

Physicochemical Properties and Molecular Mechanics of Some Thiohydantoin Derivatives Complexes.

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ABSTRACT

The organic ligands Cinnamaldehydethiosemicarbazone(1), 3-(3-Phenyl-allylideneamino)-2-thioxoimidazolidine-4-one (2), [4-Oxo-3-(3-phenyl-allylideneamino)-2-thioxoimidazolidin-1-yl]-acetic acid (3), 1-(1-aza-4-phenylbuta-1,3-dienyl)-2-methylthio-2-imidazolin-5-one (4) and 1-(1-aza-4-phenylbuta-1,3-dienyl)-2-methylthio-2-imidazolin-5-one (5) were prepared and characterized using spectroscopic and physico-chemical methods (Scheme 1). The modeling of the synthesized compounds (1 and 2) and the computation of the steric, Van der Waals, bending and stretching energy were calculated using the Molecular Mechanical method (MM2) using CS cheme Office program. For each conformation of the synthesized compounds (1, 2), the minimum energy one was determined and listed. The complexes of the compound 1 and 2 with Zn(II), Cu(II) and Ni(II) were prepared and characterized. The postulated spatial arrangements have been confirmed using the molecular modeling program, elemental analysis (CHNM %), conductance, IR, thermal analysis and mass spectra.

Key words: Complexes, Molecular Mechanics, Thiohydantoin, Thermal Analysis.

INTRODUCTION

The thiohydantoin and its derivatives have long history in the chemistry field (Schlack 1926; Johnson *et al.*, 1911). Among the known thiohydantoin, 2-thiohydantoin is most notably known due of their wide applications as hypolipidemic (Elwood *et al.*, 1972), anticarcinogenic (Al-Obaid *et al.*, 1996), antimutagenic (Takahashi *et al.*, 1998), antithyroidal (Marx *et al.*, 1970; Cheymol *et al.*, 1951) antiviral (e.g., against herpes simplex virus, HSV) (El-Barbary *et al.*, 1994), human immunodeficiency virus (HIV) (Chérouvrier *et al.*, 2004; Khodair *et al.*, 1997) and tuberculosis, antimicrobial (antifungal and antibacterial) (Marton *et al.*, 1993), anti-ulcer and anti-inflammatory agents, as well as pesticides. The reaction of the potassium salt of 3-phenyl-5(Z)-(pyridin-2-ylmethylene) -2- thioxoimidazolidin -4- one (KL) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in MeCN results in formation of the neutral complex $\text{Co}^{\text{II}}\text{L}_2$. According to single-crystal X-ray analysis, the Co^{II} centre is coordinated to four nitrogen atoms of two organic ligands and has a distorted tetrahedral geometry (Majouga *et al.*, 2005).

The synthesis, characteristics, properties and reactions with metallic ions of the furfural-, thiophenal-, pyrrolal-, cinnamal-, acetal-, and propional-derivatives of 2-thiohydantoin have been studied by González and co-worker (González *et al.*, 1982). The reagents exhibit two *pK* values in aqueous solution, and sensitive colour reactions with Pd(II), Cu(I), Cu(II), Ag(I) and Hg(II). A comparison has been made of the reactivity of all the 2-thiohydantoin derivatives (González *et al.*, 1982).

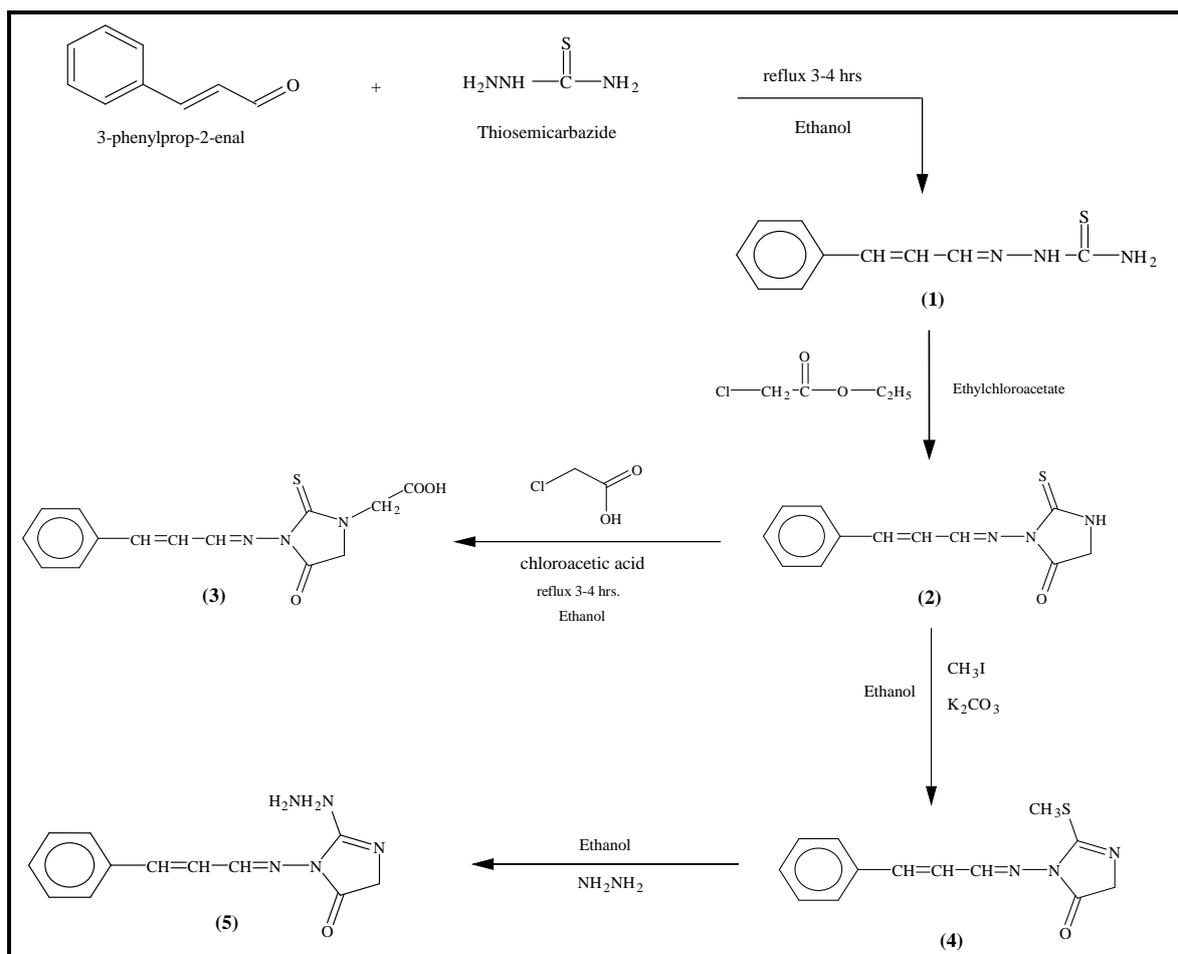
A series of Cu^{II} , Ni^{II} , and Co^{II} complexes with 5-(pyridylmethylidene)-substituted 2-thiohydantoin (L) were synthesized by the reactions of the corresponding organic ligands with $\text{MCl}_2 \cdot n\text{H}_2\text{O}$. The resulting complexes have the composition LMCl_2 (M = Cu or Ni) or L_2MCl_2 (M = Co). The reactions with N(3)-unsubstituted thiohydantoin afford complexes containing four-membered metallocycles, in which the

metal ion is coordinated by the S and N(3) atoms of the thiohydantoin ligand. The reactions of N(3)-substituted thiohydantoin give complexes in which the S and N(1) atoms are involved in coordination. IR spectroscopy studies demonstrated that the pyridine nitrogen atom is not involved in coordination. Based on the results of electrochemical study of the ligands and complexes by cyclic voltammetry and calculation of their frontier orbital's by the PM3(tm) method, the mechanism of oxidation and reduction of these compounds was proposed. In the first reduction and oxidation steps, the metal atom in the copper and nickel complexes remains, apparently, intact, and these processes occur with the involvement of the ligand fragments, *viz.*, the coordinated thiohydantoin ligand and chloride anion, respectively.

In the cobalt complexes, the first reduction step occurs at the ligand; the first oxidation state, at the metal atom. Measurements of the contact angle of aqueous wetting and electrochemical study demonstrated that carboxy-containing 2-thiohydantoin and their complexes can be adsorbed on the cystamine-modified gold surface. The structures of the complexes on the surface differ from the structures of these complexes in solution (Beloglazkina *et al.*, 2006).

Due to the versatile important of the thiohydantoin derivatives, this work dealing the reaction of 3-phenylpropanal (cinnamaldehyde) and thiosemicarbazide, which was carried out in ethanol, the compound (1) was formed which act the starting compound for the formation of the compounds (2-5) (Scheme 1). The modeling of the compounds under investigation also, the computation of the steric, Van der Waals, bending and stretching energy were calculated using the Molecular Mechanical method (MM2). The metal (Zn(II), Cu(II) and Ni(II)) complexes of the compound 1 and 2 were prepared by mixing the ethanolic solution of the ligand (0.002 mol) with the solution of the metal nitrate (0.001 mol) Schemes 2, 3.

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Scheme (1): The stepwise preparation of the compounds (1-5).

MATERIALS AND METHODS

Chemicals

Metal salts were obtained from Aldrich. All reagents used were of AR grade. All organic solvents were of analytical grade and purified by standard methods.

Preparation of the Ligands

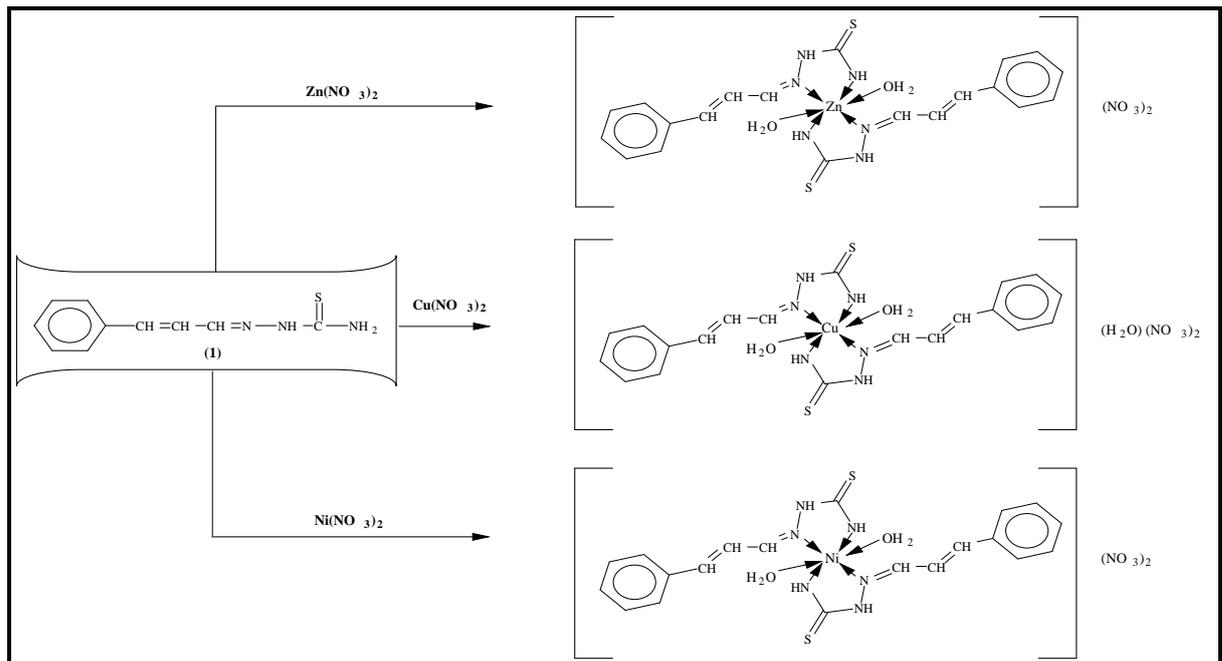
A mixture of 3-phenyl-propanal (cinnamaldehyde) (0.01 mol) and thiosemicarbazide (0.01 mol) in ethanol (50 ml) was refluxed for nearly 4 hrs. The reaction container was cooled, solid product directly formed. The resulting solid was filtered, washed by ethanol, dried and crystallized from hot CHCl_3 . The pale yellow crystal of the formed compound (1) has 70% yield and m.p. 108 °C. A mixture of compound (1) (0.01 mol) and ethylchloroacetate (0.01 mol) in ethanol (50 ml) in presence of fused sodium acetate (0.03 mol) was refluxed for 4 hrs.

The reaction mixture was cooled to room temperature after that poured into water. The resulting (compound 2) solid was filtered off, washed with hot water, dried and recrystallized from methanol. The formed compound (2) is yellow crystals, yield 60%, m.p. 213°C. A mixture of

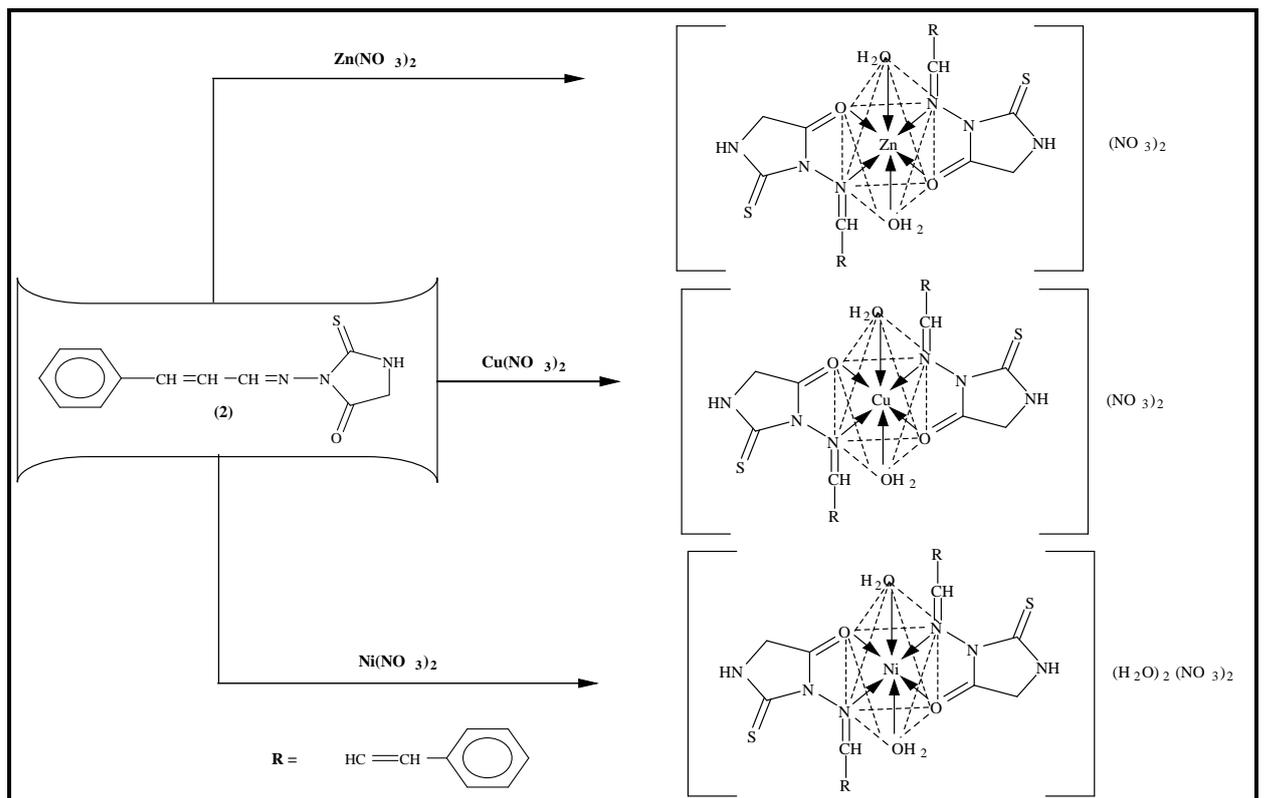
compound (2) (0.01 mol) and chloroacetic acid (0.01 mol) in ethanol (50 ml) in presence of trimethylamine (1 ml) was refluxed for 4 hrs. The reaction mixture was cooled and poured into ice containing diluted HCl.

The resulting solid crude was filtered off, washed with water, dried and purified by re-crystallization from methanol. The formed compound (3) is yellow crystals, yield 61%, m.p. 233°C. A mixture of compound (2) (0.01 mol), methyl iodide (0.01 mol) and anhydrous potassium carbonate (0.03 mol) in ethanol (50 ml) was refluxed for 4 hrs. The reaction mixture was cooled and poured into water. The resulting solid crude was filtered off, washed with water, dried and purified by re-crystallization from ethanol. The formed compound (4) is pale yellow crystals, yield 65%, m.p. 145 °C.

A mixture of compound (4) (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (50 ml) was refluxed for 4 hrs. The solid product was formed after cooling. The resulting solid crude was filtered off, washed with ethanol-water mixture, dried and purified by re-crystallization from ethanol. The formed compound (5) is pale yellow crystals, yield 55%, m.p. 160 °C.



Scheme (2): The postulated structure of the L1-M(II) complexes.



Scheme (3): The postulated structure of the L2-M(II) complexes

Preparation of Complexes

To the ethanolic solution of the ligand (1) (0.002 mol) (0.41 g dissolved in 20 ml ethanol) or the ethanolic solution of the ligand (2) (0.002 mol) (0.491 g dissolved in 20 ml ethanol), a solution of metal nitrate (0.001 mol) (0.297 g for Zn(II), 0.241 g for Cu(II) and 0.29 g for Ni(II) in ethanol (10 ml), was added with continuous stirring. The reaction mixture was heated under refluxing for 2 hr. The formed solid complexes were separated by filtration, washed with hot ethanol and dried in vacuum at room temperature. The physicochemical properties of the synthesized complexes were collected in table (3).

Instrumentation

Elemental analyses were carried out using a Heraeus CHN Rapid Analyzer. Thermal analyses of the complexes were carried out on a Shimadzu DTA-50 instrument using a platinum cell under nitrogen atmosphere at a heating rate of 10°C/min. The conductance measurements of 1×10^{-3} M solutions of the complexes in DMSO were performed using a WTW model LF-42 Conductivity Bridge fitted with a LTA-100 conductivity cell. IR spectra were recorded in the range of 4000-400 cm^{-1} in KBr discs on a Perkin-Elmer 1430 spectrophotometer. $^1\text{H-NMR}$ measurements were carried out on the Varian Gemini-200 using the suitable solvent (DMSO) and TMS as internal reference. The entire chemical shift (δ) are given down field relative to the tetramethylsilane (TMS). Mass spectra were measured using GC-MSQP 1000EX Shimadzu mass spectrometer instrument.

RESULTS AND DISCUSSION

Organic ligands

The pale yellow crystal of the formed compound (1) has 70% yield and m.p. 108 °C. The elemental analysis of the formed compound as follow: Calculated $\text{C}_{10}\text{H}_{11}\text{N}_3\text{S}$ (Mwt = 205.28): C, 58.51; H, 5.40; N, 20.47 and found: C, 58.31; H, 5.15; N, 20.41. IR (KBr) was reported and the fundamental bands of NH and NH_2 appeared at 3416, 3259, 3152 cm^{-1} , C=N stretching band appeared at 1627 (sh), 1591 (s) and C=S at 1370 cm^{-1} as medium band (m). $^1\text{H-NMR}$ (DMSO- d_6) shown that, NH proton appeared at chemical shift = 11.50 ppm as (s, 1H, NH), the aromatic and olefinic protons come to resonate at δ = 6.81 - 8.40 as (m, 8H, Aromatic and olefinic protons), the peak which appeared at δ = 4.59 ppm belongs the NH_2 protons as (s, 2H, NH_2). Mass spectra (m/z)(%): 206(82), 205(100), 183(75), 145(15), 130(65), 115(80), 103(40), 87(30), 77(48), 65(20), 51(30), 39(25), 28(10). The formed compound (2) has yellow crystals shape, yield 60%, m.p. 213 °C. The elemental analysis of the formed compound as follow: Calculated $\text{C}_{12}\text{H}_{11}\text{N}_3\text{OS}$ (Mwt = 245.30): C, 58.76; H, 4.52; N, 17.13 and found: C, 58.61; H, 4.61; N, 16.89. IR (KBr) was reported where, NH appeared at 3417 (w), 3039 (w), C=O at 1706 (s), C=N appeared at 1643 cm^{-1} as strong band (s)

meanwhile C=S appeared at 1335 cm^{-1} as medium band (m). $^1\text{H-NMR}$ (DMSO- d_6) shown that, the band which appeared at δ = 11.30 could be labeled as (s, H, NH), at 6.41 - 8.35 as (m 8H, aromatic and olefinic protons), at 2.60 as (s, 2H, $-\text{CH}_2-$). Mass spectra (m/z)(%): 246($\text{M}+1$, 82), 245($\text{M}+$, 81), 244(80), 218(25), 184(11), 174(12), 171(10), 170(30), 145(18), 144(12), 143(15), 142(25), 130(35), 129(60), 119(25), 116(25), 115(85), 104(15), 103(25), 91(30), 77(18), 69(20), 51(25).

The formed compound (3) has yellow crystals shape, yield 61%, m.p. 233 °C. The elemental analysis of the formed compound as follow: Calculated $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$ (M wt = 303.34): C, 55.43; H, 4.32; N, 13.85 and found: C, 55.21; H, 4.22; N, 13.67. IR (KBr) was reported, C=O stretching band appeared at 1705 cm^{-1} (s), C=N at 1640 cm^{-1} (s) and C=S at 1338 cm^{-1} (m). Mass spectra (m/z)(%): 304($\text{M}+1$, 12), 303($\text{M}+$, 30), 256(15), 231(15), 207(15), 175(11), 159(12), 145(13), 130(25), 129(15), 115(73), 103(11), 102(20), 77(30), 76(6), 61(100), 51(13).

The formed compound (4) has pale yellow crystals shape, yield 65%, m.p. 145 °C. The elemental analysis of the formed compound as follow: Calculated $\text{C}_{13}\text{H}_{13}\text{N}_3\text{OS}$ (Mwt = 259.33): C, 60.21; H, 5.05; N, 16.20 and found: C, 60.32; H, 5.26; N, 16.34. IR (KBr) was reported, C=O and C=N stretching bands appeared at 1716(s) and 1671 cm^{-1} (s), respectively. Mass spectra (m/z)(%): 260($\text{M}+1$, 15), 259($\text{M}+$, 39), 258(98), 232(10), 144(5), 130(25), 129(20), 115(98), 103(11), 102(10), 89(16), 78(10), 77(23), 63(13), 51(16).

The formed compound (5) has pale yellow crystals shape, yield 55%, m.p. 160 °C. The elemental analysis of the formed compound as follow: Calculated $\text{C}_{12}\text{H}_{13}\text{N}_5\text{O}$ (Mwt = 243.26): C, 59.25; H, 5.39; N, 28.79 and found: C, 59.36; H, 5.24; N, 28.84. IR (KBr) was reported, NH and NH_2 stretching bands appeared at 3037, 2962 and 2768 cm^{-1} , C=O appeared at 1705 cm^{-1} (s) and C=N appeared at 1645 cm^{-1} (s). Mass spectra (m/z)(%): 244($\text{M}+1$, 25), 243($\text{M}+$, 22), 232(10), 184(18), 130(20), 129(19), 116(30), 115(100), 103(13), 102(12), 89(13), 77(25), 63(13), 51(30).

Modeling and molecular mechanical calculation

The obtained results of the modeling and computational process of the compound 1 (conformations 1b - 1bd) using MM2 process, could be discussed according to the following findings:

1-The values of the angles and the bonds length reveal clearly the position of the bonds and the atoms in the molecule which give some idea about the reactivity of the molecules, which is important in the drug design and generally in the synthesis of the organic compounds.

2-The obtained conformation 1-b has total steric energy value, calculated corresponding to the summation of the individual energy which came from the stretching, bending, stretching-bending and the electrostatic force which present in the molecule at all (Allinger *et al.*, 1989; Lii *et al.*, 1989; Möllhoff *et al.*, 2001; Gresh *et al.*, 2007; Hofmann *et al.*, 2007).

3- Different conformations (1-bb, 1-bc and 1-bd) were obtained from the rotation through the bond N10-N11.

4- The obtained steric energy was summarized in table (1).

5- The values of the energy terms shown in table (1) are approximate and can vary slightly based on the type of processor used to calculate them.

6- From the total energy, -4.4624, -4.4624, -4.5004 and -1.7191 kcal/mol for 1-b, 1-bb, 1-bc and 1-bd conformations respectively, we could deduce that:

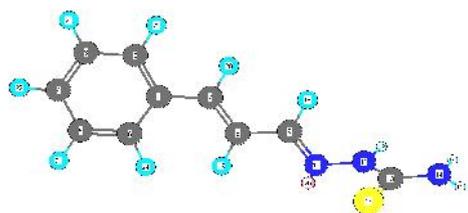
- The stable conformation belongs to the 1-bd form (which gave the minimum steric effect).
- The 1-b, 1-bb and 1-bc nearly has the same reactivity.

7- It is clear that the torsion term of -11.6878, -11.6878, -11.3463 and -9.3852 kcal/mol for 1-b, 1-bb, 1-bc and 1-bd respectively act as the dominates of the steric energy. This term is due to the deforming torsional angles in the molecule from their ideal values.

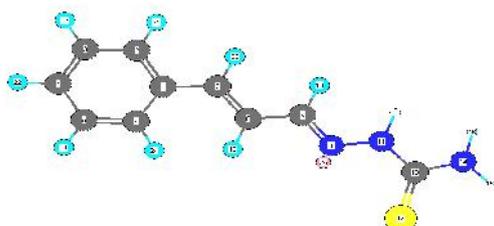
8- Also 1,4 VDW force play important role in the total steric energy. This term is due to the H-H repulsion contribution.

Table (1): Variation of the steric energy with the spatial arrangement.

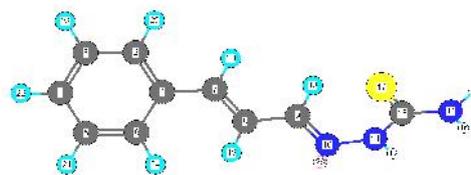
Energy Type	Comp.1-b	Comp.1-bb	Comp.1-bc	Comp.1
Iteration No.	97	97	215	59
Stretch	0.3081	0.3080	0.2927	0.2931
Bend	1.6980	1.6981	1.6454	1.7840
Stretch-Bend	0.0234	0.0234	0.0218	0.0240
Torsion	-11.6878	-11.6878	-11.3463	-9.3852
Non-1,4	-0.6543	-0.6543	-0.7351	-0.4402
VDW	5.8485	5.8485	6.0117	5.4982
1,4 VDW	0.0017	0.0017	-0.3906	0.5070
Dipole/Dipole				
Total	-4.4624	-4.4624	-4.5004	-1.7191



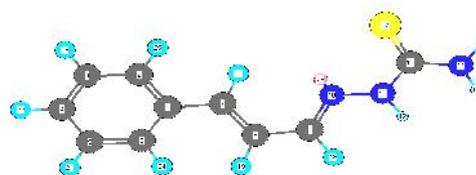
Conformation 1-b: XZ view



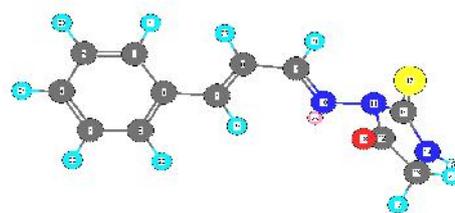
Conformation 1-bb: XZ view



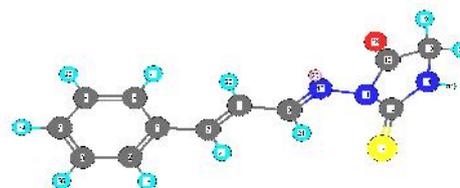
Conformation 1-bc: XZ view



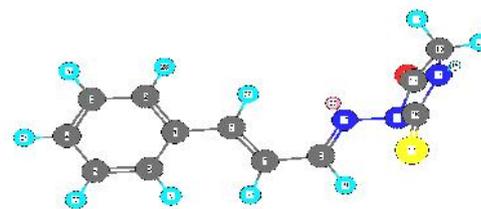
Conformation 1-bd: XZ view



Conformation 2-bb: XZ view



Conformation 2-b: XZ view



Conformation 2-bc: XZ view

The variation of the steric energy with the spatial arrangements for the compound 2, which summarized in table (2), could be discussed as the following:

1. The stability of the conformations under consideration (2-b, 2-bb and 2-bc) (which has the minimum steric energy) could be arranged in the following order: 2-b > 2-bc > 2-bb.
2. It is clear that the torsion term of -11.7552, -8.5020, -9.5684 kcal/mol for 2-b, 2-bb and 2-bc respectively, act as the dominates of the steric energy. This term is due to the deforming torsional angles in the molecule from their ideal values.
3. The contribution of the bend term play also the second dominates of the steric energy. 8.6244, 8.2210 and 8.5105 kcal/mol for 2-b, 2-bb and 2-bc respectively.
4. Also 1,4 VDW force play important role in the total steric energy.
5. The high value of the bending and 1,4 VDW energy may be due to the presence of the five ring structure (Schlick, 2000).
6. The 2-b conformation (which has the minimum steric energy) has nearly perpendicular plans, one of them the plane of the five rings and the other the plane of the benzene ring and the rest of the molecule.

Table (2): Variation of the steric energy with the spatial arrangement for the compound - 2.

Energy Type	Comp.2-b	Comp.2-bb	Comp.2-bc
Iteration No.	242	314	78
Stretch	0.8168	0.9910	0.9479
Bend	8.6244	8.2210	8.5105
Stretch-Bend	-0.4475	-0.6219	-0.5687
Torsion	-11.7552	-8.5020	-9.5684
Non-1,4	-1.3154	-1.4830	-1.2746
VDW	6.6396	6.6825	6.6998
1,4 VDW	2.3626	2.2481	2.3122
Dipole/Dipole			
Total	4.9253	7.5357	7.0587

(The energy unit is kcal/mol).

Synthesis of solid complexes

General Properties

The reactions of compound 1 (L1) and the compound 2 (L2) (Scheme 2, 3) with $Zn(NO_3)_2$, $Cu(NO_3)_2$ and $Ni(NO_3)_2$ in ethanol-water medium gave 1:2 (metal:ligand) complexes. The purity of the prepared complexes confirmed by chemical analysis, melting point and TLC (silica gel GF 254 type 60, mesh size 50-250, eluted with H_2O -ethanol 30:70). The complexes were found to be either yellow or green coloured non-hygroscopic powders, moderately soluble in hot water, methanol, ethanol, dimethylformamide (DMF) and dimethylsulfoxide (DMSO). They were insoluble in benzene and petroleum ether.

Elemental Analysis

The Elemental Analysis (C, H, N, M %) of the solid complexes show 1:2 (metal:ligand) stoichiometry (Table 3).

Molar Conductance

The molar conductance of the complexes in DMSO (0.001M) (Table 3) indicate that all compounds behaves as electrolytes with the structure $A_2^+.2B^-$, where A_2^+ refers to the coordination sphere of the formed complexes and B^- refers to the ionization sphere ($B = NO_3^-$) (Orabi, 1998; Geary, 1971).

Infrared Spectra

The significant IR data of the (L1) and (L2) ligands as well as these of their complexes are listed in table (4). The band which appeared at 3600 - 2750 cm^{-1} range which is present in all complexes as a medium broad band may be due to the coordinated and crystallized water molecules.

The carbonyl group of the ligand (2), which found at 1706 cm^{-1} as strong band, exerted shifts to lower wave number for the complexes 2-1, 2-2, and 2-3 as 1684, 1690 and 1692 cm^{-1} respectively. The shift of the stretching vibration of this group to lower wave number for these complexes indicating, the sharing of this group (C=O) in the chelation process as chelation center. Upon complexation of ligand (1) and (2) with the studied metal ions, the bands which appeared at 1627 and 1591 cm^{-1} for the first ligand are shifted to lower frequency which indicate the contribution of C=N group in coordination.

The same behaviour is obtained for ligand (2), where also the band at 1643 cm^{-1} is shifted to lower frequency (Curtis *et al.*, 1965). The stretching vibration band of the C=S group appeared at 1370 and 1335 cm^{-1} for ligands (1) and (2) respectively, which gave nearly no shifts in the complexes under consideration which reveal the un sharing of this group in the complexation process. Bands due to the stretching or deforming of the coordinate bond are generally found at the low-frequency end of the infrared range, both the heavy metal atom and the nature of the coordinate bond being responsible for this. The M-O and M-N stretching vibration band appeared as weak band as shown in the table (4) (Ram *et al.*, 1986; Socrates, 1980).

Thermal Analysis (DTA/TGA)

The thermal analysis technique of thermogravimetry (TG) is one in which the change in sample mass is recorded as a function of the temperature. The water content in the formed complexes was determined using gravimetric analysis (Vogel, 1978). The decomposition temperature for the 2-1 and 2-2 complexes indicate that, the H_2O molecules present in the coordination sphere of the complexes, meanwhile the Ni(II)-L2 complex (2-3) has coordinated water and water of crystallization as shown in the table (5) and figures (1-3).

Table (3): Physical Data and Chemical Analysis of the ligands (1) and (2) and their metal complexes.

No	Formula	M.wt.	Color	m.p °C	C %		H %		N %		M %		H ₂ O%		Cond moh /cm
					Clc.	F.	Clc.	F.	Clc.	F.	Clc.	F.	Clc.	F.	
1	C ₁₀ H ₁₁ N ₃ S	205.28	Yellow	108	58.51	58.31	5.40	5.15	20.47	20.41	-	-	-	-	-
1-1	[Zn(C ₁₀ H ₁₁ N ₃ S) ₂ (H ₂ O) ₂](NO ₃) ₂	636.00	yellowish	280	37.77	37.52	4.12	4.05	17.62	17.91	10.28	5.67	5.32	5.32	183
1-2	[Cu(C ₁₀ H ₁₁ N ₃ S) ₂ (H ₂ O) ₂](H ₂ O)(NO ₃) ₂	652.17	green	245	36.83	36.91	4.33	4.35	17.18	16.94	9.74	8.28	8.42	8.42	165
1-3	[Ni(C ₁₀ H ₁₁ N ₃ S) ₂ (H ₂ O) ₂](NO ₃) ₂	629.30	green	261	38.17	38.04	4.16	4.21	17.81	17.74	9.33	5.73	5.41	5.41	148
2	C ₁₂ H ₁₁ N ₃ OS	245.30	yellow	213	58.76	58.61	4.52	4.61	17.13	16.89	-	-	-	-	-
2-1	[Zn(C ₁₂ H ₁₁ N ₃ OS) ₂ (H ₂ O) ₂](NO ₃) ₂	716.04	Yellow	240	40.26	40.11	3.66	3.74	15.65	15.44	9.13	5.03	4.88	4.88	171
2-2	[Cu(C ₁₂ H ₁₁ N ₃ OS) ₂ (H ₂ O) ₂](NO ₃) ₂	714.19	darkgren	287	40.36	40.25	3.67	3.88	15.69	15.76	8.90	5.04	5.31	5.31	159
2-3	[Ni(C ₁₂ H ₁₁ N ₃ OS) ₂ (H ₂ O) ₂](H ₂ O) ₂ (NO ₃) ₂	745.37	Greenish	255	38.67	38.78	4.06	3.95	15.03	14.88	7.87	9.66	9.45	9.45	152

Table (4): IR spectra for the ligands (1) and (2) and their metal complexes.

	L1	1-1	1-2	1-3	L2	2-1	2-2	2-3
H ₂ O	-	3620-2750 br	3610-2850 br	3610-2800 br	-	3600-2875 br	3605-2900 br	3612-2900 br
C=O	-	-	-	-	1706 s	1684 s	1690 s	1692 s
C=N	1627 sh 1591 s	1602 s 1510 s	1610 s 1508 s	1611 s 1510 s	1643 s	1620 s	1625 s	1630 s
C=S	1370 m	1373 m	1368 s	1372 m	1335 m	1333 m	1335 m	1331 m
MO	-	-	-	-	-	510 w	512 w	518 m
MN	-	482 w	490 w	491 w	-	485 w	490 w	480 w

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

The % of the H₂O which librated at the decomposition temperature was in good agreement with the result obtained by using (C, H, N, M, H₂O %) analysis, tables (3,5). The thermogravimetric studies of the complexes gave more insight on their molecular structure. Thethermogravemetric curves of the Zn(II) complexe figure (1) showed that, a well-defined endothermic peak at 240 °C of DTA thermo gram without any weight loss in TG thermo gram. This could be probably due to some phase transition in the solid state structure. Zn(II)-L2, Cu(II)-L2 and Ni(II)-L2 complexes gave a well-defined endothermic peak at temperatures of 140, 150 and 180°C respectively (table 5).

This could due to the liberation of coordinated water [Orabi, 1998; Rakha *et al.*, 1987). Such a peak was well observed in the TG curves. The % obtained from the TG thermo grams was go well with the data obtained by (C, H, N, M, H₂O %) analysis. The endothermic peak which appeared at 110 °C for the Ni(II)-L2 (2-3) complex could be due to the liberation of the water of the crystallization (30,38). The decom-position product % which obtained from the TG thermo gram go well with the calculated % for the postulated strucutre (Scheme 2,3). Zn(II)-L2, Cu(II)-L2 and Ni(II)-L2 complexes gave a well-defined endothermic peak at 372, 351 and 364 °C respectively. This could due to the partial decomposition of the organic ligand.

The obtained results suggested the following thermal stability order of the different species (table 5).

1- thermal stability of the coordinated water:



2- thermal stability of the ligand in the form of complexes



Mass spectra

The mass spectra of the L1-M(II) complexes reveals the peak of M⁺-2H₂O for Zn(II) and Ni(II) complexes meanwhile Cu(II) gave peake at M⁺-3H₂O (Fig. 4-6)

Molecular Modeling

The postulated spatial arrangements have been confirmed using the molecular modeling program CS Cheme office. The program has been applied on many different arrangements for each ligand, the most stable one (which gave the minimum molecular energy) being presented in scheme (2,3).

Finally, from the elemental analysis, conductance, IR, thermal analysis, mass spectra and molecular modeling calculation, could be assignement the structure of the formed complexes from the ligands (1) and (2) as shown in the schemes 2, 3.

Table (5): The thermal analysis (DTA and TG) for the Synthesized L2-M(II) Complexes.

Comp. No.	Complex name	Tem. Peak T(°C)	Peak Type	Wt. loss%		Assignment
				Calcd.	Found	
2-1	$[\text{Zn}(\text{C}_{12}\text{H}_{11}\text{N}_3\text{OS})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	140	Endo	5.03	4.90	Coordinated H ₂ O
		240	Endo	-----	-----	Phase transition
		372	Exo	-----	56.20	Partial ligand decomposition
2-2	$[\text{Cu}(\text{C}_{12}\text{H}_{11}\text{N}_3\text{OS})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	150	Endo	5.04	5.10	Coordinated H ₂ O
		351	Exo	-----	57.00	Partial ligand decomposition
2-3	$[\text{Ni}(\text{C}_{12}\text{H}_{11}\text{N}_3\text{OS})_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2(\text{NO}_3)_2$	110	Endo	4.83	5.01	Water of crystallization
		180	Endo	4.83	5.00	Coordinated H ₂ O
		364	Exo	-----	55.02	Partial ligand decomposition

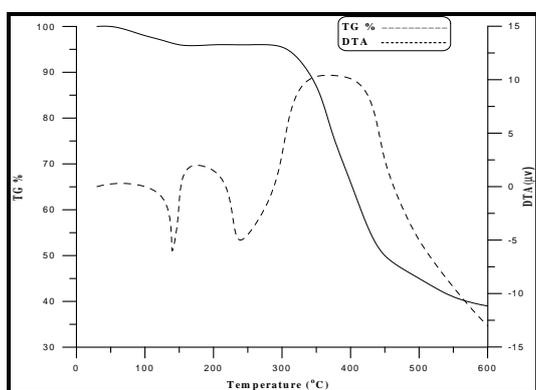


Figure (1): Thermal analysis (TG/DTA) of the L2-Zn(II) complex (complex 2-1).

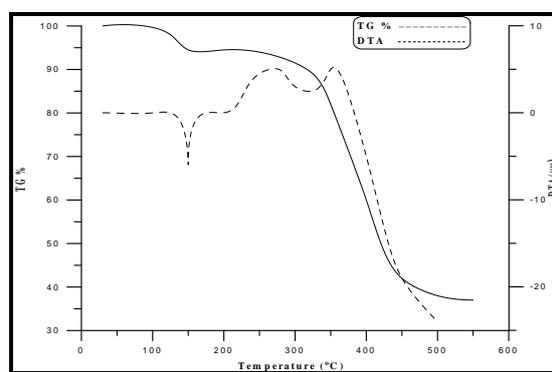


Figure (2): Thermal analysis (TG/DTA) of the L2-Cu(II) complex (complex 2-2).

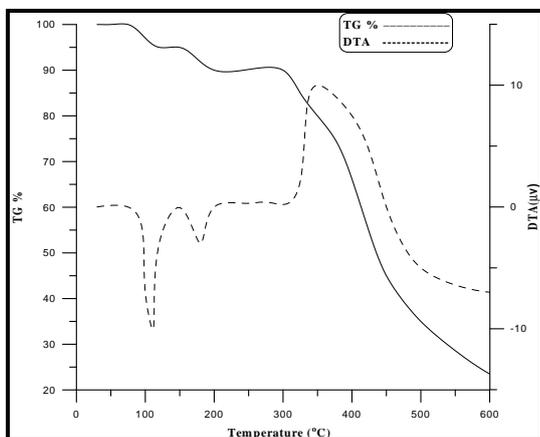


Figure (3): Thermal analysis (TG/DTA) of the L2-Ni(II) complex (complex 2-3).

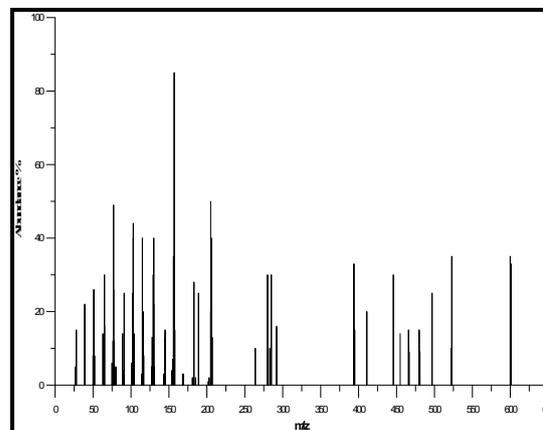


Figure (4): Mass spectra of the L1-Zn(II) complex (complex 1-1).

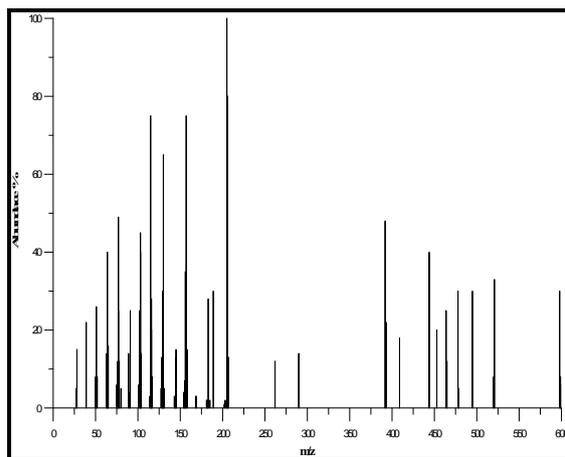


Figure (5): Mass spectra of the L1-Cu(II) complex (complex 1-2).

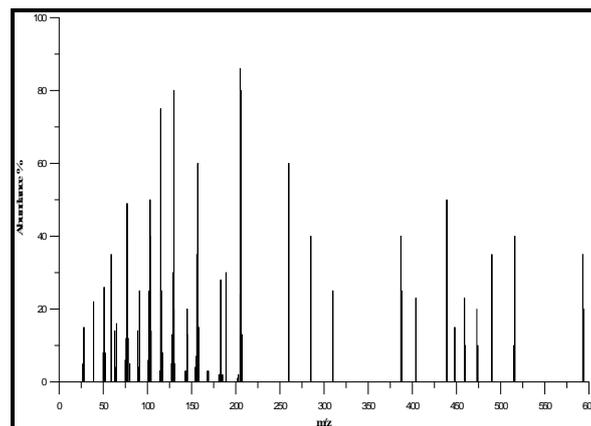


Figure (6): Mass spectra of the L1-Ni(II) complex (complex 1-3).

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