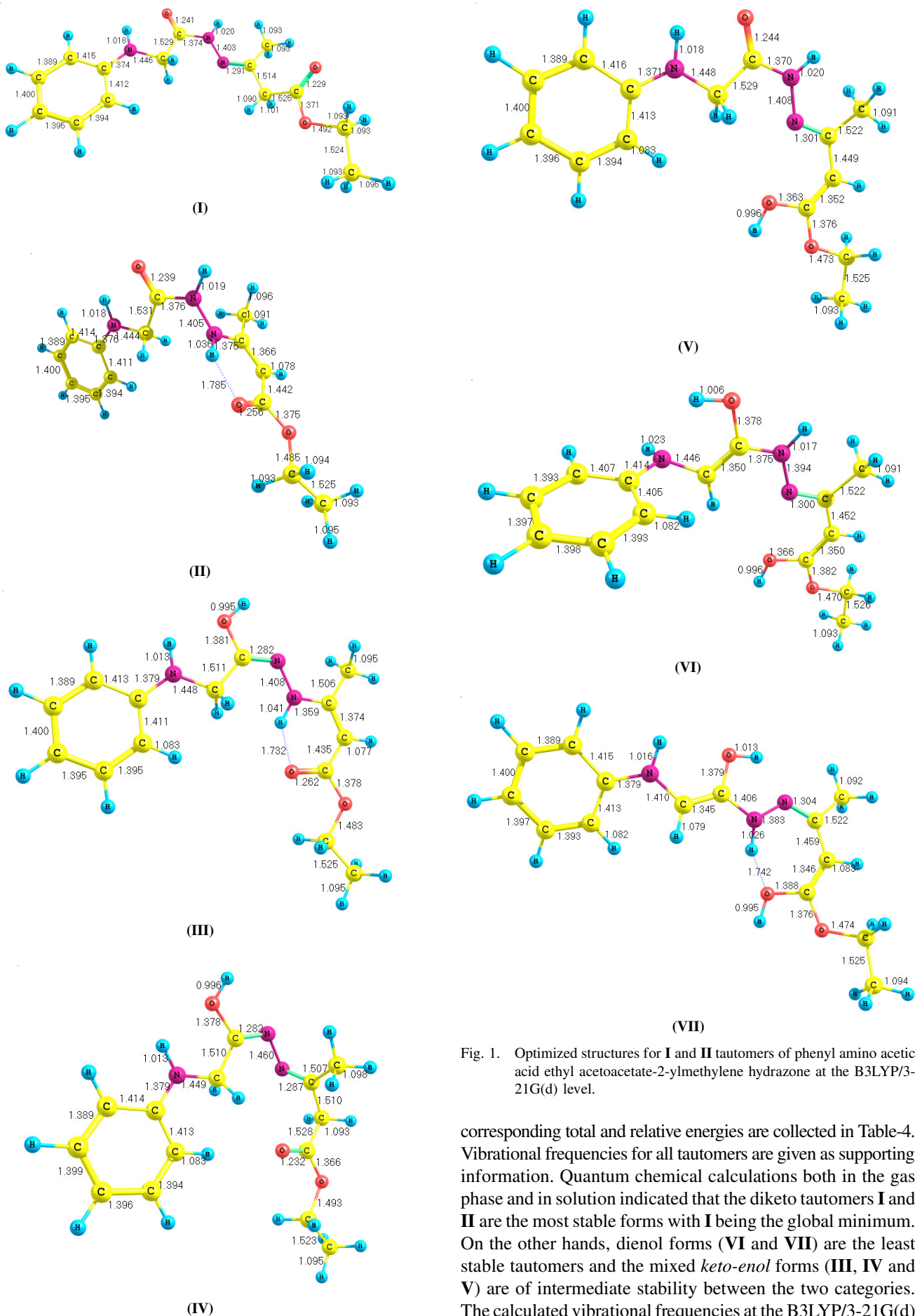


Fig. 1. Optimized structures for **I** and **II** tautomers of phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone at the B3LYP/3-21G(d) level.

corresponding total and relative energies are collected in Table-4. Vibrational frequencies for all tautomers are given as supporting information. Quantum chemical calculations both in the gas phase and in solution indicated that the diketo tautomers **I** and **II** are the most stable forms with **I** being the global minimum. On the other hands, dienol forms (**VI** and **VII**) are the least stable tautomers and the mixed *keto-enol* forms (**III**, **IV** and **V**) are of intermediate stability between the two categories. The calculated vibrational frequencies at the B3LYP/3-21G(d)

level agree very well with the reported experimental data after scaling the computed values by 0.962 to account for anharmonicity of the calculated frequencies. The calculated IR spectra for tautomer **I** are 3378, 3342  $\text{cm}^{-1}$  for the two NH bonds, 3098-3058  $\text{cm}^{-1}$  for C-H aromatic and 1675 and 1669  $\text{cm}^{-1}$  for the two C=O groups. The higher energy barrier of 42-66 kcal/mol between the most stable conforms at different levels of theory in the gas phase and in DMSO prevents their transformation at temperature range used in the experimental work reported here. These finding confirm the existence of only the diketo form in the gas phase and in DSMO. The only way of forming slightly less stable tautomers, like **I** and **III** is only through tunneling which is efficient with higher barriers at low temperature.

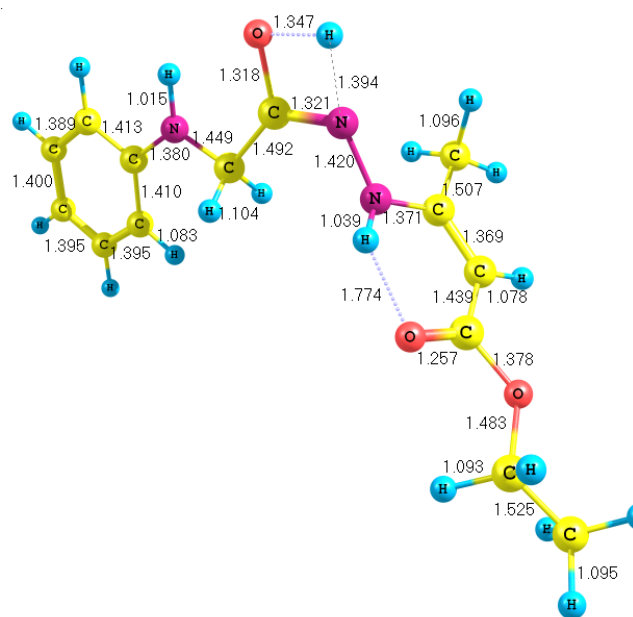
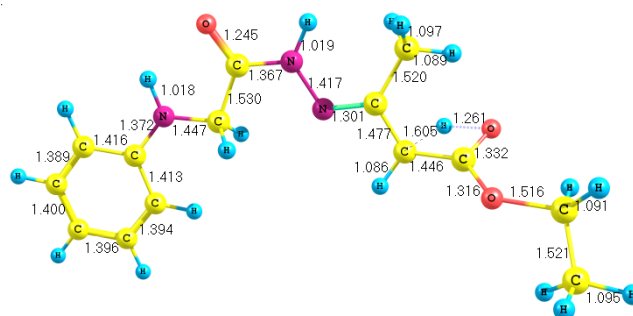
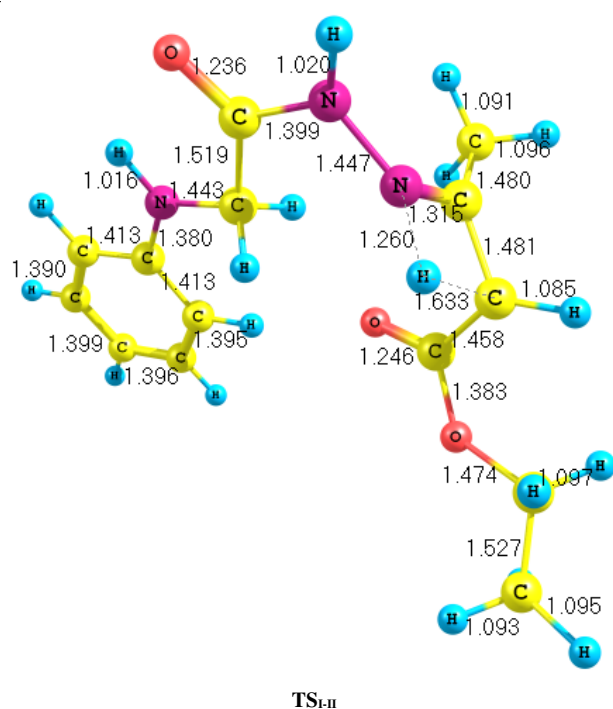


Fig. 2. Optimized structures for transition states at the B3LYP/3-21G(d) level

The analytical and spectral data of the prepared complexes (Tables 1-3) showed that the complexes No **1**, **2**, **3**, **4** and **5**

TABLE-4 TOTAL ( $E_e$ , au), ZPE (au) AND RELATIVE ( $\Delta E$ , kcal/mol) ENERGIES CALCULATED FOR DIFFERENT TAUTOMERS OF PAAEH* AT B3LYP <sup>a</sup>										
Property/species	I	II	III	IV	V	VI	VII	TS <sub>I-V</sub>	TS <sub>I-II</sub>	TS <sub>II-III</sub> <sup>b</sup>
$E_e/3-21G(d)$	-929.71522	-929.72336	-929.70109	-929.68811	-929.67586	-929.63480	-929.64488	-929.60081	-929.61765	-929.64989
ZPE/3-21G(d)	0.32332	0.32456	0.323212	0.32223	0.32259	0.32122	0.32172	0.3176	0.31774	0.31879
$H_{298}/3-21G(d)$	-929.37038	-929.37774	-929.35658	-929.34422	-929.33167	-929.29187	-	-929.28321	-929.29991	-929.30991
$\Delta E_0/3-21G(d)$	0	-4.34	8.79	16.32	24.24	49.14	43.13	68.20	57.72	42.48
$\Delta H_{298}/3-21G(d)$	0	-4.62	8.66	16.41	24.29	49.27	43.13	68.20	57.72	42.56
$\Delta E_c/3-21G(d)$	0	-5.11	8.86	17.01	24.70	50.47	44.14	71.79	61.23	46.11
$E_e/(6-31+G(d))/3-21G(d)$	-934.88671	-934.88591	-934.86764	-934.85798	-934.84760	-934.80592	-934.80551	-934.77100	-934.77895	-934.81185
$\Delta E_e/(6-31+G(d))/3-21G(d)$	0	0.50	11.96	18.03	24.54	50.70	50.95	72.61	67.62	46.470
$E_c/(6-31+G(d))(DMSO)/3-21G(d)$	-934.89594	-934.89393	-934.87403	-934.86354	-934.85928	-934.81713	-934.81676	-934.78240	-934.78987	-934.81773
$\Delta E_c/(6-31+G(d))(DMSO)/3-21G(d)$	0	1.26	13.75	20.33	23.00	49.45	49.68	71.24	66.56	47.82
$\Delta E_0/(6-31+G(d))/3-21G(d)$	0	1.28	11.89	17.34	24.08	49.376940	49.94	69.01	64.12	42.85
$\Delta E_0/(6-31+G(d))(DMSO)/3-21G(d)$	0	2.03	13.68	19.642	22.54	48.13	48.68	67.65	63.056	44.20

<sup>a</sup> $E_e = E_c + ZPE$ ;  $H_T$  (enthalpy) =  $E_{\text{thermal}} + nRT$ ;  $E_{\text{thermal}} = ZPE + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$ . <sup>b</sup>Calculated with respect to II. \*Phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene.

are formed in stoichiometric ratios (M:L) of 1:1 for M=Co(II), Cu(II), Fe(III) and Ni(II) or 1:2(M:L) for M=Zn(II). Molar conductance indicates that the mononuclear Cu(II), Fe(III) and Ni(II) complexes are electrolytes in DMF<sup>28</sup>, whereas the Co(II) chloride complexes are non-electrolytes.

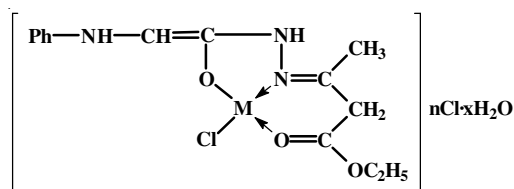
The investigated metal complexes exhibit change in  $\nu(\text{N-H})$  and  $\nu(\text{C-H})$  band due to the appearance of new band in 3400-3000  $\text{cm}^{-1}$  region assigned to  $\nu(\text{O-H})$  of coordinated water<sup>32</sup>. The absence of  $\nu(\text{C=O})$   $\beta$ -diketone band in all complexes except complexes No **1**, **4** and **6** indicated that the coordination are formed through the enol form of  $\beta$ -diketone part. The negative shift of the  $\nu(\text{C=O})$  band of hydrazide part indicates that  $\nu(\text{C=O})$  group are coordinated in complexes No **1**, **4**, **5** and the  $\nu(\text{C=O})$  band of hydrazide part disappeared and a negative shift in  $\nu(\text{C=O})$  of  $\beta$ -diketone part is found. In all complexes negative shift are detected for  $\nu(\text{C=N})$  stretching vibrations which suggests a coordination through nitrogen of C=N group<sup>28</sup>. All of the investigated complexes give new bands at 521-510<sup>33</sup>, 430-420 and 330-310  $\text{cm}^{-1}$  assigned to  $\nu(\text{M-O})$ ,  $\nu(\text{M-N})$ , respectively but  $\nu(\text{M-Cl})$ <sup>34</sup> appeared in complexes No **1**, **2** and **4**.

All the complexes display bands around 500 nm may be assigned to charge transfer (CT) transitions arising from metal-ligand interaction (Table-3)<sup>35</sup>. The bands at  $\approx 450$  and 413-344 nm may be attributed to  $n-\pi^*$ <sup>28</sup> and  $\pi-\pi^*$  transitions, respectively, of conjugated C=N group<sup>28</sup>. The bands at 302-240 nm which may be attributed to  $\pi-\pi^*$  transition of ketoimine group<sup>36</sup>. The observed magnetic moment values for Co(II) complexes are 4.9 BM (Table-1). These value are within the expected range of 4.7-5.2 BM<sup>4,37</sup> for octahedral Co(II) complex also the BM values of Ni(II) complex 2.3 BM are accepted for hexa-coordinate octahedral geometries<sup>37,38</sup>. The magnetic moment of copper(II) complex indicate the presence of one unpaired electron and square planar  $d^9$  complex are expected<sup>28</sup> and also the values of BM of Fe(III) complexes are acceptable for square planar geometries.

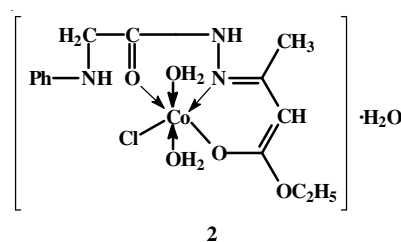
The thermogravimetric analysis of solid complexes given in Tables 5 and 6 showed that all the complexes are thermally stable up to 60  $^{\circ}\text{C}$ <sup>35</sup>. The presence of an endothermic peak within 60-140  $^{\circ}\text{C}$ <sup>28</sup> in DTA indicates the beginning of dehydration which is accompanied with a weight loss in TGA. The removal of coordinated water molecules takes place at 140-300  $^{\circ}\text{C}$ <sup>28</sup> and an additional weight loss was observed which may be attributed to the removal of HCl molecule and appeared as exothermic peak in DTA. The percentage weight losses and

the number of dehydrated and coordinated water are listed in Table-5. The complexes were heated up to 800  $^{\circ}\text{C}$  where metal oxides were not reached<sup>39</sup>.

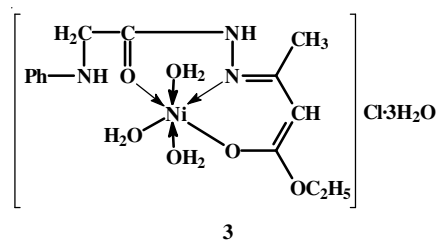
Based on the elemental, spectrophotometric analyses (IR, UV-vis, TGA, DTA) and magnetic moments, the resulting complexes have the following structures:



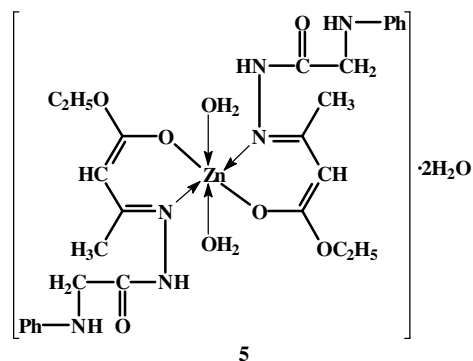
M = Cu<sup>2+</sup> or Fe<sup>3+</sup>, n = 0 for Cu<sup>2+</sup>, n = 1 for Fe<sup>3+</sup>  
x = 4 for Fe<sup>3+</sup> complex and 1 for Cu<sup>2+</sup>  
**1, 4**



**2**



**3**



**5**

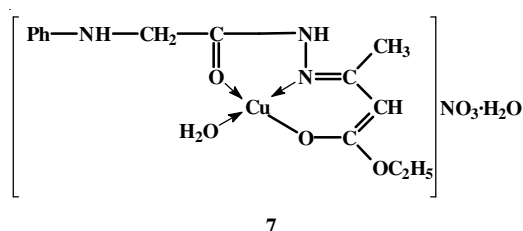
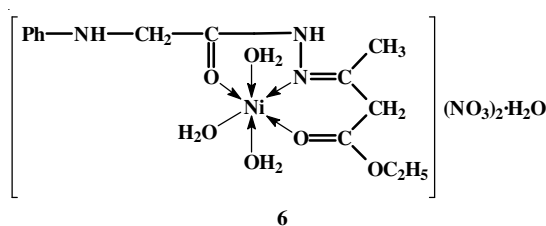
TABLE-5  
THERMAL ANALYSIS TGA OF THE INVESTIGATED COMPLEXES

No.	Compound	Lattice water			Number of H <sub>2</sub> O	Coordinated water			Number of H <sub>2</sub> O
		Temperature rang ( $^{\circ}\text{C}$ )	Weight loss (%)			Temperature range ( $^{\circ}\text{C}$ )	Weight loss		
			Found.	Calcd.			Found.	Calcd.	
C-1	[HLFeCl]Cl.4H <sub>2</sub> O	50-130 130-200	4.7 13.0	3.8 11.3	1	—	—	—	—
C-2	[HLCuCl.2H <sub>2</sub> O].H <sub>2</sub> O	50-130	4.1	4.2	3	130-250	8.7	8.5	2
C-3	[HLNi.3H <sub>2</sub> O]Cl.3H <sub>2</sub> O	50-140	9.4	11.3	1	140-350	20.3	18.9	3**
C-4	[HLCuCl].H <sub>2</sub> O	100-250	2.8, 12.3	2.2, 11.6	3	—	—	—	—
C-5	[(HL) <sub>2</sub> Zn.2H <sub>2</sub> O].2H <sub>2</sub> O	70-140	4.6	5.2	1/2, 1/2**	140-320	4.0	5.2	2
C-6	[H <sub>2</sub> LNi.3H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub> .H <sub>2</sub> O	50-170	3.3	3.4	2	170-300	11.2	10.2	3
C-7	[HLCuH <sub>2</sub> O]NO <sub>3</sub> .H <sub>2</sub> O	50-100	3.1	4.1	1	100-250	20.2	18.5	1*

\*Loss of Coordinated H<sub>2</sub>O + aniline. \*\*Loss of Coordinated H<sub>2</sub>O + HCl

TABLE-6  
THERMAL ANALYSIS DTA OF THE METAL COMPLEXES

No	Compound	Temperature	Assignment	
C-1	[HLFeCl]Cl·4H <sub>2</sub> O	Endo.	70	Loss of one molecule of latt. water
		Endo.	200	Loss of three molecule of latt. water
		Exo.	375.7	Thermaldecomposition
		Exo.	506.8	Thermal decomposition
		Exo.	641.5	Thermal decomposition
C-2	[HLCuCl·2H <sub>2</sub> O]·H <sub>2</sub> O	Endo.	52.7	Loss of one molecule of latt. water
		Endo.	170.0	Loss of two molecule of coord.water
		Endo.	449	Thermal decomposition
		Endo.	700	Thermal decomposition
C-3	[HLNi·3H <sub>2</sub> O]Cl·3H <sub>2</sub> O	Endo.	68.1	Loss of three molecule of latt. water
		Exo.	381.8	Loss of three molecule of coord. water + HCl
		Exo.	430.1	Thermal decomposition
		Exo.	495	Thermal decomposition
C-4	[HLCuCl]·H <sub>2</sub> O	Endo.	55.1	Loss of half molecule of latt.water
		Exo.	297	Loss of half molecule of latt. water + HCl
		Exo.	504	Thermal decomposition
C-5	[(HL) <sub>2</sub> Zn·2H <sub>2</sub> O]·2H <sub>2</sub> O	Endo.	101.9	Loss of two molecule of latt. water
		Exo.	370.8	Loss of two molecule of coord. water + Thermal decomposition
		Exo.	421.4	Thermal decomposition
		Exo.	524.3	Thermal decompositio
C-6	[H <sub>2</sub> LNi·3H <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Endo.	50	Loss of one molecule of latt. water
		Exo.	296	Loss of three molecule of coord. water
		Exo.	340	Thermal decomposition
		Endo.	391	Thermal decomposition
		Endo.	444	Thermal decomposition
C-7	[HLCuH <sub>2</sub> O]NO <sub>3</sub> ·H <sub>2</sub> O	Endo.	50	Loss of one molecule of latt. water
		Endo.	150	Loss of one molecule of coord. water
		Exo.	314	Thermal decomposition



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