

Spectroscopic, thermal and toxicity studies of some 2-amino - 3- cyano - 1, 5 –diphenylpyrrole containing Schiff bases copper (II) complexes.

Research Article

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Abstract: Two novel Schiff base ligands of 2-amino-3-cyano-1,5-diphenylpyrrole and salicylaldehyde (HL¹) or 2- hydroxy1-naphthylaldehyde (HL²) and their copper(II) complexes have been synthesized and characterized by elemental analyses, spectral (UV–Vis, IR, EPR, Mass (for ligands)), thermal (DTA-TGA) methods, magnetic and conductance measurements. IR results demonstrate the bidentate binding of the Schiff base ligands involving azomethine nitrogen, phenolic or naphtholic oxygen and suggest the presence of HL² and complexes (1, 2, 4 and 8) in enolimine-ketonamine tautomeric forms in the solid state. The EPR spectral data of complexes (2, 5, 6) show that the metal – ligand bonds have considerable covalent character. The thermal studies show that complexes (1, 2, 4 and 8) that are present in enolimine-ketonamine tautomeric forms exhibit lower thermal stability. The effect of synthesized ligands (HL¹, HL²) and complexes (1, 5) were tested on the mortality of entomopathogenic nematodes (EPN) (*Heterorhabditis bacteriophora* and *Steinernema carpocapsae*). The study shows that the mortality of the nematodes increased with increasing concentrations of copper(II) ion, ligands and complexes. Copper(II) ion was the most toxic for EPN.

Keywords: Copper(II) complexes • EPR spectra • Schiff base ligands • Thermal analysis (DTA/TG) • Nematodes

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1. Introduction

Schiff bases have been extensively employed in the understanding of molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, etc. [1–5]. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest of Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [6–11].

In addition, copper(II) complexes possess a wide range of biological activity and are among the most potent anti-viral, anti-tumor and anti-inflammatory agents; they also play a central role in biological redox metal enzymes like plastocyanin, hemocyanin, azurin, galactose oxidase and others [12]. In recent years, considerable interest has developed in copper complexes with mixed donor ligands as structural models for the active site of copper proteins [13,14] and, moreover, copper is an essential micronutrient for feeding as well as a cofactor of several enzymes involved in oxidative metabolism like β -hydroxylases, quercetinase, ceruloplasmin, cytochromoxidase, monoaminoxidase, superoxydismutase, ascorbic acid oxidase and

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tyrosinase [15-17]. The catalytic role of these enzymes is a two-step process, *i.e.*, the reduction of Cu^{2+} ion to Cu^+ ion and the fixation of molecular oxygen [18]. The rutine-Cu(II) complex shows their higher activity as antioxidants and anti-free radical agents than free rutine [19-21]. A survey of the literature reveals that no work has been carried out on the synthesis of metal complexes with Schiff bases derived from 2-amino-3-cyano-1,5-diphenylpyrrole. The present manuscript is devoted to the synthesis, spectroscopic, thermal and toxicity studies of new Schiff base ligands of 2-amino-3-cyano-1,5-diphenylpyrrole and salicylaldehyde (HL^1) or 2-hydroxy-1-naphthylaldehyde (HL^2) and their copper(II) complexes. Entomopathogenic nematodes (Heterorhabditidae and Steinernematidae) have been studied extensively for biological control of numerous insect pests in a wide range of commodities [22,23] and are promising alternatives to synthetic insecticides [24]. These nematodes are unique because they possess many important traits: they are environmentally safe, easy to apply, have a wide host range including the majority of insect orders and families, kill insects within 24-48 h, and form a durable infective juvenile stage which can persist in nature. In addition, they are safe to vertebrates, plants and non-target organisms [25,26]. Also, they are compatible with many chemical pesticides [27,28]. Many biotic and abiotic soil components affect nematode activity; among them is copper(II) ion. Copper is an essential element and required by all organisms. However, elevated concentrations of copper in soils are toxic and may result in a range of effects including reduced biological activity and subsequent loss of fertility [29]. Toxicity studies of Cu(II) ion, ligands and complexes (1,5) on *Heterorhabditis bacteriophora* and *Steinernema carpocapsae* juveniles were evaluated via the effect of all tested materials on mortality of EPN.

2. Experimental Procedures

2.1. Material

All organic compounds and solvents were purchased from Fluka and Merck. The metal salts $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and CuBr_2 were obtained from Fluka and used for complex preparation without further purification. 2-amino-3-cyano-1,5-diphenylpyrrole was synthesized following the reported procedures [30].

2.2. Analytical and physical measurements

The elemental analysis (C and H) were carried out at the Micro Analytical Center, Cairo University, Giza, Egypt. Copper(II) content in the complexes was determined via iodometric method. Halide ions were determined by Volhard's method, and qualitative tests for chloride in complex (5) indicated no chloride ions. The FT-IR measurements were performed ($4000\text{--}400\text{ cm}^{-1}$) in KBr discs using Nenexeus-Nicolidite-640-MSA FT-IR, Thermo-Electronics Co. The UV-Visible absorption spectra were measured in both methanol and in Nujol mull using 4802 UV/Vis double beam spectrophotometer. The EPR spectra were recorded using a Varian E-109C model X-band spectrometer. The magnetic field modulation frequency was 100 KHz and the microwave power was around 10 mW. Mass spectra were recorded at 70 eV and 300°C on an MS 5988 Hewlett-Packard mass spectrometer. Molar conductivities were measured in methanol or acetonitrile solution of the complexes (10^{-3} M) using Cyber Scan CON/510 Conductivity/TDS/ $^\circ\text{C}/\text{F}^\circ$ meter Umedic/Germany (EUTECH). Magnetic susceptibilities of the complexes were measured by the modified Gouy method at room temperature using a Magnetic Susceptibility Johnson Matthey Balance. The effective magnetic moments were calculated using the relation $\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2}$ B.M., where χ_m is the molar susceptibility corrected for diamagnetism of all atoms in the compounds using Selwood [31] and Pascal's constants. Thermal analysis (DTA/TGA) were obtained by using a Shimadzu DTA/TG-50 Thermal analyzer with a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere with a following rate of 20 mL min^{-1} .

For toxicity studies, one Egyptian *Heterorhabditis* species and one imported *Steinernema* species were used. The *Heterorhabditis* species was defined as *Heterorhabditis bacteriophora* [32]. The *Steinernema* species was *Steinernema carpocapsae* (ALL) strain obtained from Germany.

2.3. Preparation of the Schiff bases (HL^1 and HL^2)

The Schiff base ligands were prepared by the condensation of equimolecular amounts of 2-amino-3-cyano-1,5-diphenylpyrrole with salicylaldehyde (HL^1) or 2-hydroxy-1-naphthylaldehyde (HL^2) in 25 mL absolute ethanol and a trace amount of P_4O_{10} was added. The resulting mixture was refluxed for 1-4 h. The solid products (yellow or orange for HL^1 and HL^2 , respectively), were filtered off, washed several times with ethanol and vacuo dried over P_4O_{10} . (M.P = $210, 222^\circ\text{C}$ for HL^1, HL^2 , respectively).

2.4. Preparation of solid complexes

The solid complexes were prepared by mixing hot alcoholic solutions of copper(II) salts (chloride, nitrate, acetate or bromide for complexes 1, 2, 3 and 4, respectively) with either HL¹ or HL² ligand under study (1:1 molar ratio). The reaction mixture was magnetically stirred for 3-8 days. Petroleum ether (60-80) was added to assist precipitation. The solid complexes were filtered off, washed several times with ethanol and vacuo dried. Attempts to prepare nickel(II) and cobalt(II) complexes were unsuccessful.

2.5. Preparation of the tested samples for toxicity study

The hydrated copper(II) chloride (CuCl₂•2H₂O) was dissolved in distilled water. Redistilled water was used for the control. Ligands (HL¹ and HL²) and complexes (1, 5) were dissolved in distilled water and dimethylsulfoxide (DMSO) in a ratio of (1000 mL: 5 mL), respectively at the following concentrations (1.5, 7.5, 11 mg L⁻¹). Redistilled water and DMSO were used for the control.

2.6. Toxicity study

The toxicity study was performed according to Jawraska *et al.* [33].

2.7. Data analysis

Data expressed in percentages were transformed to arcsine values to ensure normality. Statistical significance was determined by analysis of variance (Duncan's multiple range tests and T- test to differentiate between the means at P<0.05) using software package Costat (Cohort Inc., Berkeley, CA, USA). Results are recorded as mean ± standard deviation (SD) [34].

3. Results and Discussion

The ligands (HL¹, HL²) and their copper(II) complexes (Scheme 1) have been synthesized and characterized by elemental analyses, molar conductivity measurements, magnetic susceptibility measurements, EPR, mass spectra (for ligands), electronic and IR spectral data and thermal analysis (DTA/TGA). The complexes are air stable, non- hygroscopic, soluble in MeOH and/or CH₃CN but insoluble in most common organic solvents, and freely soluble in coordinating solvents such as DMF, DMSO. TLC of the complexes and their elemental analyses were satisfactory evidence for their purity. The molar conductivity values (Table 1) of 10⁻³ M solution indicate that the complexes are non-electrolytes [35].

3.1. IR spectra

The mode of binding of both Schiff base ligands to the copper(II) ion was elucidated by recording the IR spectra of the complexes as compared with the spectra of the free ligands (Table 2). The spectra of both free ligands HL¹ and HL² show strong bands at 1621 and 1620 cm⁻¹ (characteristics of the ν(C=N) (azomethine) stretching mode for HL¹ and HL²) respectively [12,36,37] indicating the formation of the Schiff bases. These bands are shifted towards lower frequencies in the spectra of all copper(II) complexes, 1585-1565 and 1615-1601 cm⁻¹ compared with the free Schiff bases indicating the involvement of the azomethine nitrogen in chelation with the copper(II) ion [38]. The broad band at 3422-3124 cm⁻¹ in the IR spectra of ligands HL¹ and HL² was assigned to ν(O-H) (phenolic or naphtholic) of the aldehyde moiety [39,40]. The observed low value of this band is due to the intramolecular hydrogen bonding between the hydrogen atom of the -OH group and the azomethine nitrogen atom, ν(OH...N = C). This band was shifted to lower frequencies in all copper(II) complexes (except for complex 5), suggesting the involvement of the -OH group in coordination. For complex 5, the ν(O-H) for the ligand disappears, suggesting coordination through deprotonated naphtholic oxygen. The Ar-O stretching frequency appears as a strong band within the 1318-1277 cm⁻¹ as reported for similar ligands [41]. The Ar-O stretching frequency is shifted to a lower frequency in the 1310-1230 cm⁻¹ which confirms the participation of the oxygen atom of the aldehyde moiety in coordination to the copper(II) ion. [36]. The coordination of the azomethine nitrogen and phenolic or naphtholic oxygen are further supported by the appearance of two peaks at 663-564 cm⁻¹ and 540-409 cm⁻¹ due to ν(Cu-O) and ν(Cu-N) stretching vibrations [42,43] that are not observed in the infrared spectra of the free ligands. For HL² ligand, new bands appear at 3300, 1677 and 1597 cm⁻¹ attributable to ν(NH), ν(C=O) and δ(NH) vibration modes, respectively, suggesting the presence of the HL² ligand in an enolimine-ketonamine tautomeric interconversion form [40,44,45]. The lower value of ν(C=O) is due to the intramolecular hydrogen bonding between the hydrogen atom of the -NH group and the oxygen atom of the naphtholic moiety, ν(NH...O = C) (Scheme 1). The free ligands exhibit a strong band at 2213 cm⁻¹, assigned to ν(C≡N) at the 3-position of the pyrrole ring [46]. In all the copper(II) complexes, no significant change was observed, symbolizing that the cyano nitrogen was not involved in the coordination. In addition, the presence of ν(C≡N) at the same position rules out the possibility of its change to CO-NH₂ by promotion of water to the cyano group [47]. For

Table 1. Color, elemental analysis and molar conductivity for ligands (HL¹) and (HL²) and their copper(II) complexes

No	Compound	Yield (%)	Color	Decomp. Temp./ °C	Analysis			$\Lambda_{\text{M}}^{\circ}$
					Calc. (F) %			
					C	H	M	
	HL ¹	84.1	Yellow	210 ^m	80.00 (80.10)	4.68 (4.40)	–	–
1	[Cu (HL ¹)(Cl) ₂]	73.3	Brownish green	100	57.88 (58.37)	3.42 (3.00)	12.8 (12.9)	43.79 [•]
2	[CuHL ¹ (NO ₃) ₂].H ₂ O.EtOH	70.7	Brownish green	131	50.77 (51.06)	4.08 (4.00)	10.3 (10.1)	20.94 [•]
3	[Cu(HL ¹)(L ¹) ₂]	82.3	Brownish red	310	75.09 (76.40)	4.26 (4.30)	5.5 (5.9)	3.22 [•]
4	[Cu HL ¹ (Br) ₂].4H ₂ O	65.4	Dark green	151	43.74 (43.76)	3.79 (3.88)	9.6 (9.9)	18.87 [•]
	HL ² .1.5 EtOH	89.3	Orange	222 ^m	77.19 (77.60)	5.81 (5.70)	–	–
5	[Cu(L ²) ₂]	77.4	Dark green	270 ^m	75.71 (74.42)	4.06 (4.29)	7.2 (7.3)	5.55 [•]
6	[Cu(HL ²)(L ²)NO ₃]	76.4	Brownish green	284 ^m	70.69 (70.75)	3.89 (4.67)	6.7 (6.4)	3.18 [•]
7	[Cu(HL ²)(L ²)(OAc)]	75.9	Dark brown	331 ^m	73.45 (72.86)	4.22 (4.23)	6.7 (6.5)	3.49 [•]
8	[CuHL ² (Br) ₂].2H ₂ O.1/2 EtOH	81.5	Dark brown	95	50.05 (49.21)	3.74 (3.79)	9.1 (9.4)	15.29 [•]

[•] Ohm⁻¹ cm² mol⁻¹ in 10⁻³ M.sol.; [•] in MeOH; [•] in CH₃CN; ^m Melting

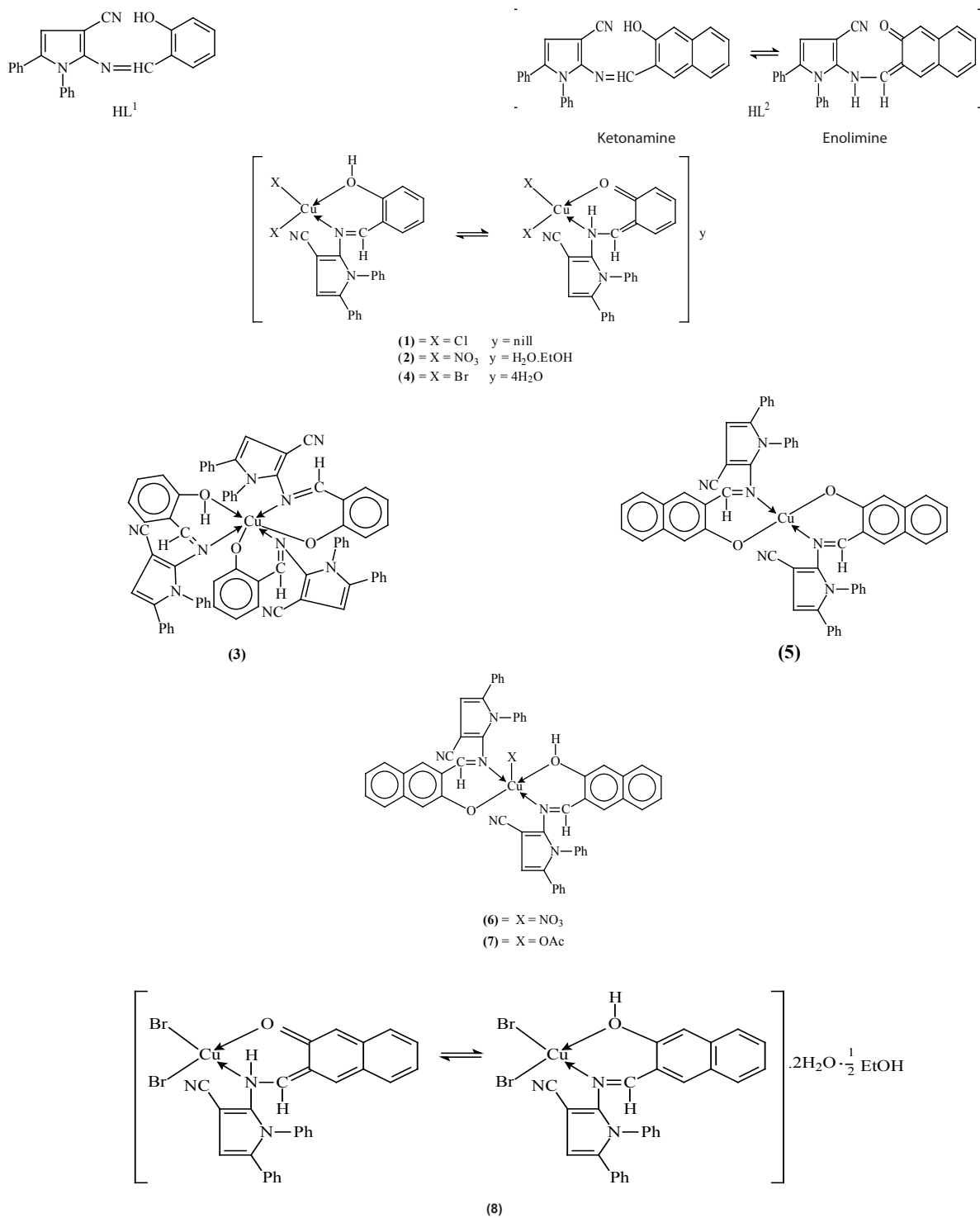
the complexes (1, 2, 4 and 8), the IR spectra show additional bands at 3228-3196, 1680-1675 and 1618-1581 cm⁻¹ attributable to $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ and $\delta(\text{NH})$ vibration modes, respectively, suggesting the presence of these complexes also in an enolimine-ketonamine tautomeric interconversion form (Scheme 1), which is further supported by their lower thermal stability (vide thermal analysis). The IR spectra of the nitrate complexes (2, 6) show bands due to NO₃⁻ stretching vibrations at (1386-1369) cm⁻¹ (ν_s), (1298-1255) cm⁻¹ (ν_1), (1139-1052) cm⁻¹ (ν_2) and (836- 833) cm⁻¹ (ν_3). The values of ($\nu_s - \nu_1$) i.e. (88,114) cm⁻¹ suggest the monodentate coordination of NO₃⁻ ions [21, 48-50]. The cetate complex (7) shows bands at 1570 and 1369 cm⁻¹ assigned to $\nu_{\text{as}}(\text{OAc})$ and $\nu_s(\text{OAc})$, respectively, with a difference of 201 cm⁻¹ indicating a monodentate manner [51,52]. The spectra of some complexes show a very broad band observed in the region between 3500-2905 cm⁻¹ comprising of both –OH (aldehyde moiety, solvent) and –NH stretching absorptions. Bands in the region 1585-1559 cm⁻¹ are due to aromatic (C=C) stretching absorption. From the IR spectra, we can conclude that both Schiff base ligands act as monobasic or neutral bidentate ligands, coordinating to copper(II) ion through the oxygen of the aldehyde moiety and imine nitrogen.

3.2. Mass spectroscopy

The EI mass spectra of free ligands, HL¹, HL² confirm their proposed formulae by showing a molecular ion peak at 363 and 413 amu (calculated 363 and 413 amu), with an abundance of 80.1% and 80.01% for HL¹ and HL² respectively, which coincides with their formulae weight. Their proposed pathway fragmentation pattern is depicted in Scheme 2.

3.3. Electronic spectra and magnetic susceptibility

The electronic spectra of the ligands in methanol and their copper(II) complexes in mulls are summarized in Table 2. The band at 475-460 nm in the spectrum of HL² ligand may be assigned to enolimine-ketonamine tautomeric equilibria [44]. All the complexes show an intense band in the 350–300 nm range which is assigned to n- π^* transition associated with the azomethine linkage [53]. The spectra of the complexes show intense bands at the high-energy region (in the 487–358 nm range), which can be assigned to charge transfer. The electronic spectra of Cu(II) complexes (1, 2, 4 and 8) exhibit a broad band at 680-800 nm indicating square planar geometry [52,54-56]. In the case of complex (3), two transitions were observed at 740 and at 545-450 nm



Scheme 1. Suggested structures of the ligands (HL^1 , HL^2) and their Cu(II) complexes (1-8)

Table 2. Infrared spectral bands (cm^{-1}), magnetic moment (BM) and electronic spectral data (nm) for (HL^1) and (HL^2) ligands and their copper(II) complexes.

No.	Compound	$\nu(\text{OH}) / \nu(\text{H}_2\text{O}, \text{EtOH})$	$\nu(\text{N-H})$	$\nu(\text{C=O})$ (tout.)	$\nu(\text{C=N})$	$\delta(\text{N-H})$	$\nu(\text{M-O})$	$\nu(\text{M} \leftarrow \text{N})$	$\mu_{\text{eff}}(\text{BM})$	(d-d) transition mulls(nm)
	HL^1	3124(m)	-	-	1621(s)	-	-	-	-	-
1	$[\text{Cu}(\text{HL}^1)(\text{Cl})_2]$	3338	3204	1680(s)	1582(sh)	1618(s)	635(w)	540(sh)	2.0	800, 520, 415, 370
2	$[\text{Cu}(\text{HL}^1)(\text{NO}_3)_2] \cdot \text{H}_2\text{O} \cdot \text{EtOH}$	3375, 2932	3196	1680(s)	1585(sh)	1618(s)	643(sh)	460(w)	2.0	700, 510, 490, 480
3	$[\text{Cu}(\text{HL}^1)(\text{L}^1)_2]$	3100	-	-	1599(s)	-	663(w)	522(m)	1.9	740, 545, 450
4	$[\text{Cu}(\text{HL}^1)(\text{Br})_2] \cdot 4\text{H}_2\text{O}$	3500-3414	3228	1675(sh)	1583(sh)	1614(s)	566(sh)	409(sh)	1.98	800, 475, 455-400
	$\text{HL}^2 \cdot 1.5 \text{ EtOH}$	3500-3422, 2905	3300	1677(m)	1620 (s)	1597(m)	-	-	-	-
5	$[\text{Cu}(\text{L}^2)_2]$	-	-	-	1615 (sh)	-	564(m)	502(m)	2.0	700, 480, 460
6	$[\text{Cu}(\text{HL}^2)(\text{L}^2)\text{NO}_3]$	4000-3300	-	-	1601 (m)	-	565(m)	500(m)	2.0	900, 740, 620
7	$[\text{Cu}(\text{HL}^2)(\text{L}^2)(\text{OAc})]$	3400	-	-	1601 (m)	-	565(m)	500(m)	2.0	910, 729, 580
8	$[\text{Cu}(\text{HL}^2)(\text{Br})_2] \cdot 2\text{H}_2\text{O} \cdot 1/2 \text{ EtOH}$	3413-3350, 2935	3200	1679(w)	1602(sh)	1581(sh)	583(w)	495(sh)	1.9	680, 470-405

(sh) shoulder; (s) strong; (m) medium; (w) weak

Table 3. EPR parameters of copper(II) complexes.

No.	Compound	$g_{\parallel}$	$g_{\perp}$	g_{iso}	G	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel} / A_{\parallel}$ cm	α^2
2	$[\text{CuHL}^1(\text{NO}_3)_2] \cdot \text{H}_2\text{O} \cdot \text{EtOH}$	2.18	2.05	2.09	3.67	190	25	80	112	0.774
5	$[\text{Cu}(\text{L}^2)_2]$	2.25	2.05	2.11	5	190	25	80	112	0.805
6	$[\text{Cu}(\text{HL}^2)(\text{L}^2)\text{NO}_3]$	2.25	2.04	2.11	6.25	120	10	46.66	178	0.637

Table 4. DTA and TG data of the investigated copper(II) complexes.

No.	Compound	Temp. /C°		Wt loss/ %		Reaction	Leaving species	
		Calc.(F)	TGA	DTA				
1	[Cu (HL ¹)(Cl) ₂]	HL ¹	200 -216*(Max=210)	-	-	c	.-	
			216 - 800**	216 - 624	100 (100)	d	gradual decomposition	
			100 - 270.*	100 - 230	14.5 (14.7)	d	2HCl	
			270 - 800•	230 - 800 at 800	69.5 (69.0) 16.0 (16.3) °	d	gradual decomposition. ≡ CuO	
2	[CuHL ¹ (NO ₃) ₂]. H ₂ O•EtOH		27 - 110*	27 – 110	7.5 (7.7)	b	EtOH	
			110 - 130*	110 - 130	2.9 (2.8)	c	H ₂ O	
			131 - 800*	131 – 550 at 550	76.6 (76.2) 13.0 (13.3)°	d	gradual decomposition. ≡ CuO	
3	[Cu(HL ¹)(L ¹) ₂]		310 - 450* 450 - 730•	310 - 450 450 - 650 at 650	23.5 (23.7) 68.9 (68.1) 7.6 (8.2) °	d d	Pyrrole moiety(C ₁₈ H ₁₂ N ₃) completion of the decomposition process ≡ CuO _{1.5}	
4	[Cu HL ¹ (Br) ₂].• 4H ₂ O		30 - 150* 151 - 370* 370-800•	30 -150 151- 370 370-1000 at 1000	10.9 (10.6) 12.3 (12.2) 55.0 (55.4) 21.8 (21.8)°	a d d	4H ₂ O HBr gradual decomposition. ≡ CuBr	
5	HL ² •1.5 EtOH		140 -160* 210 -230*max=222 231 -520.* 520 -800•	140-160 161-230 231 -520 520-713	- 14.3 (14.3) 53.3 (53.3) 32.4 (32.4) 100 (100)	- c+ b d d	phase change 1.5 EtOH pyrrole moiety(C ₁₇ H ₁₁ N ₃) naphthyl moiety(C ₁₁ H ₉ O)	
5	[Cu(L ²) ₂]		203* 270 - 800*•	- 270 - 800	- 64.8 (65.6)	c d	- decomposition	
6	[Cu(HL ²)(L ²) NO ₃]		230 * 284 - 490• 491 - 700*	- 284 - 490 491 - 680 at 680	- 54.1 (53.7) 32.7 (33.0) 13.2 (13.3)°	c d d	- 2 pyrrole moiety(C ₃₄ H ₂₂ N ₆) 2 naphthyl moiety(C ₂₂ H ₁₅ O ₂) ≡ Cu(NO ₃)	
7	[Cu(HL ²)(L ²)(OAc)]		230 * 331 - 550*• 550 - 760*	- 331 – 620 620 -760 at 760	- 54.3 (54.8) 32.8 (32.5) 12.9 (12.7) °	c d d	- 2 pyrrole moiety(C ₃₄ H ₂₂ N ₆) 2 naphthyl moiety(C ₂₂ H ₁₅ O ₂) ≡ Cu(OAc)	
8	[CuHL ² (Br) ₂].•2H ₂ O• 1/2 EtOH		26 - 94* 95 -200• 200 -800*	26 - 94 95 - 200 200 -800 at 800	8.5 (8.6) 11.6 (11.8) 59.3 (57.8) 20.6 (21.4) °	a + b d d	1/2 EtOH + 2H ₂ O HBr gradual decomposition. ≡ CuBr	

* Endo; • Exo; ° Final product percent; a Dehydration; b Desolvation; c Melting; d- decomposition, HL¹= (C₂₄H₁₇N₃O); HL²= (C₂₈H₁₉N₃O)

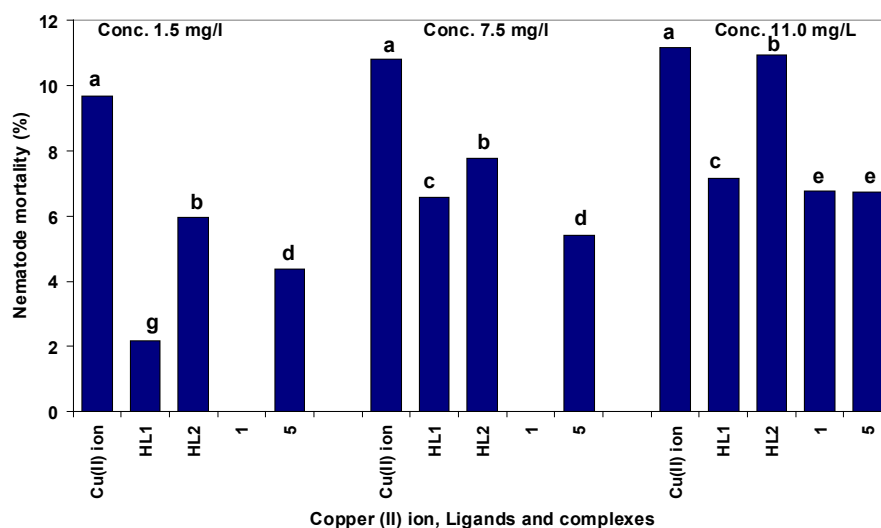


Figure 1. Mortality of *Heterorhabditis bacteriophora* after 48 h as a function of different concentrations of Cu(II) ion, ligands (HL¹, HL²) and complexes (1, 5).

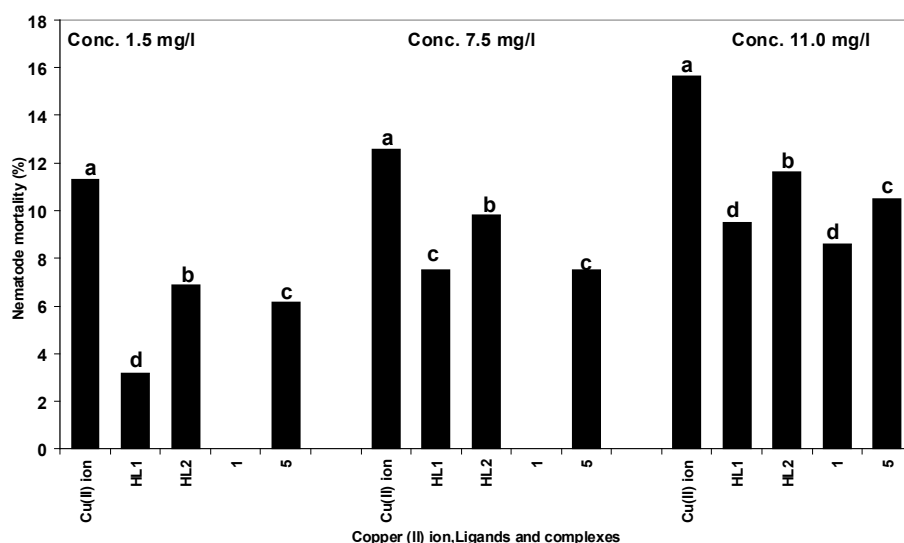


Figure 2. Mortality of *Heterorhabditis bacteriophora* after 96 h as a function of different concentrations of Cu(II) ion, ligands (HL¹, HL²) and complexes (1, 5).

indicating octahedral geometry [57,58]. The electronic reflectance spectra of the copper(II) complexes (6, 7) were analyzed to three Gaussian components which were consistent with square-pyramidal copper(II) complexes (Table 2). In the C_{4v} symmetry the three bands are assigned ${}^2B_1 \rightarrow {}^2E_1$ (Δ_1), ${}^2B_1 \rightarrow {}^2B_2$ (Δ_2) and ${}^2B_1 \rightarrow {}^2A_1$ (Δ_3) transition, respectively [59,60]. The room temperature magnetic moments were measured for all complexes and are summarized in Table 2. The observed values (ranging from 1.98 to 2.0 BM) are

normal for monomeric Cu(II) complexes with an $S = 1/2$ spin state and did not indicate anti-ferromagnetic coupling of spin at this temperature. The slightly higher magnetic moment observed for some complexes could be associated with spin-orbital contribution [61].

3.4. Electron Paramagnetic Resonance (EPR)

The X-band EPR spectra of copper(II) complexes (2, 5, 6) have been recorded in the solid state at room temperature. The various Hamiltonian parameters have

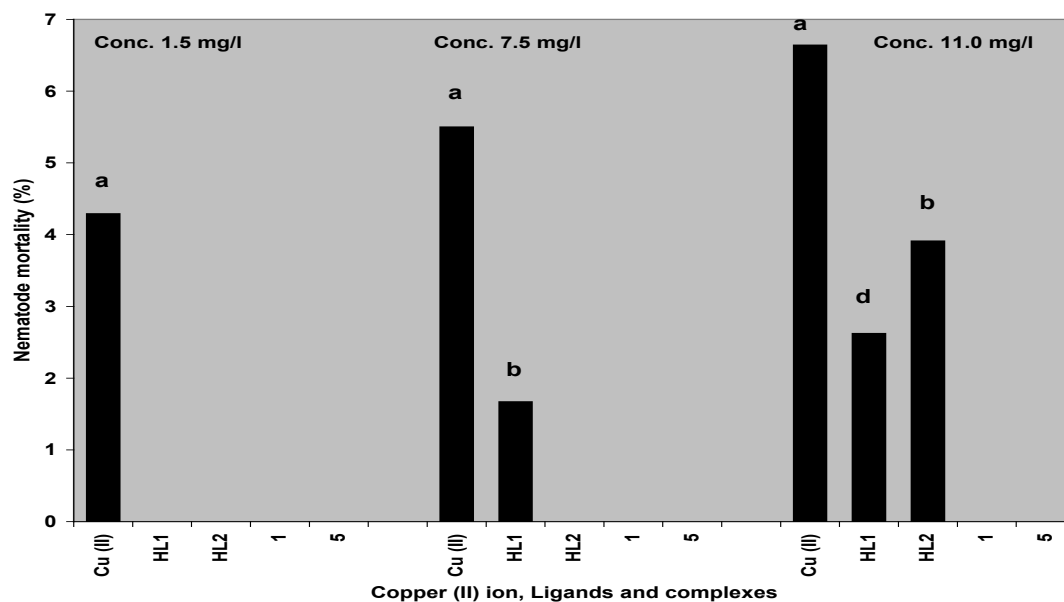


Figure 3. Mortality of *Steienernema carpocapse* after 48 h as a function of different concentrations of Cu(II) ion, ligands (HL¹, HL²) and complexes (1, 5).

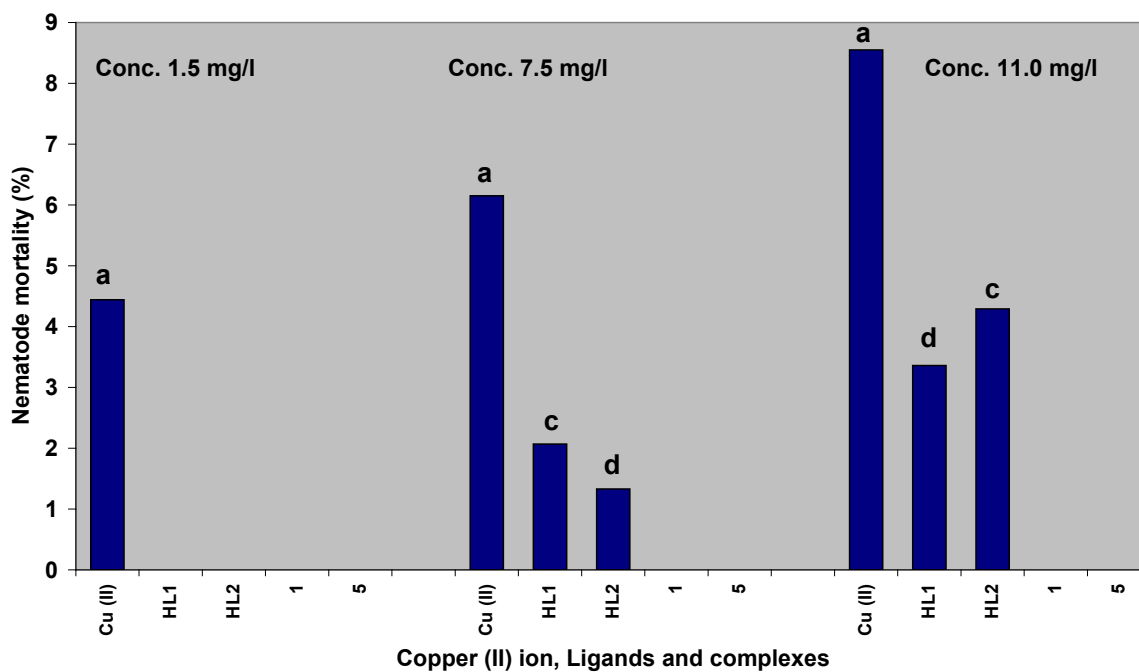
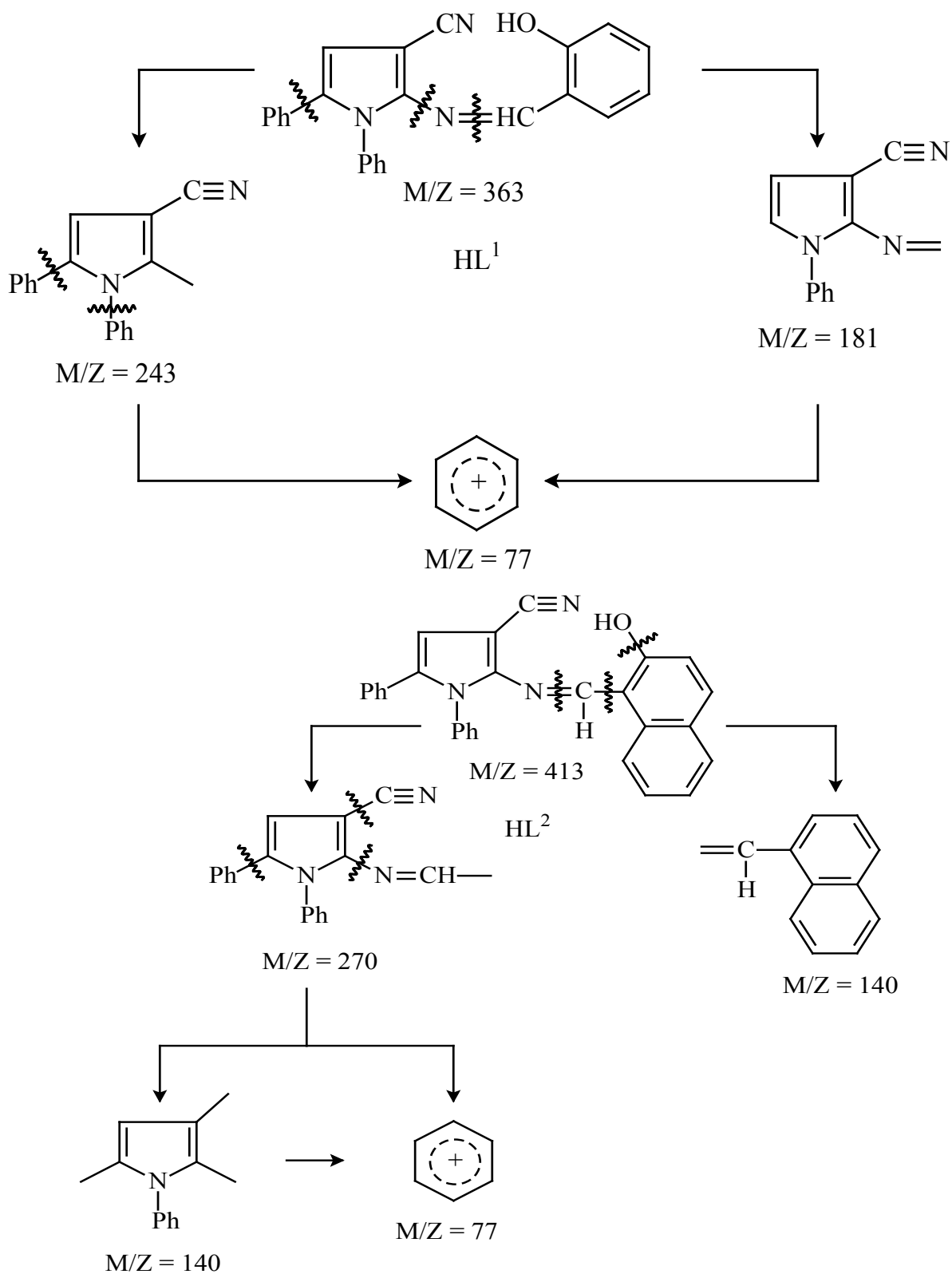


Figure 4. Mortality of *Steienernema carpocapse* after 96 h as a function of different concentrations of Cu(II) ion, ligands (HL¹, HL²) and complexes (1, 5)

The columns followed by the same letter are not significantly different but the columns followed by different letters are significantly different ($P=0.05$) according to the Duncan multiple-range test (Figs.1-4).



Scheme 2. The fragments observed in mass spectra of HL¹ and HL².

been calculated [62,63] (Table 3). In all complexes, the $g_{\parallel}$ values are less than 2.3 with the trend $g_{\parallel} > g_{\perp} > 2.0023$. This result shows that the complexes are largely covalent [64] and that the $d_{x^2-y^2}$ is in the ground state with d^9 $[Cu^{2+}]$ configuration i.e $(eg)^4, (a_{1g})^2 (b_{2g})^2 (b_{1g})^1$. Further, the values are consistent with Cu-N and Cu-O bonded copper complexes [65]. The empirical factor $F = g_{\parallel}/A_{\parallel}$ cm values were considered as a diagnostic of stereochemistry. The $g_{\parallel}/A_{\parallel}$ cm ratios for complexes (2, 5) in this study (112 cm) are within the 105–135 cm range seen for square planar complexes [66]. On the other hand, the ratio calculated is 178 cm for complex (6) which lies within the range 150–250 cm expected for tetragonal distorted complexes. Apart from this, the covalency parameter (α^2) has been calculated using Kivelson and Neiman equations [67]. The covalency parameter ($\alpha^2 = 0.805 - 0.637$) indicates considerable covalent character for the metal–ligand bond [68]. The g_{iso} values and the geometric parameter G , i.e., the measurement of exchange interaction between the copper centers were evaluated by using the expressions:

$$g_{iso} = \frac{g_{\parallel} + 2g_{\perp}}{3}, \quad G = \frac{g_{\parallel} - 2.003}{g_{\perp} - 2.003}$$

The complexes in the present study show the value of $G = 3.67$ – 6.25 , which indicates no effective interaction. Thus, based on the spectral and analytical data (Table 1,2,3), tentatively proposed structures of the ligands and their copper(II) complexes are depicted in Scheme 1.

3.5. Thermal analysis

The thermal properties of the studied ligands HL^1 , HL^2 and their copper(II) complexes were investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), under nitrogen atmosphere from 25 to 800°C; important data are summarized in Table 4.

3.5.1. Ligands HL^1 , HL^2

For the Schiff base ligand HL^1 , the DTA curve shows an endothermic peak at 210°C due to the melting of the organic ligand. It can be seen that the TGA curve of HL^1 shows no mass loss up to 216°C, indicating the absence of water molecule and/or any other adsorptive solvent molecules. The thermogram shows one decomposition step that begins at 216°C with a total mass loss of 100.0% (found 100.0%). This mass loss may be due to the successive losses of $C_{24}H_{17}N_3O$ molecule as gases at the given temperature range. The DTA curve of Schiff base ligand HL^2 shows a weak endothermic peak at 150°C, and the TGA thermogram shows no mass loss at that temperature;

this peak may be assigned to an enolimine-ketonamine tautomeric equilibria. The DTA curve shows a second endo peak at 222°C, with mass loss (estimated mass loss 14.3%; theoretical 14.3%) This result is in good agreement with the loss of one and a half molecules of ethanol per ligand molecule along with the melting point of the organic ligand. These results are in accordance with the composition of the ligand determined by elemental analysis and IR spectroscopy. The Schiff base ligand HL^2 refers to two stages of mass loss at the temperature range between 231–713°C. These stages involved mass loss of 100.0% (found 100.0%) for the first and second steps of decomposition, respectively. These mass losses may be due to the successive losses of $C_{28}H_{19}N_3O$ molecule as gases at the given temperature range.

3.5.2. Complexes

The thermal analysis data are presented in Table 4. The correlations between the different decomposition steps of the complexes with their corresponding mass loss are discussed in terms of the proposed formulae of the complexes. DTA curves of complexes (2, 4, 8) are generally characterized by endothermic peaks in the temperature range of 26–150°C, assigned to loss of solvents for crystallization, which results from TG mass loss in that temperature range. The lower and wide range of temperature of desolvation indicates that, the solvents of crystallization are physically bound [69–72]. As shown from DTA curves, the desolvation process was followed by other asymmetric endo and/or exothermic peaks, that are assigned to material decomposition, as indicated from TG mass loss in that temperature range. The thermal behavior of complexes (1, 2, 4 and 8) that are present in the enolimine-ketonamine tautomeric forms are almost the same, and the DTA/TGA curves are very similar to each other and display a lower thermal stability (95–151°C). The lower thermal stability of these complexes may be due to the pseudo removal of the aromaticity of the phenolic or naphtholic moiety in the ketonamine form and confirms the presence of these complexes in enolimine-ketonamine tautomeric forms. As the temperature is increased, the DTA/TGA curves exhibit a gradual decomposition over a large temperature range. The thermal behavior of the complexes (3, 5–7) are also almost the same; the DTA/TGA curves are very similar to each other and display one or two decomposition steps with a higher thermal stability (270–331°C). The higher thermal stability of HL^1 complex (3) (310°C) may be due to the presence of three six membered chelate rings around $Cu(II)$ ion. For HL^2 complexes (5–7), the observed higher thermal stability may be due to the

presence of two six membered chelate rings in each complex. Complex (5) is thermally less stable (270°C) than the nitrate complex (6) which in turn thermally less stable (284°C) than the cetate complex (7) (331°C). This reflects the effect of the type and the presence of the anions on the thermal stability of complexes. The final solid thermoproduct was examined by IR spectroscopy and it is likely to be CuO for complexes (1, 2), CuO_{1.5} for complex (3), CuBr for complex (4, 8), Cu(NO₃) for complex (6), and Cu(OAc) for complex (7).

3.6. Toxicity study

The effect of the tested copper(II) ion, ligands and complexes (1, 5) on *Heterorhabditis bacteriophora* mortality after 48 h were highly variable. The Cu(II) ion followed by HL² appeared to be toxic for *H. bacteriophora* juveniles. The mortality of the nematodes increased and the increase was gradual with increasing concentrations for all the tested materials except for complex (1), where a sharp increase in mortality was cleared from median concentration to high concentration. At low concentration, Cu(II) ion appeared to be the most toxic for the nematode juveniles followed by HL², complex (5), then HL¹. Complex (1) showed no toxicity at low and median concentration but toxicity appeared at high concentration. The rank of toxicity slightly differed at higher concentrations. Cu(II) ion also scored the highest toxicity followed by HL², HL¹, complex (5) then complex (1) (Fig. 1). The percent mortality of the juveniles increased at 96 h of exposure to Cu(II) ion, HL², HL¹, complex (5) and complex (1) with the same rank of 48 h (Fig. 2).

For *Steinernema carpocapsae* at 48h, Cu(II) ion was the only toxic species for the juveniles at low concentration. This toxicity increased with increasing concentrations. The mortality appeared at the median

concentration in HL¹ (Fig. 3). For HL², the toxicity started only at higher concentrations. All the tested complexes (1, 5) have no effect on mortality on *S. carpocapsae* (Fig. 3). The same rank of mortality at 48 h occurred at 96 h with increasing values of percent mortality of the nematode juveniles (Fig. 4). The increased mortality of *S. carpocapsae* observed for Cu(II) ion at high concentration occurred randomly in nature. Unlike the finding of Jaworska *et al.* [33] in which *H. bacteriophora* was more resistant than *S. carpocapsae* to copper(II) ions, the reverse was found in the present study where *S. carpocapsae* was more resistant to Cu(II) ion, ligands and complexes than *H. bacteriophora*. An elevated copper(II) ion concentration has been shown to reduce beneficial mycorrhizal association [73]. Also, it has been noted that earth worms exhibit chronic toxic responses at relatively low concentrations of copper (<4-16 mg kg⁻¹) [74].

4. Conclusions

Novel copper(II) complexes of bidentate Schiff base ligands obtained by the condensation of salicylaldehyde or 2-hydroxy-1-naphthaldehyde with 2-amino-3-cyano-1,5-diphenylpyrrole have been isolated and studied. As demonstrated from IR spectroscopy, complexes (1, 2, 4, 8) are present in enolimine-ketonamine tautomeric form and thermal analysis shows that these complexes have lower thermal stability. EPR spectral data of complexes (2, 5, 6) indicate that the metal-ligand bonds have considerable covalent character. The toxicity study results indicate that copper pollutants affect nematode density and biological activity in the natural environment, but combinations of copper with ligands to form complexes reduce this harmful effect.

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