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Synthesis and characterization of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of PAAEH

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ABSTRACT

Phenyl amino acetic acid ethyl acetoacetate-2-ylmethylene hydrazone (PAAEH) 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, VIS-UV, electrical conductivity, magnetic moment and thermal analyses (DTA, TGA). All of the investigated complexes are mononuclear. The ligand behaves as di- or tridentate 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. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Complexes;
Spectral studies;
Conductivity;
Thermal analyses;
Synthesis;
DFT 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^[1-3]. β -Diketone Hydrazone derivatives are known to act as good chelating agents^[4-7] and show immense antitumor activity^[8-16]. These compounds and their metal complexes are used as antituberculosis agents^[17]. Furthermore, some hydrazones are used as quantitative analytical reagents, especially in colorimetric and fluorimetric determination of metal ions^[18,19]. 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 (PAAEH) ligand both in the gas phase and in DMSO using quantum chemical calculations. Secondly to investigate the interaction of PAAEH with the title metal ions 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 complexes as promising active species.

MATERIALS AND METHODS

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. ^1H NMR spectra in DMSO recorded using Varian EM-390, 90-MHz NMR spectrometer. Molar conductance was measured on a Bibby conductometer using 10^{-3} 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 hrs. 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 1h. A white solid so obtained was isolated, dried and dissolved in ethanol (20 ml) and then treated with ethylacetocacetate (0.01 mol). The reaction mixture was refluxing for 2 hrs. The resulting product was filtered off and crystallized from ethanol and dried under vacuum P_4O_{10} . 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 hrs. The precipitated products were removed by filtration washed several times with EtOH and dried in vacuo over P_4O_{10} .

Methods of quantum chemical calculations

All electronic structure calculations were performed using the Gaussian98W suite of programs^[20]. Geometry optimizations for seven tautomers of PAAEH have been performed using Density Functional Theory (DFT) at the B3LYP level^[21-23] 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^[24]. Vibrational analyses indicated that all tautomers are minima on the potential energy surface of PAAEH (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^[25].

RESULTS AND DISCUSSION

The analytical and spectral data of PAAEH and its complexes are given in TABLES 1, 2, and 3. The ^1H NMR spectrum of the ligand in DMSO at room temperature showed signals at 9.5^[26] and 8.8 ppm for two NH groups. Also multiplet signals of aromatic protons appeared at 6.6-7.5 ppm^[27]. The triplet and quartet signals appeared at 3.3 and 1.3 ppm are assigned to CH_3 and CH_2 of the ester group. The spectrum also showed signals at 1.8 ppm^[28] and 4-4.5 ppm due to CH_3 and CH_2 groups

The IR spectrum of the ligand (TABLE 2) showed a strong bands at 3393, 3180 and 3032 due to two $\nu(\text{N-H})$ and $\nu(\text{C-H})$ vibration respectively. The band at 1736 and 1674 cm^{-1} is assigned to the two group of $\nu(\text{C=O})$ ^[29]. A strong band observed at 1607 cm^{-1} cor-

TABLE 1 : Elemental analysis of the ligand and its complexes.

NO.	Compound	Color	M.wt	C %		H %		N %		Cl %		M %		m.p. °C
				Found	calc.	Found	calc.	Found	calc.	Found	calc.	Found	calc.	
	(H ₃ L)	p.yellow	277	61.1	60.7	7.5	6.9	16.2	15.2	-	-	-	-	235
C-1	[HLFeCl] Cl.4H ₂ O	d.brown	476	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 ₂ O] H ₂ O	gray	424	40.6	39.6	5.1	5.7	11.0	10.0	8.7	8.4	14.5	13.9	>310
C-3	[HLNi.3H ₂ O]Cl.3H ₂ 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 ₂ O	Brown	393	43.0	42.7	4.7	5.1	10.2	11.2	10.3	10.6	17.0	16.1	>310
C-5	[(HL) ₂ Zn.2H ₂ O] 2H ₂ O	p.yellow	689.5	49.5	49.0	5.2	6.1	12.3	12.2	-	-	10.2	9.5	>310
C-6	[H ₂ L Ni.3H ₂ O] (NO ₃) ₂ H ₂ O	green	531.7	31.7	31.4	4.9	5.1	12.9	13.2	-	-	11	10.8	>31
C-7	[HL CuH ₂ O] NO ₃ H ₂ O	Brown	437.5	38.5	38.4	4.5	5.0	12.3	12.8	14.9	14.5	-	-	>310

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TABLE 2 : Important IR spectral bands of the ligand and its complexes.

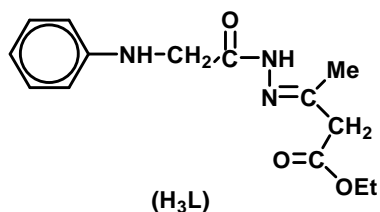
NO.	Compound	ν_{O-H}	$\nu_{NH,CH}$	$\nu_{C=O}$ diketone-	$\nu_{C=O}$ hydrazide	$\nu_{C=N}$	ν_{N-N}	ν_{M-O}	ν_{M-N}
	(H ₃ L)		3393 (S) 3180 (S) 3032 (S)	1736 (S)	1674 (S)	1607 (S)	1032 (S)	-	-
C-1	[HLFeCl] Cl.4H ₂ O	3000-3400 (br)		1720 (S)		1589 (S)	1100 (m)	521 (m)	430 (m)
C-2	[HLCoCl.2H ₂ O] H ₂ O	3261 (br)		-	1605 (S)	1551 (S)	1115 (m)	512 (m)	430 (m)
C-3	[HLNi.3H ₂ O]Cl.3H ₂ O	3100-3400 (br)		-	1603 (S)	1560 (S)	1098 (m)	516 (m)	420(m)
C-4	[HLCuCl] H ₂ O	3200-3300	3217 (m) 3000 (w)	1724 (S)		1600 (m)	1098 (m)	511 (m)	430 (m)
C-5	[(HL) ₂ Zn.2H ₂ O]2H ₂ O	3327 (S)	-	-	-	1552 (S)	1103 (S)	510 (w)	430(m)
C-6	[H ₂ L Ni.3H ₂ O] (NO ₃) ₂ H ₂ O	3440 (br)		1710 (m)	1627 (m)	1590 (m)	1100 (m)	514 (m)	
C-7	[HL CuH ₂ O] NO ₃ H ₂ O	3214 (br)		-	1640 (m)	1600 (m)	1100 (m)	507 (m)	

TABLE 3 : Electronic spectra, conductivity and magnetic moments of the investigated complexes.

NO.	Compound	λ_{max}, nm	$\Lambda_m, \mu S$	μ_{eff} (B.M)
C-1	[HLFeCl] Cl.4H ₂ O	344,310,304,290,250	42.3	4.7
C-2	[HLCoCl.2H ₂ O] H ₂ O	391,350,331,310,303,274,240	13.9	5.1
C-3	[HLNi.3H ₂ O]Cl.3H ₂ O	413,350,341,310,302,275,242	81.5	2.3
C-4	[HLCuCl] H ₂ O	351,344,310,303,289,255	20.3	1.97
C-5	[(HL) ₂ Zn.2H ₂ O] 2H ₂ O	369,350,303,289,243	5.0	Dia
C-6	[H ₂ L Ni.3H ₂ O] (NO ₃) ₂ H ₂ O	600,410,309,302	168.3	2.4
C-7	[HL CuH ₂ O] NO ₃ H ₂ O	530,420,308,301,251,211	73.6	2.2

responds to $\nu(C=N)$ vibration^[30]. The band appeared at 1032 cm^{-1} is assigned to $\nu(N-N)$ vibration^[26,31].

Depending on these data the following structure is suggest



Optimized structures of seven different PAAEH tautomers and related transition states are displayed in Figures 1 and 2. The 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 $3342, 3378\text{ cm}^{-1}$ for the two NH bonds, $3098-3058\text{ cm}^{-1}$ for C-H aromatic, and 1675 and 1669 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.

The analytical and spectral data of the prepared complexes (TABLES 1, 2, and 3) showed that the complexes no 1,2,3,4 and 5 are formed in stoichiometric ratios (M:L) of 1:1 for M=Co(II), Cu(II), Fe(III), and

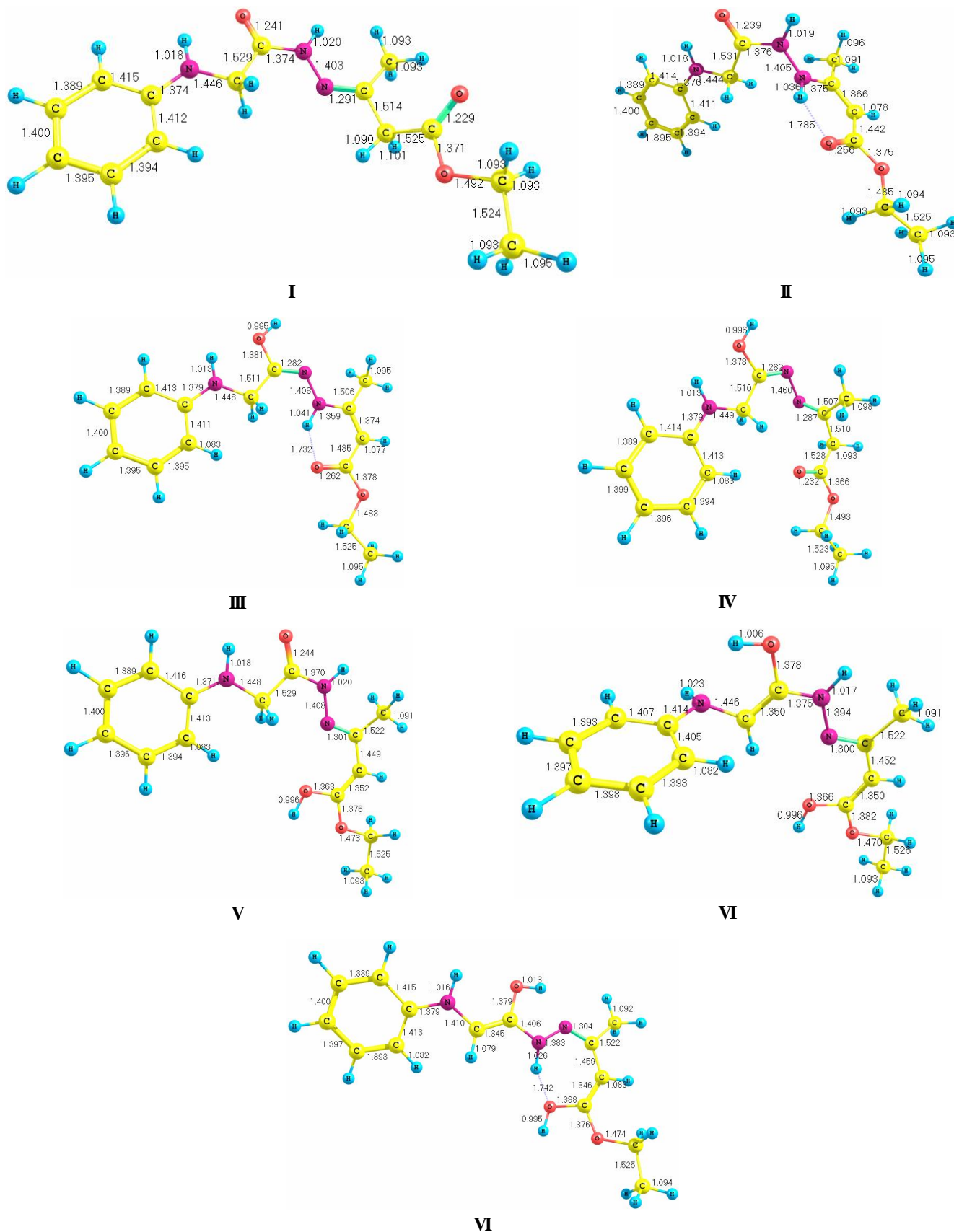


Figure 1 : Optimized structures for I and II tautomers of PAAEH at the B3LYP/3-21G(d) level.

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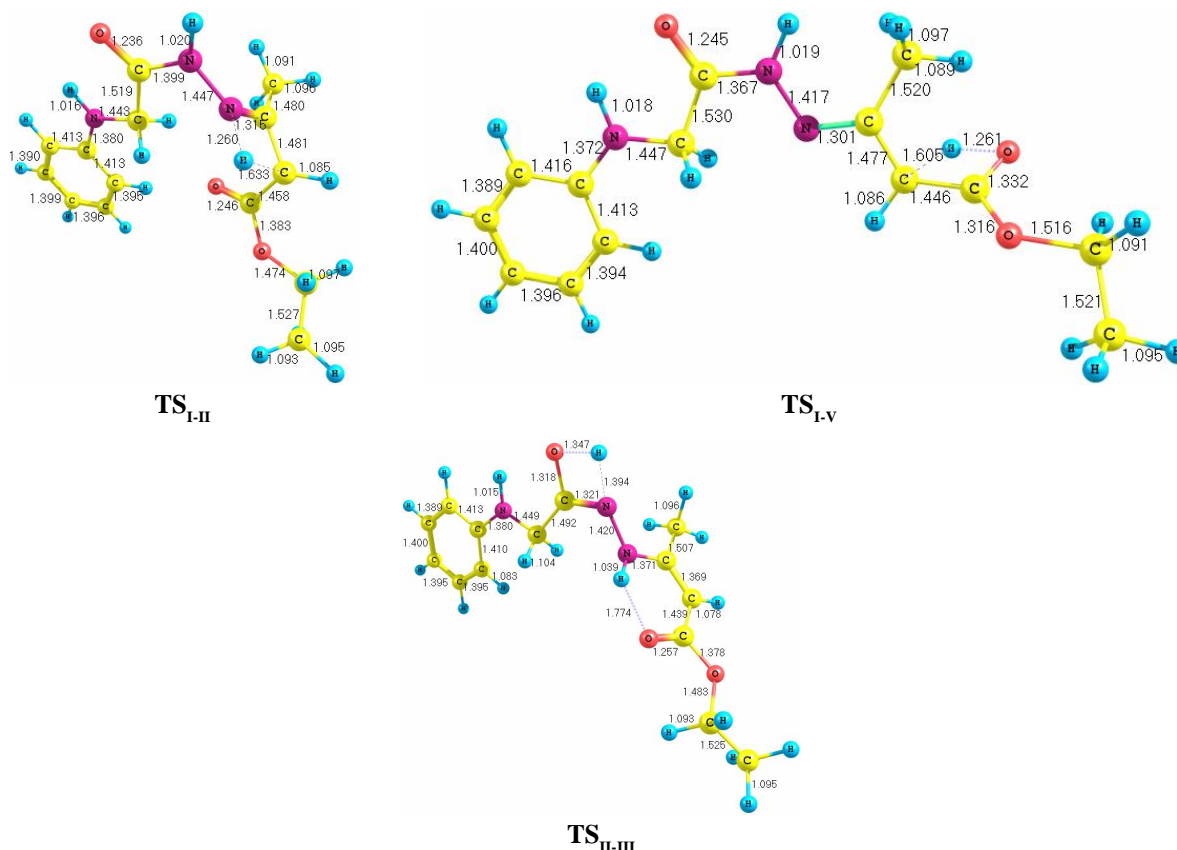


Figure 2 : Optimized structures for transition states at the B3LYP/3-21G(d) level.

TABLE 4 : Total (E_c , au), ZPE (au) and relative (ΔE , kcal/mol) energies calculated for different automers of PAAEH at B3LYP^a

Property/species	I	II	III	IV	V	VI	VII	TS _{I-V}	TS _{I-II}	TS _{II-III} ^b
$E_c/3-21G(d)$	-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	49.27	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
$E_c/(6-31+G(d))/3-21G(d)$	-934.88671	-934.88591	-934.86764	-934.85798	-934.84760	-934.80592	-934.80551	-934.77100	-934.77895	-934.81185
$\Delta E_c/(6-31+G(d))/3-21G(d)$	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

^a $E_0 = E_c + ZPE$; H_f (enthalpy) = $E_{\text{thermal}} + nRT$; $E_{\text{thermal}} = ZPE + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$. ^b calculated with respect to II.

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^[28], whereas the Co(II) chlorid complexes are non-electrolytes.

The investigated metal complexes exhibit change in $\nu(N-H)$ and $\nu(C-H)$ band due to the appearance of new band at 3400-3000 cm^{-1} assigned to $\nu(O-H)$ of

coordinated water^[32]. The absence of $\nu(C=O)$ β -diketone band in all complexes except complexes no 1, 4 and 6 indicated that the coordination are formed through the enol form of β -diketone part. The negative shift of the $\nu(C=O)$ band of hydrazide part indicates that $\nu C=O$ group are coordinated but in complexes no1, 4,5 and the $\nu(C=O)$ band of hydrazide part dis-

appeared and a negative shift in $\nu(\text{C}=\text{O})$ of β -diketone part is found. In all complexes negative shift are de-

TABLE 5 : Thermal analysis TGA of the investigated complexes

NO.	Compound	Lattice water			Coordinated water				
		Temp. rang.	wt. loss		No. of H ₂ O	Temp. rang.	wt. loss		No. of H ₂ O
			Found	Calc.			Found	Calc.	
C-1	[HLFeCl]Cl.4H ₂ O	50-130	4.7	3.8	1	-	-	-	
		130-200	13.0	11.3	3	-	-	-	
C-2	[HLC _o Cl.2H ₂ O] H ₂ O	50-130	4.1	4.2	1	130-250	8.7	8.5	2
C-3	[HLNi.3H ₂ O]Cl.3H ₂ O	50-140	9.4	11.3	3	140-350	20.3	18.9	3**
C-4	[HLCuCl] H ₂ O	100-250	2.8	2.2	½	-	-	-	-
			12.3	11.6	½**				
C-5	[(HL) ₂ Zn.2H ₂ O] 2H ₂ O	70-140	4.6	5.2	2	140-320	4.0	5.2	2
C-6	[H ₂ L Ni.3H ₂ O] (NO ₃) ₂ H ₂ O	50-170	3.3	3.4	1	170-300	11.2	10.2	3
C-7	[HL CuH ₂ O] NO ₃ H ₂ O	50-100	3.1	4.1	1	100-250	20.2	18.5	1*

* Loss of Coordinated H₂O + aniline ** Loss of Coordinated H₂O + HCl

TABLE 6 : Thermal analysis DTA of the complexes.

No	Compound	Temp.	Assignment
C-1	[HLFeCl] Cl.4H ₂ O	Endo. 70	Loss of one molecule of latt.water
		Endo. 200	Loss of three molecule of latt.water
		Exo. 375.7	Thermal decomposition
		Exo. 506.8	Thermal decomposition
		Exo. 641.5	Thermal decomposition
C-2	[HLC _o Cl.2H ₂ O] H ₂ 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 ₂ O]Cl.3H ₂ 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
C-4	[HLCuCl] H ₂ O	Exo. 495	Thermal decomposition
		Endo. 55.1	Loss of half molecule of latt.water
		Exo. 297	Loss of half molecule of latt.water + HCl
C-5	[(HL) ₂ Zn.2H ₂ O] 2H ₂ O	Exo. 504	Thermal decomposition
		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
C-6	[H ₂ L Ni.3H ₂ O] (NO ₃) ₂ H ₂ O	Exo. 524.3	Thermal decomposition
		Endo. 50	Loss of one molecule of latt.water
		Exo. 296	Loss of three molecule of coord.water
C-7	[HL CuH ₂ O] NO ₃ H ₂ O	Exo. 340	Thermal decomposition
		Endo. 391	Thermal decomposition
		Endo. 444	Thermal decomposition
		Endo. 50	Loss of one molecule of latt.water
C-7	[HL CuH ₂ O] NO ₃ H ₂ O	Endo. 150	Loss of one molecule of coord.water
		Exo. 314	Thermal decomposition

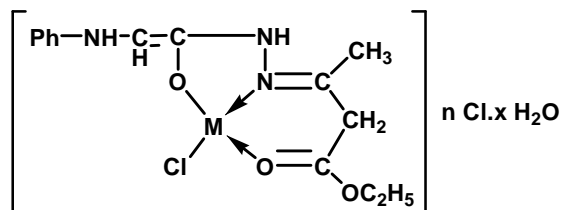
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tected for $\nu(\text{C}=\text{N})$ stretching vibrations which suggests a coordination through nitrogen of $\text{C}=\text{N}$ group^[28]. All of the investigated complexes give new bands at $(521-510 \text{ cm}^{-1})$ ^[33], $(430-420 \text{ cm}^{-1})$ and $(330-310 \text{ cm}^{-1})$ assigned to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ respectively but $(\text{M}-\text{Cl})$ ^[34] 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)^[35]. The bands at $\cong 450$ and $413-344 \text{ nm}$ may be attributed to $n-\pi^*$ ^[28] and $\pi-\pi^*$ transitions, respectively, of conjugated $\text{C}=\text{N}$ group^[28]. The bands at $302-240 \text{ nm}$ which may be attributed to $\pi-\pi^*$ transition of ketoimine group^[36]. The observed magnetic moment values for Co(II) complexes are 4.9 B.M (TABLE 1). These value are within the expected range of 4.7-5.2 B.M^[4,37] for octahedral Co(II) complex also the B.M. values of Ni(II) complex 2.3 B.M are accepted for hexa-coordinate octahedral geometries^[37,38]. The magnetic moment of copper(II) complex indicate the presence of one unpaired electron and square planar d^9 complex are expected^[28] and also the values of B.M. of Fe(III) complexes are acceptable for square planar geometries.

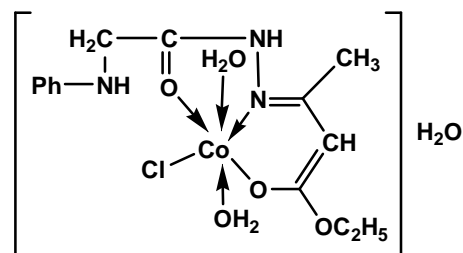
The thermogravimetric analysis of solid complexes given in TABLES 5 and 6 showed that all the complexes are thermally stable up to 60°C ^[35]. The presence of an endothermic peak within $60-140^\circ\text{C}$ ^[28] in DTA indicates the beginning of dehydration which is accompanied with a weight loss in TGA. The removal of coordinated water molecules takes place at $140-300^\circ\text{C}$ ^[28] 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°C where metal oxides were not reached^[39].

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

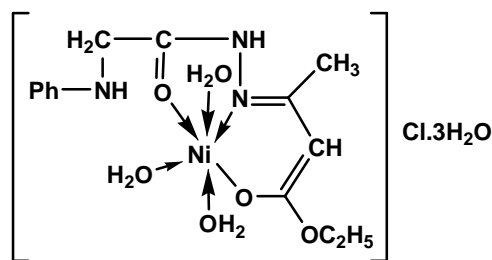


M = Cu+2 and Fe+3, n = 0 for Cu+2
X = 4 for Fe+3 complex and 1 for Cu+2

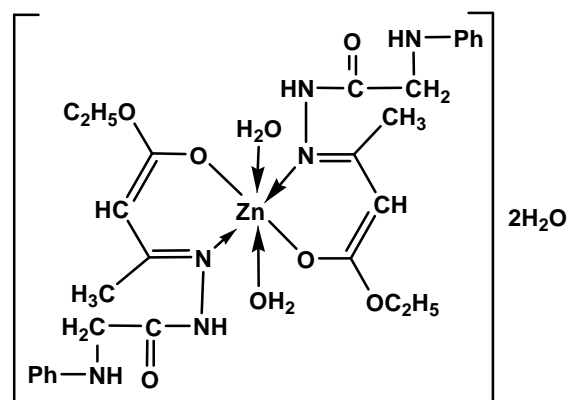
Complexes no 1,4



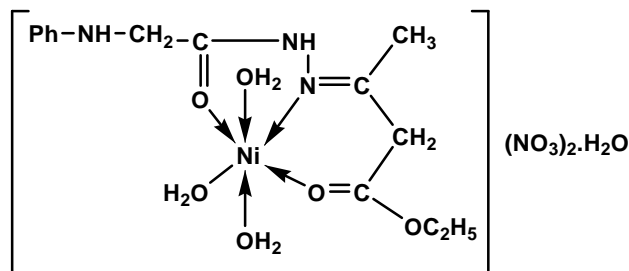
Complexes no 2



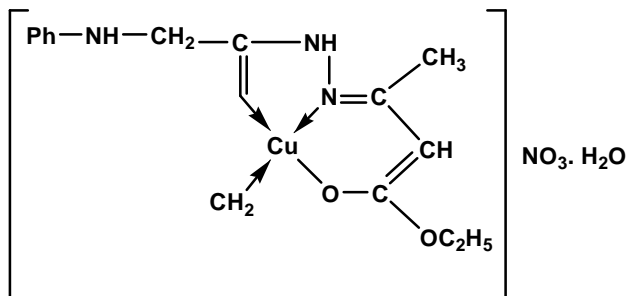
Complexes no 3



Complexes no 5



Complexes no 6



Complex no 7

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