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Green Synthesis Approach For Thiosemicarbazone Derivative Cu (II) Complexes With Elaborated Spectral, Theoretical Studies

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ABSTRACT

A high-yield synthesis method for the one-pot synthesis of (Z)-2-(4-(diethylamino)benzylidene)hydrazine-1-carbothioamide (HL) and its Cu(II) complexes were developed using ball milling under solvent-free conditions. HL and its Cu(II) complexes were characterized by elemental analysis, UV-Vis absorption spectra, Fourier transform infrared spectroscopy (FT-IR), mass spectra, (¹H-, ¹³C-) nuclear magnetic resonance spectroscopy (NMR), electronic absorption spectral studies as well as magnetic studies, X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). The FTIR spectra confirmed the formation of HL and its Cu(II) complexes. XRD revealed the polycrystalline nature of the ligand (HL) while Cu(II) complex in amorphous nature. HL exhibited a spherical like ball morphology, whereas the Cu(II) complexes had a plates or network structures.

Keywords: Thiosemicarbazone complexes; X-ray powder diffraction (XRD); Scan electron microscope (SEM); Molecular modelling.

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INTRODUCTION

Ball milling is a mechanical procedure broadly utilized for grinding to acquire powders with fine particles [1-4]. In traditional strategies, reactants are broken apart by solvent molecules. On the other hand, reactants are broken utilizing mechanical powers in ball milling, resulting in an amorphous mixture of all reagents and a large surface area for the reaction. Solvent free ball milling has been rarely applied in organic synthesis. In any case, this system has increased extensive consideration in view due to its simplicity, low cost and environment friendliness and its capability to achieve high yields.

Extensive center has been coordinated towards the utilization of chelating agents containing sulfur and nitrogen in analytical, biological and structural studies of metal complexes. The chelating agents containing sulphur have many applications due to the strong ability of the electron-donating property. Thiosemicarbazones have a remarkable place among chelating agents containing sulphur and nitrogen atoms. These chelating agents form complexes with many metal ions by bonding with thionate or thione sulphur and hydrazine nitrogen atoms [5-9]. Recently, many authors have reported the complexation of thiosemicarbazones with several metal ions [10-19]. As one of the first transition metals, copper was already very early for investigations used in the field of coordination chemistry. Not only because its abundance in the earth's crust and its easy accessibility. The interest on transition metal complexes especially with copper has in recent years. A large number of publications produced, from a variety of motivations have arisen. The fields of application of copper complexes are very diverse. They range from catalysis in organic chemistry to materials research towards medically relevant complexes.

EXPERIMENT

Material

All the solvents and reagents used were of reagent grade / molecular biology grade, and used as commercially purchased without further purification. Spectroscopy grade solvents were used for spectral measurements while metal salts were purchased from sigma Aldrich and were used as received.

Synthesis of ligand and their Cu(II) complexes

Synthesis of ligand

(Z)-2-(4-(diethylamino)benzylidene)hydrazine-1-carbothioamide

An equimolar of thiosemicarbazide (0.95 g, 1 mmol) and p-diethylaminobenzaldehyde (0.15 g, 1 mmol) was placed into stainless steel vials with 31 g of stainless steelballs (12 mm in diameter). The vials was closed then placed in an SPEX 8000 mixer. The pure form of compound HL was obtained after 90 min of milling without further purification.

Synthesis of Cu(II) complexes

All complexes were prepared by placed equimolar amounts of the ligand (HL) and $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ into stainless steel vials with 31 g of stainless steelballs (12 mm in diameter). The vials was closed then placed in an SPEX 8000 mixer. The pure forms of complexes were obtained after 120 min of milling without further purification.

Molecular modeling

An attempt to gain better insight on the molecular structure of the ligand and its complexes, geometric optimization and conformational analysis has been performed using semi-empirical PM3 and AM1 methods [20] using the hyperchem series of programs forcefield as implemented in hyperchem 8 [21]. Molecular mechanics technique was used to investigate rapidly the geometries of the suggested structures of the metal complexes. The low lying conformers obtained from this search were then optimized at AM1 and PM3, (Polak-Ribiere) RMS 0.01 kcal.

Analyses of the complexes

Elemental analyses

Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 Series II Analyzer. The analysis for the metal content and halide in complexes were carried out by the standard method.

Physico-chemical measurements

The ball mill used in this study was an SPEX 8000 mixer with 10 cm³ stainless steel vials. Melting points were determined using a Stuart Melting point apparatus SMP10. Infrared spectra were recorded on a Perkin–Elmer FTIR spectrometer 2000 as KBr pellets in the 4000–400 cm⁻¹ spectral range. ¹H and ¹³C NMR measurements at room temperature were obtained JEOL NMR ECA-500MHz, using a 5 mm probe head in D₂O-DMSO. The electronic spectra of ligand and its metal complexes were recorded in DMSO solution on a Unicam UV–Vis spectrophotometer UV2, in the range 200–900 nm. Magnetic moment values were evaluated at room temperature (25±1°C) using a Johnson Matthey magnetic susceptibility balance using Hg[Co(SCN)₄] as calibrant. Thermo gravimetric analysis (TGA, DTG, 20 – 1000 °C) was performed using DTG-50 Shimadzu thermo gravimetric analyzer at heating rate 10 °C/min and nitrogen flow rate of 20 ml/min. Powder XRD (PAN analytical X'Pert PRO, Boulder, CO, USA) was carried out using Cu-K α radiation at 40 kV and 40 mA. The scans were typically performed over a 2θ range of 10 to 80 at a speed of 0.02/s. The morphology of the powder was examined by SEM (JSM-6380LA, JEOL -Japan Electron Optics Laboratory, Tokyo, Japan).

RESULTS AND DISCUSSION

The prepared complexes are non-hygroscopic, insoluble in water and most organic solvents yet dissolvable in DMF or DMSO. Crystals suitable for X-ray measurements cannot be isolated. The elemental analysis data of the ligand (HL) and Cu(II) complexes were ordered in (Table 1). All the solid complexes have been isolated in a pure state. The compositions of the isolated complexes are agreed with the proposed formulae on the basis of the comparison between the calculated and found data listed in (Table 1).

Spectral studies

¹H- ¹³C NMR spectra

The ¹H NMR spectrum of HL in DMSO-d₆ (Fig.1) was recorded; it showed signals at: δ 1.222 ppm (4H, s, two CH₂), δ 2.948 ppm (6H, s, two CH₃), δ 6.695 ppm (2H, s, NH₂-CS), δ 11.149 ppm (1H, s, N-NH-CS), δ 7.973 ppm (1H, s, Ph-CH-C), δ 7.735 (2H, Ph, d), δ 7.557 ppm (2H, Ph, d). The peaks due to NH protons disappeared on addition of D₂O, which suggests that they are easily exchangeable.

The most significant features of the ¹³C NMR spectrum of HL (Fig. 2) were detected; it shows signals at: (39.083, 39.123) ppm for two CH₃, (42.083, 42.123) ppm for two CH₂, (111.653) ppm for C₂, C₄, (121.395) ppm for C₆, (128.567) ppm for C₁, C₅, (143.286) ppm for C₃, (151.360) ppm for C₁₀ and (177.935) ppm.

Infrared spectra

The principle infrared bands of HL and its metal complexes are recorded in (Table 2).

The IR spectrum of the ligand HL shows bands at 3365 and 3243 cm⁻¹ which are assigned to ν (NH₂) and ν (NH) groups, respectively. The bands due to ν (C=S) appeared at 812 cm⁻¹ and the band at 1585 cm⁻¹ is assigned to ν (C=N)(azomethine) group. The bands located at 1476, 1290, 950 and 761 cm⁻¹ assigned to thioamide I-IV vibrations have substantial contributions from ν (C=N), δ (C-H), δ (N-H) and ν (C=S) vibrations [22].

The possibility of thione/thiol tautomerism (HN-C=S/N=C-SH) in the solid state is ruled out, since no band characteristic for a thiol group (2500-2650 cm⁻¹) is found in the spectrum of the ligand [23].

In all Cu(II) complexes ν (NH) appears at nearly the same or slightly higher frequencies, suggesting that this group does not take part in bonding. Whereas, the bands attributed to thione sulphur (C=S) and

azomethine nitrogen (C=N) groups appears at 800-805 and 1568-1572 cm^{-1} , respectively [24]. In all the complexes $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ is shifted to lower frequency indicating coordination of thiophen sulphur and azomethine nitrogen to the metal. So, the ligand acts as a neutral bidentate ligand via the thiophen sulphur and azomethine nitrogen. Also, the spectra of Cu(II) complexes show new bands in (500–513) and (403–427) cm^{-1} region assignable to $\nu(\text{Cu}-\text{O})$ and $\nu(\text{Cu}-\text{N})$, respectively [25,26]. The appearance of new bands in $[\text{Cu}(\text{HL})_2(\text{SO}_4)]$ complex at 1050 and 913 cm^{-1} assignable to the SO stretching vibrations suggest bidentate sulphate [27].

Electronic Spectra and magnetic measurements

The tentative assignments of the significant electronic spectral absorption bands of HL metal complexes and their magnetic moments are given in (Table 3).

The magnetic susceptibility (μ_{eff}) for Cu(II) complexes varies between 1.75 and 2.20 B.M., when spin–spin coupling between unpaired electrons belonging to different copper ions is absent, depending on the geometries of the complexes due to the difference in orbital contribution [28]. The observed μ_{eff} values for the Cu(II) complexes in this study are in the 1.88–2.10 B.M. range, corresponding to one unpaired electron. The Cu(II) complexes generally show a broad band in the 13,000– 18,000 cm^{-1} region assigned to the envelop of ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g + {}^2\text{B}_{2g} + {}^2\text{A}_{1g}$ transitions [29]. In the present study, all Cu(II) complexes showed a broad band in the 16,100–16,873 cm^{-1} region in DMSO with a shoulder in the 14,178–14,383 cm^{-1} regions, suggesting a distorted octahedral geometry for all the complexes.

THERMAL STUDIES

The TG–DTA results for HL and its Cu(II) complexes was depicted in (Table 4). The results were in good agreement with the proposed formulae. From table 4 we concluded that there were general decomposition manners; the ligand decomposed in two main steps whereby, the complexes decomposed in three main stages. The first stage for all studied complexes is the loss of hydrated water molecules at 60–120 $^\circ\text{C}$, followed in a second decomposition stage by the loss of the coordinated water, chloride, nitrate or sulphate ions at 120–350 $^\circ\text{C}$, after that, the deligation process started at a temperature range of 200–800 $^\circ\text{C}$, finally metal oxide formation takes place. It is clear that, the TG thermograms for the investigated complexes displayed high residual part reflecting a higher thermal stability owing to the existence of five membered rings.

MOLECULAR MODELING

The atomic numbering scheme and the theoretical geometry structures for the HL and its Cu(II) complexes were calculated (Structures 1-4). The molecular parameters: total energy, binding energy, isolated atomic energy, electronic energy, heat of formation, dipole moment, HOMO and LUMO were calculated and represented in Table 5. A comparison between the bond length of the ligand and its complexes were illustrated. All the active groups taking part in coordination have bonds longer than that already exist in the ligand (like C=N and C=S). Analysis of the data in (Table 5) and (Tables 1S - 8S supplementary materials) including the bond lengths and bond angles, one can conclude the following remarks:

- 1- Bond lengths of C(12)-S(13), C(10)-N(15) and N(11)-N(15) become slightly longer in complexes as the coordination takes place via N atom of C=N and S atom of C=S groups.
- 2- There is some changes change in bond angles of the HL upon coordination; the largest change affects N(14)-C(12)-N(11), N(15)-N(11)-C(12), N(11)-N(15)-C(10) and S(13)-C(12)-N(11) angles which are reduced or increased on complex formation as a result of bonding with Cu ions.
- 3- The bond angles in all complex are adopted an octahedral arrangement predicting $\text{sp}3\text{d}^2$ hybridization [28-31].

Generally, the bond length of M–N is smaller than that of M–S. This is attributed to the electronegativity difference between the sulfur and nitrogen atoms.

XRD Analysis

XRD was carried out to identify the polycrystalline or amorphous nature of the synthesized samples. Figure 3 a,b show XRD patterns of HL and its $[Cu(HL)_2Cl_2](H_2O)_2$ complex, respectively. The free ligand was polycrystalline while Cu(II) complex was amorphous in nature. This can be explained by distortion of the crystallinity of ligand due to complexation to the Cu(II) ions. The dominant XRD peak at $27.74^\circ 2\theta$ was observed for HL, while the peak for its Cu(II) complex was observed at $43.18^\circ 2\theta$. Therefore, the structural phase changes occurred with the chelation of Cu(II) with HL, which was apparent by the shift in the dominant 2θ value to the higher energy side. The structural properties of HL and its Cu(II) complex have not been reported in the literature so far. Therefore, crystal growth experiments are in progress for the determination of the crystal structure of HL and its Cu(II) complex, intending for a better understanding of the structural properties.

SEM Analysis

SEM images were performed to examine the morphological variation and microstructure of the synthesized samples. Figure 4 a-f present the low and high magnified images of free ligand and its Cu(II) complexes. These images showed that the free ligand (HL) possesses a spherical like ball morphology on the micrometer scale. An abrupt change in its morphology was observed after the chelation of Cu(II) to HL. The figures showed that Cu(II) complexes had a plates or network structures.

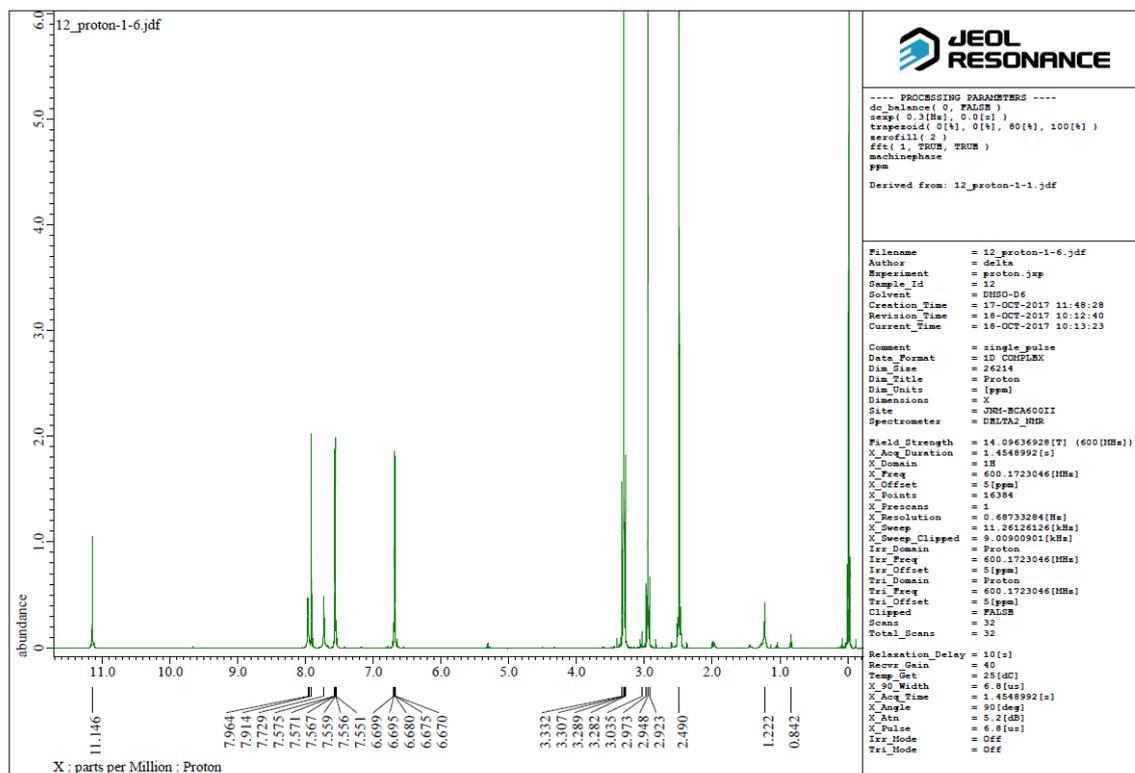


Fig. 1 1H NMR spectrum of HL

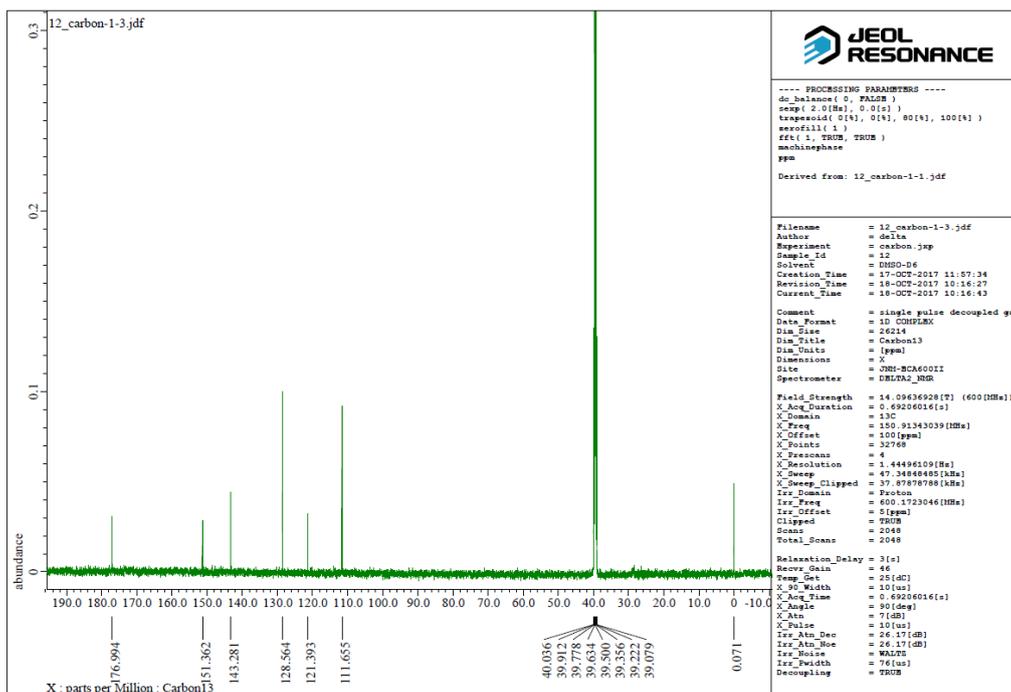


Fig. 2 ¹³C NMR spectrum of HL

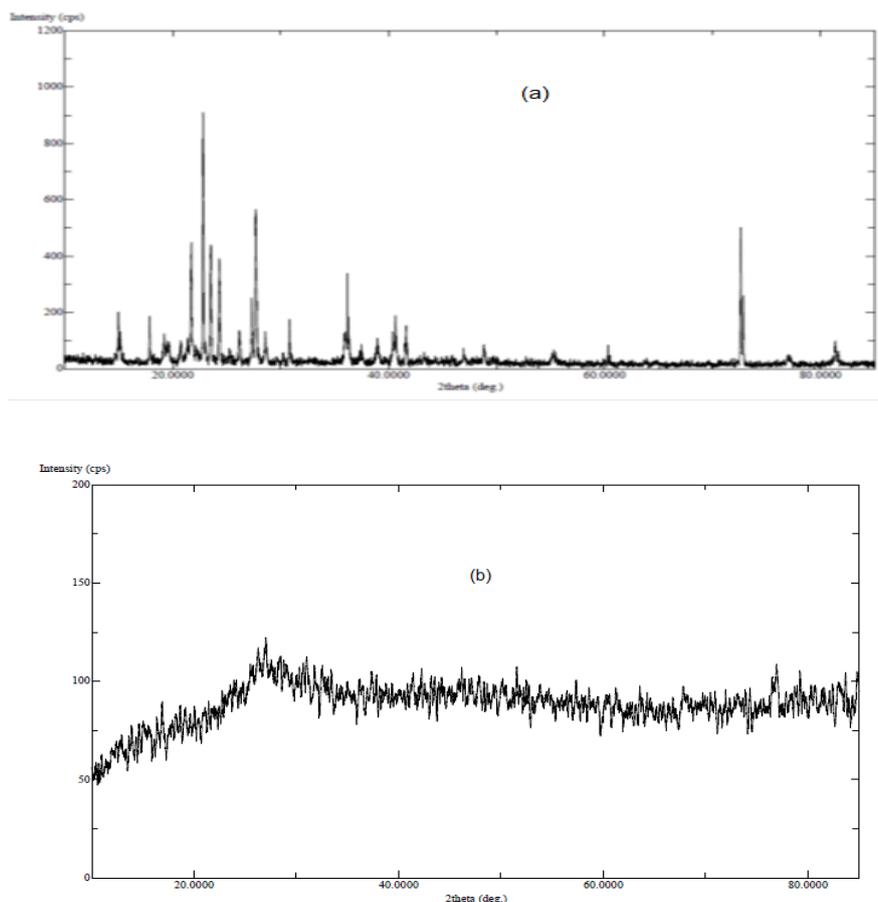


Fig. 3. XRD patterns of (a) HL and (b) [Cu(HL)₂Cl₂](H₂O)₂.

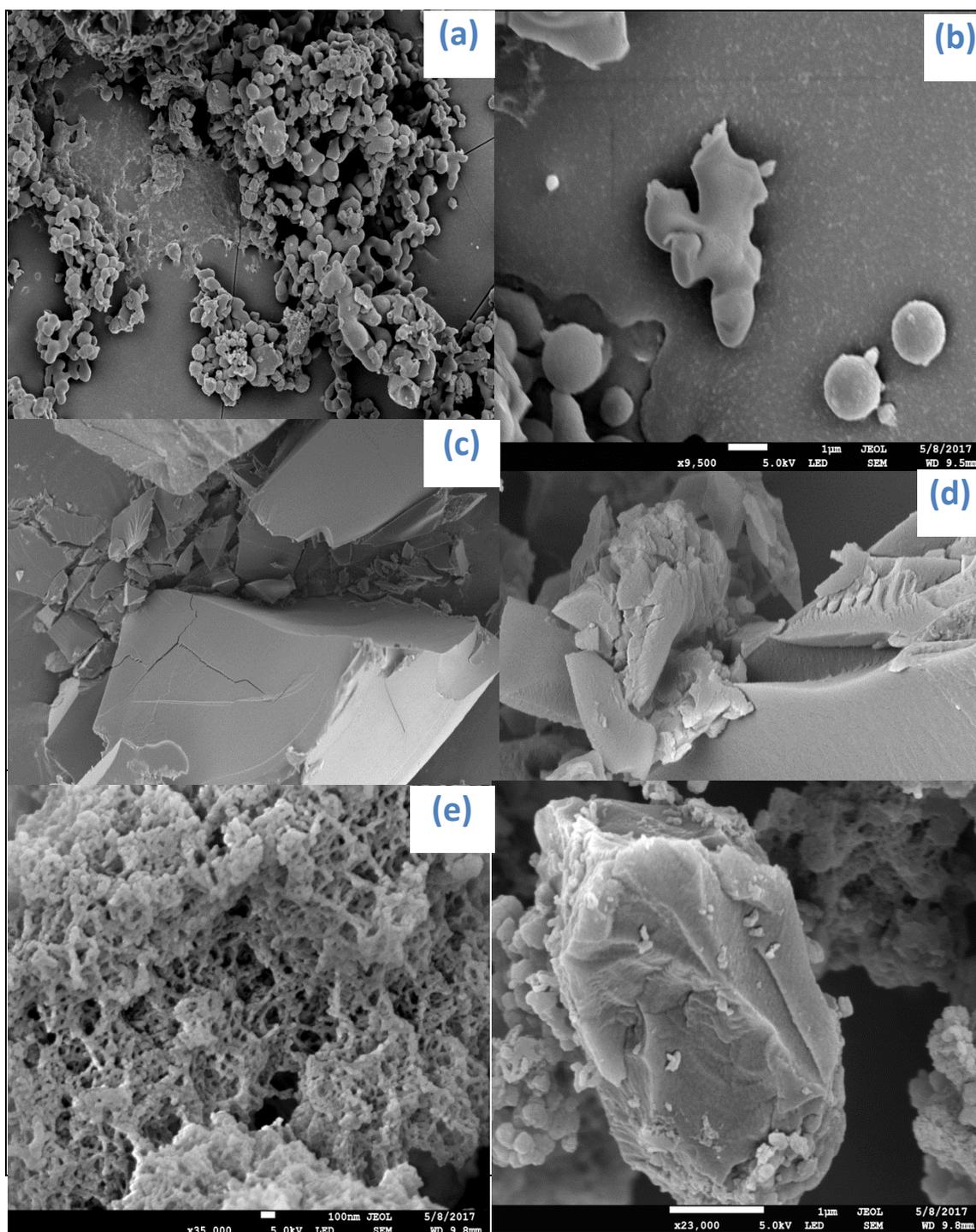
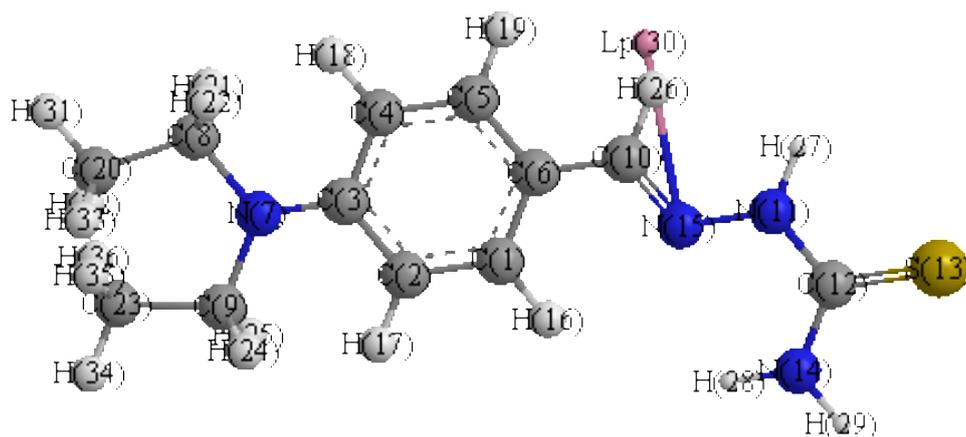
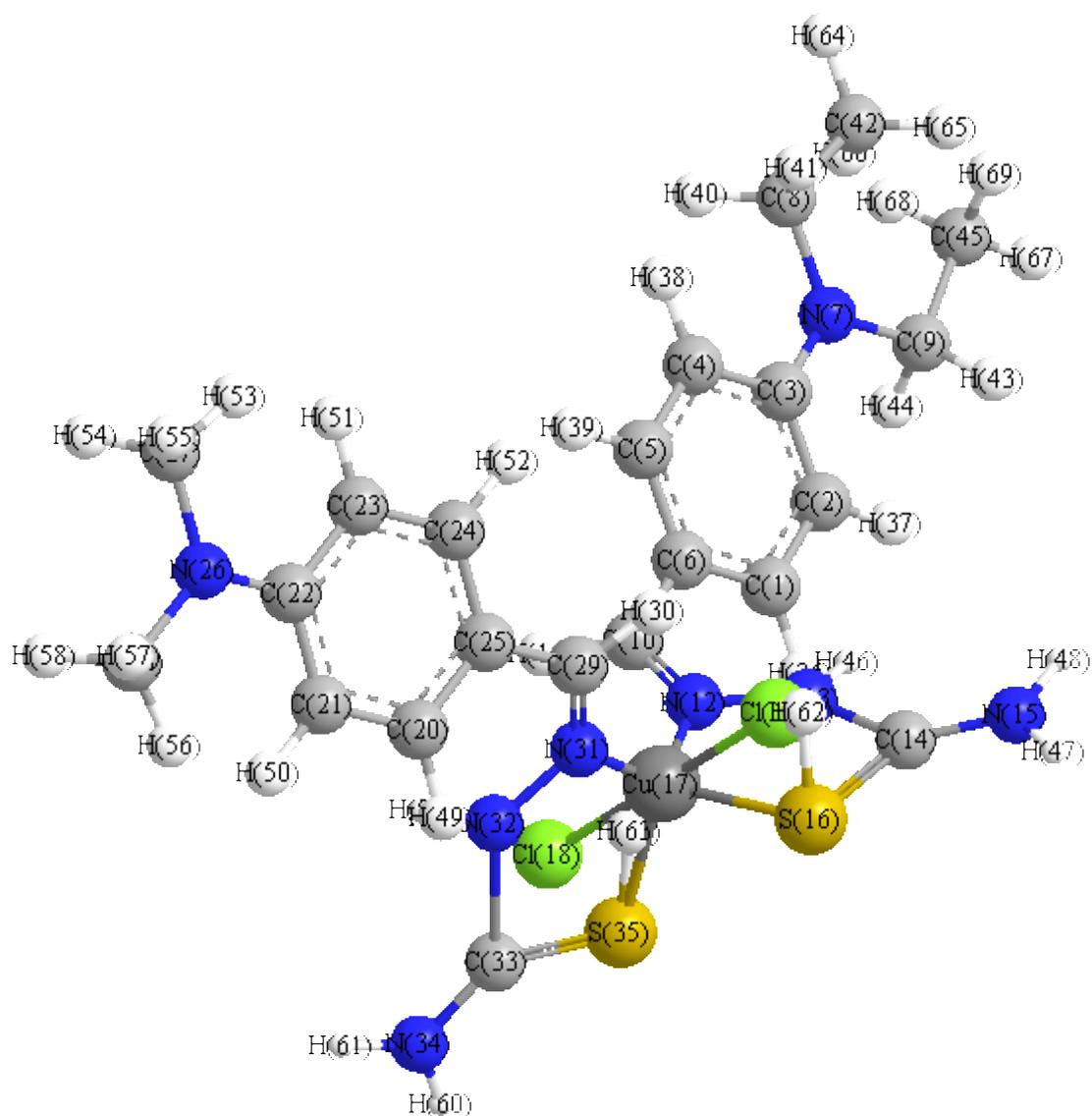


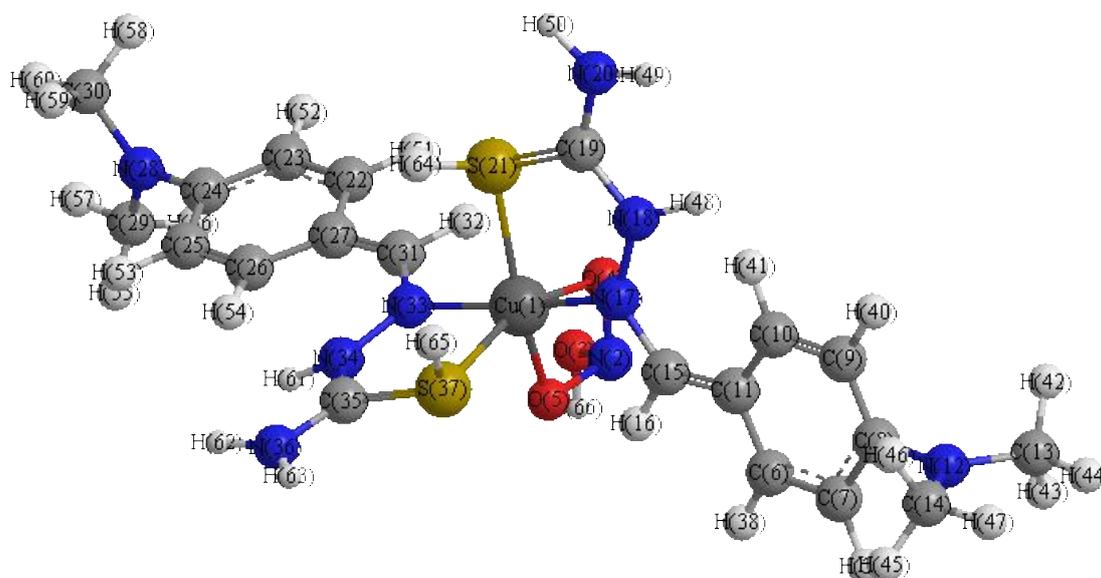
Fig. 4. SEM images of (a,b) HL, (c,d) $[Cu(HL)_2(NO_3)]$ and (e,f) $[Cu(HL)_2(SO_4)]$.



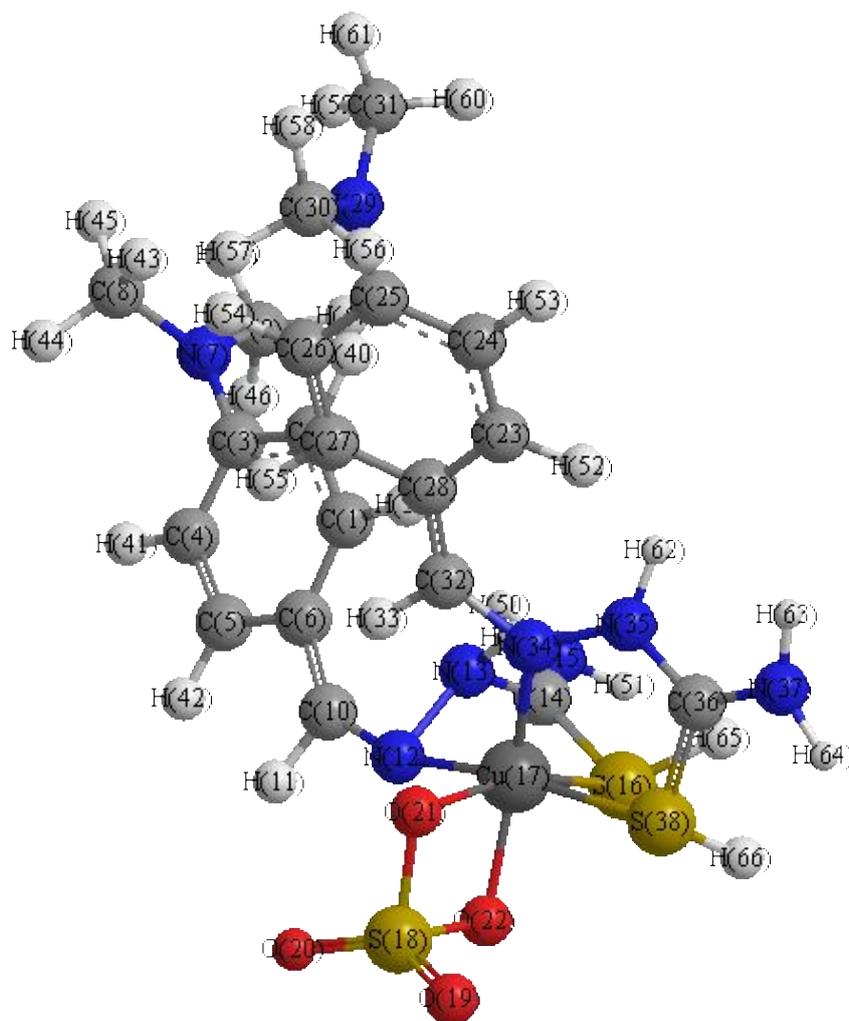
Structure 1. Molecular modelling of HL



Structure 2. Molecular modelling of [Cu(HL)₂Cl₂](H₂O)₂



Structure 4. Molecular modelling of [Cu(HL)₂(NO₃)]



Structure 4. Molecular modelling of [Cu(HL)₂(SO₄)]

Table 1. Analytical and physical data of HL and its metal complexes

Compound, Empirical formula, (F.Wt)	Color	M.P. (°C)	% Found (Calcd.)					Yield%
			C	H	N	M	Cl	
HL C ₁₀ H ₁₄ N ₄ S (222.31)	Yellow	220	53.78 (54.03)	6.48 (6.35)	24.98 (25.20)	-	-	90
[Cu(HL) ₂ Cl ₂](H ₂ O) ₂ C ₂₀ H ₃₂ Cl ₂ CuN ₈ O ₂ S ₂ (615.10)	Pale Brown	>300	39.47 (39.05)	4.89 (5.24)	18.55 (18.22)	10.52 (10.33)	11.21 (11.35)	81
[Cu(HL) ₂ (NO ₃)] C ₂₀ H ₂₈ CuN ₉ O ₃ S ₂ (570.17)	Dark Green	>300	42.37 (42.13)	4.59 (4.95)	22.35 (22.11)	11.02 (11.15)	-	85
[Cu(HL) ₂ (SO ₄)] C ₂₀ H ₂₈ CuN ₈ O ₄ S ₃ (604.22)	Brown	>300	39.97 (39.76)	4.34 (4.67)	18.87 (18.55)	10.23 (10.52)	-	83

Table 2. Principle infrared bands of HL and its Cu(II) complexes

Compound	$\nu(\text{C}=\text{N})^a$	$\nu(\text{C}=\text{S})$	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$
HL	1585	812	3365	3243	-	-
[Cu(HL) ₂ Cl ₂](H ₂ O) ₂	1565	801	3370	3244	505	421
[Cu(HL) ₂ (NO ₃)]	1538	803	3373	3242	508	415
[Cu(HL) ₂ (SO ₄)]	1572	802	3375	3245	510	408

a: azomethine

Table 3. Electronic spectra and Magnetic moment of Cu(II) Complexes.

Compound	Band position (cm ⁻¹)	$\mu_{\text{eff.}}$ (B.M.)
[Cu(HL) ₂ Cl ₂](H ₂ O) ₂	14328; 16687	1.88
[Cu(HL) ₂ (NO ₃)]	14273; 16598	1.95
[Cu(HL) ₂ (SO ₄)]	14481; 16685	2.10

Table 4. TGA and DTA data for HL and its Cu(II) complexes

Compound	Temp. Range °C	% Weight loss		Assignment
		Found	Calcd.	
HL	250-350	19.78	19.92	Loss of N(CH ₃) ₂
	350-800	-	-	Start of Deligation
[Cu(HL) ₂ Cl ₂](H ₂ O) ₂	80-120	5.63	5.86	Loss of 2 mole of hydrated water
	120-280	12.56	12.24	Loss of 2 coordinated chloride ions
	280-800	-	-	Deligation

[Cu(HL) ₂ (NO ₃) ₂]	195-310	10.39	10.87	Loss of 1 coordinated nitrate group
	310-800	-	-	Deligation
[Cu(HL) ₂ (SO ₄) ₂]	180-270	15.64	15.90	Loss of 1 coordinated sulphate group
	270-800	-	-	Start of Deligation

Table 5. The molecular parameters of HL and Cu(II) complexes.

The assignment of the theoretical parameters	The compound investigated	The theoretical data
Total Energy	HL	= -51509.9848684 (kcal/mol)
Total Energy		= -82.086375799 (a.u.)
Binding Energy		= -2868.9857164 (kcal/mol)
Isolated Atomic Energy		= -48640.9991520 (kcal/mol)
Electronic Energy		= -314888.8595581 (kcal/mol)
Core-Core Interaction		= 263378.8746897 (kcal/mol)
Heat of Formation		= 87.7422836 (kcal/mol)
Dipole moment		= 5.784 (Debys)
Homo		= -8.765585 ev
Lumo		= -1.059459 ev
Total Energy		[Cu(HL) ₂ Cl ₂](H ₂ O) ₂
Total Energy	= -231.107685624 (a.u.)	
Binding Energy	= -5009.4754122 (kcal/mol)	
Isolated Atomic Energy	= -139027.3894800 (kcal/mol)	
Electronic Energy	= -1217849.510180 (kcal/mol)	
Core-Core Interaction	= 1072827.230008 (kcal/mol)	
Heat of Formation	= 57.2453081 (kcal/mol)	
Dipole moment	= 11.24 (Debys)	
Homo	= -4.673929 ev	
Lumo	= -2.11505 ev	
Total Energy	[Cu(HL) ₂ (NO ₃) ₂]	
Total Energy		= -246.175869128 (a.u.)
Binding Energy		= -6335.4595157 (kcal/mol)
Isolated Atomic Energy		= -148142.2497300 (kcal/mol)
Electronic Energy		= -1311421.486440 (kcal/mol)
Core-Core Interaction		= 1156943.7771945 (kcal/mol)
Heat of Formation		= -49.6265157 (kcal/mol)
Dipole moment		= 11.307 (Debys)
Homo		= -8.054379 ev
Lumo		= -0.9103375 ev
Total Energy		[Cu(HL) ₂ (SO ₄) ₂]
Total Energy	= -257.913745776 (a.u.)	
Binding Energy	= -6432.6771251 (kcal/mol)	
Isolated Atomic Energy	= -155410.6618320 (kcal/mol)	
Electronic Energy	= -1364876.4270609 (kcal/mol)	
Core-Core Interaction	= 1203033.0881037 (kcal/mol)	
Heat of Formation	= -133.8851251 (kcal/mol)	
Dipole moment	= 12.32 (Debys)	
Homo	= -4.357796 ev	
Lumo	= -0.8292 ev	

CONCLUSION

The present manuscript deals with the green syntheses, spectral characterizations, theoretical calculations of HL and its Cu(II) complexes. All these characterization studies conclude the synthesis of HL and its chelation with Cu(II). All the reported Cu(II) complexes are octahedral in nature. The bonding of the primary ligand with in all complexes takes place through azomethine nitrogen atoms and thione sulphur atoms. Furthermore, investigations on the crystal structures of HL and its Cu(II) complexes will be carried out to achieve a better understanding of the structural properties.

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