
SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES ON SOME TRANSITION METAL COMPLEXES OF 2-THIOXO-1,2,5,6,7,8-HEXAHYDRO-QUINOLINE-3-CARBONITRILE

ALI. M. A. HASSAN, MOSTAFA M. OMARA, ABD ELAZIZ Y. ELSID
GALAL E. GEMEIE and TARK H. ALY

Department of Chemistry, Faculty of Science, Al-Azhar University, Egypt

Abstract

Binary ligand complexes of 2-thioxo-1,2,5,6,7,8-hexahydro-quinoline-3-carbonitrile (HL^1) with Fe(III), Co(II), Ni(II) and Cu(II) ions were prepared and characterized on the basis of elemental analysis, conductivity data, IR, 1H NMR, electronic spectra and magnetic susceptibility measurements. The conductivity data obtained are interpreted on the basis of the molecular structure of the ligand complexes. The IR spectral band of the complex is assigned to the proper stretching frequencies in comparison to these of the free ligand. The various decomposition steps are determined from thermal analysis and determined the numbers of water molecules in the complexes. Kinetic parameters of the thermal decomposition have been evaluated and the data was refined using the least square method. Values of the activation energy, correlation coefficient and order of decomposition reaction were computed and discussed. Also Entropy (ΔS), enthalpy (ΔH) and free energy (ΔG) of activation were computed. The biological effects of the ligand complexes were studied.

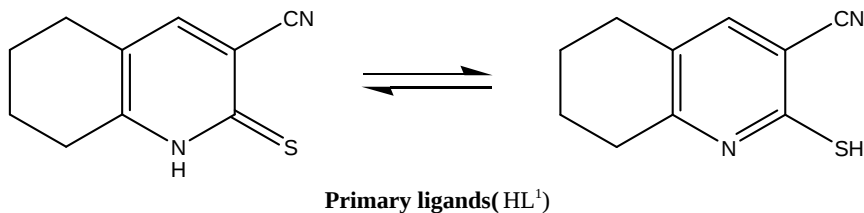
Introduction

Heterocyclic thiones form complexes with a variety of metal is potentially interesting, much of the research interest into the coordination chemistry of the heterocyclic thiones stems from the wide ranging applications of their complexes from their use as analytical reagents in gravimetric and spectrophotometric analysis[1] to industrial processes such as in metal finishing and electroplating industries[2-4]. Some of the common application include the use of heterocyclic thione complexes as polyolefin stabilizers[5,6], as a vulcanisation accelerators[7] and as metal corrosion inhibitors[8].

Experimental

- 1) Metal salts: The metal salts $Fe(NO_3)_3 \cdot 9H_2O$, $CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ used for the preparation of complexes were of general grade reagents (prolabo chemicals).
- 2) PREPARATION OF THE LIGAND [9]:
ligand (HL^1): 2-thioxo-1,2,5,6,7,8-hexahydro-quinoline-3-carbonitrile. The derived from heterocyclic compounds, which we are used, were prepared according to the literature procedure.

The ligand used in the present study has the following structures:



3) PREPARATION OF THE BINARY COMPLEXES:

The binary complexes were synthesized by adding a clear methanolic solution (25 ml) of the metal salt (1 mmole) dropwise to methanolic solution (25 ml) of the ligand (1 and 2 mmole) in 1:1 and 1:2 molar ratios (M : L) with constant stirring in one direction with heating for two hours. The precipitate was obtained then left at room temperature for 12-24 hours. The mixture was permitted to evaporate slowly at room temperature until one-third its original volume, whereby a microcrystalline solid was separated. Then the solid obtained was filtered, washed with methanol and dried in vacuo over P₄O₁₀. The binary complexes were analyzed for their carbon, hydrogen, nitrogen, sulfur, and metal contents.

4) COMPLEX SOLUTIONS:

Stock solution of complexes were prepared by dissolving the accurate weight of each in the appropriate volume solvents (DMF) solutions of required concentration were prepared by accurate dilution with the proper solvent.

5) IR spectra of the ligand and its metal complexes were recorded on Shimadzu 140 Infrared Spectrophotometer (4000 - 400 cm⁻¹) as KBr discs. The proton HNMR spectra DMSO -d₆ on a Varian FT -200 Mhz spectrometer using TMS as internal standard at Assiut university. The electronic absorption spectra were recorded with Shimadzu 2101 recording spectrophotometer. All conductance measurements reported in this study were performed using an LF Digi 550 conductance bridge with an immersion cell. The thermogravimetric analysis were determined using Shimadzu analyzer 50 H For TGA and DTA in a dynamic nitrogen atmosphere (100 ml/min). The antimicrobale activity of the ligand and their complexes was tested using the usual cup - plate diffusion technique. The culture media used are nutrient agar media supplemented with 1 g yeast/L.

Results and Discussion

The results of elemental analyses are shown in Table 1. The complexes are soluble in DMF and DMSO, but not soluble in most common organic solvents. The measured molar conductance values of Fe(III), Co(II), Ni(II) and Cu(II) complexes in DMF solution fall in the range 18.15-39.18 $\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$ (Tables 1). These values indicate that those complexes are non electrolytes, since the reasonable range for 1:1 electrolytes in DMF is 65-90 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ [10].

I – The IR Spectra

The IR spectra of the free ligands 2-thioxo-1,2,5,6,7,8-hexahydro-quinoline-3-carbonitrile (HL^1) show the appearance of absorption band at 3300 cm^{-1} in HL^1 , which can be assigned to stretching vibration of (NH) group [12]. The appearance of an absorption band at 2900 cm^{-1} in HL^1 which can be attributed to ν aliphatic structure of cyclic. Also the presence of an absorption band at 2210 cm^{-1} in HL^1 which can be attributed to stretching vibration of $\nu \text{ C}\equiv\text{N}$. The presence of an absorption band at 1240 cm^{-1} in HL^1 which can be attributed to stretching vibration of $\nu \text{ C}=\text{S}$.

The IR spectra of investigated solid complexes shows that the band at 3300 cm^{-1} in HL^1 due to stretching vibration of $\nu(\text{NH})$ group in ligand is absent in the spectra of all complexes. The disappearance of these bands is due to the displacement of the hydrogen ion from the NH group [11,13,14] through the coordination moiety. This result is confirmed by ^1H NMR data.

The band at 2240 cm^{-1} in HL^1 is attributed to stretching $\text{C}\equiv\text{N}$ and is shifted to lower frequencies due to coordination in investigated complexes, in the range $2100 - 2210 \text{ cm}^{-1}$ for HL^1 complexes.

The band at 1240 cm^{-1} in HL^1 which corresponds to stretching vibration of $\text{C}=\text{S}$ are shifted to higher or lower frequencies due to coordination with metal ions [15] in the range $1100-1210 \text{ cm}^{-1}$ for HL^1 complexes.

The appearance of a broad band in the range $3400-3500 \text{ cm}^{-1}$ is due to νOH of (H_2O) [14-16] for Cu(II)L complexes.

Also the two new bands appear for all chelates at $600-500 \text{ cm}^{-1}$ region corresponding to stretching $[\text{M}-\text{S}]$ [16-17] metal-sulphur bond and at $460-480 \text{ cm}^{-1}$ due to stretching $[\text{M}\leftarrow\text{N}]$ [16] metal-nitrogen bond. The important IR bands are listed in (Tables 2) and (Figs 1,2).

1.2 The ^1H NMR

The ^1H NMR spectrum of the ligand [9] HL^1 show characteristic signal at 1.80 ppm due to appearing the ($-\text{NH}$) proton and Moreover the appearance of the band located at 3.30 ppm may be assigned to due to the ($-\text{SH}$) proton. The band observed at 7.83 ppm may be assigned to ($-\text{CH}$ -pyridine-) proton. The important ^1H NMR spectrum bands are listed in (Table 3) for ligand HL^1 and some its complexes.

Table 1: Colour, elemental analyses, melting point and conductance value of the complexes.

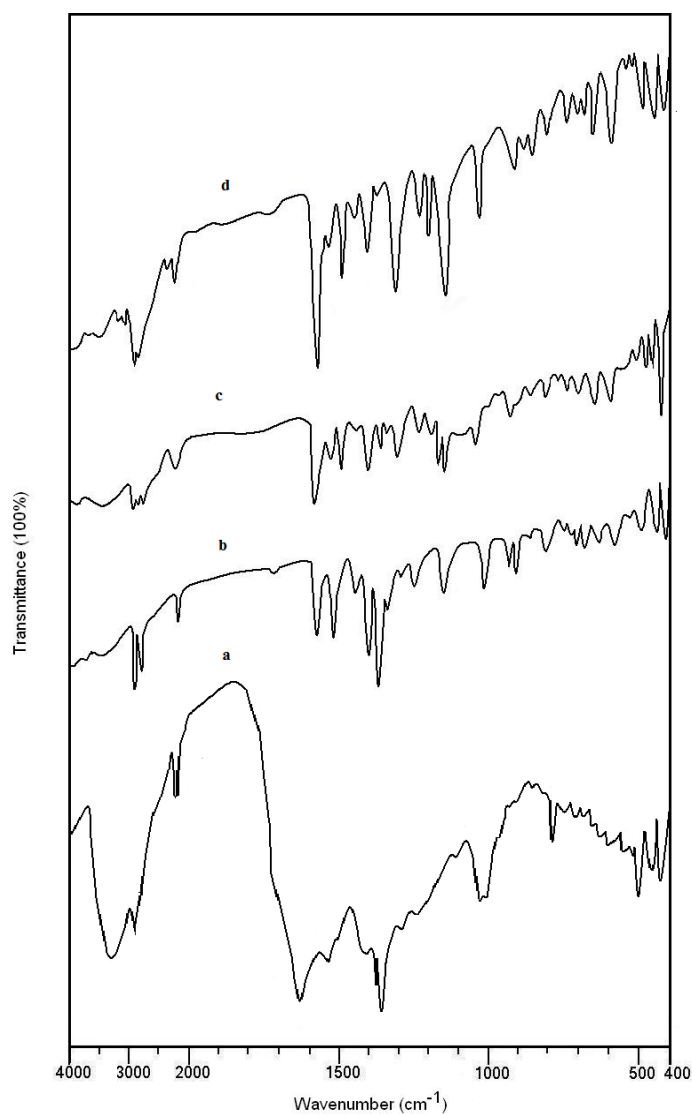
Compounds	Colour	Found (Calcd.%)					m.p. $^{\circ}\text{C}$ Decomp.	Conductance $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
		C	H	N	S	M		
HL^1 $\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}$ M.Wt=190.27	Yellow	63.18 (63.13)	4.90 (5.30)	14.80 (14.72)	16.42 (16.85)	-	250	-
$[\text{Fe}(\text{L}^1)_3]$ $\text{C}_{30}\text{H}_{27}\text{FeN}_6\text{S}_3$ M.Wt= 623.08	Brown	62.75 (57.78)	4.29 (4.36)	14.66 (13.48)	16.81 (15.39)	- (8.99)	>330	33.25
$[\text{Co}(\text{L}^1)_3]$ $\text{C}_{30}\text{H}_{27}\text{CoN}_6\text{S}_3$ M.Wt= 626.08	Yellow	61.39 (57.50)	5.15 (4.34)	14.30 (13.42)	16.68 (15.32)	4.70 (9.41)	300	26.11
$[\text{Co}(\text{L}^1)_2]$ $\text{C}_{20}\text{H}_{22}\text{CoN}_4\text{S}_2$ M.Wt= 437.49	Yellow	53.87 (54.90)	4.81 (5.03)	11.63 (12.80)	15.17 (14.63)	12.08 (12.76)	300	36.29
$[\text{Ni}(\text{L}^1)_3]$ $\text{C}_{30}\text{H}_{27}\text{NiN}_6\text{S}_3$ M.Wt= 625.08	Yellow	58.53 (57.59)	4.57 (4.35)	13.65 (13.44)	15.67 (15.34)	8.38 (9.27)	320	39.18
$[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})_2]$ $\text{C}_{10}\text{H}_{13}\text{CuN}_4\text{O}_2\text{S}$ M.Wt= 288.84	Yellow	42.90 (41.58)	4.30 (4.53)	9.73 (9.69)	10.99 (11.10)	21.44 (22.00)	330	18.15
$[\text{Cu}(\text{L}^1)_2]$ $\text{C}_{20}\text{H}_{22}\text{CuN}_4\text{S}_2$ M.Wt= 441.10	Yellow	54.94 (54.40)	4.42 (4.98)	12.68 (12.70)	14.29 (14.50)	14.11 (14.40)	>330	32.89

Table 2: Relative IR bands of ligand (HL^1) and its metal chelates (cm^{-1}).

Compounds	(H_2O)	ν NH	ν SH	ν aliphatic St. of cyclic	ν C=N	δ NH	(H_2O)	ν C=S	M-S	M-N
HL^1	-	3200	2860	2900	2240	1500	-	1240	-	-
$[\text{Fe}(\text{L}^1)_3]$		-	-	2900	2200	-		1160	500	470
$[\text{Co}(\text{L}^1)_3]$		-	-	2900	2150	-		1105	600	470
$[\text{Co}(\text{L}^1)_2]$	-	-	-	2900	2120	-		1150	600	480
$[\text{Ni}(\text{L}^1)_3]$		-	-	2900	2125	-		1120	500	470
$[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})_2]$	3500	-	-	2900	2125	-	1345	1170	600	460
$[\text{Cu}(\text{L}^1)_2]$	-	-	-	2900	2190	-		1210	600	460

Table 3: ^1H NMR spectrum data of ligand (HL^1) and its metal complexes (ppm).

Complexes	m, 2H, CH_2	m, 4H, 2CH_2	S, 1H, pyridine H-4	S, br, 1H, NH	S, br, 1H, SH	S, nH, H_2O
HL^1	1.55-1.81	2.52-2.81	7.83	1.80	3.30	-
$[\text{Co}(\text{L}^1)_3]$	1.65, 1.96	2.52-2.81	7.90	-	-	5.6
$[\text{Co}(\text{L}^1)_2]$	1.65, 1.95	2.52-2.81	7.90	-	-	5.6
$[\text{Ni}(\text{L}^1)_3]$	1.65, 1.96	2.52-2.81	7.90	-	-	5.6

**Fig. 1.** Infrared spectra of the free ligand HL^1 and its metal complexes.

(a) = Free ligand

(b) = $[\text{Fe}(\text{L}^1)_3]$ (c) = $[\text{Co}(\text{L}^1)_3]$ (d) = $[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2]$.

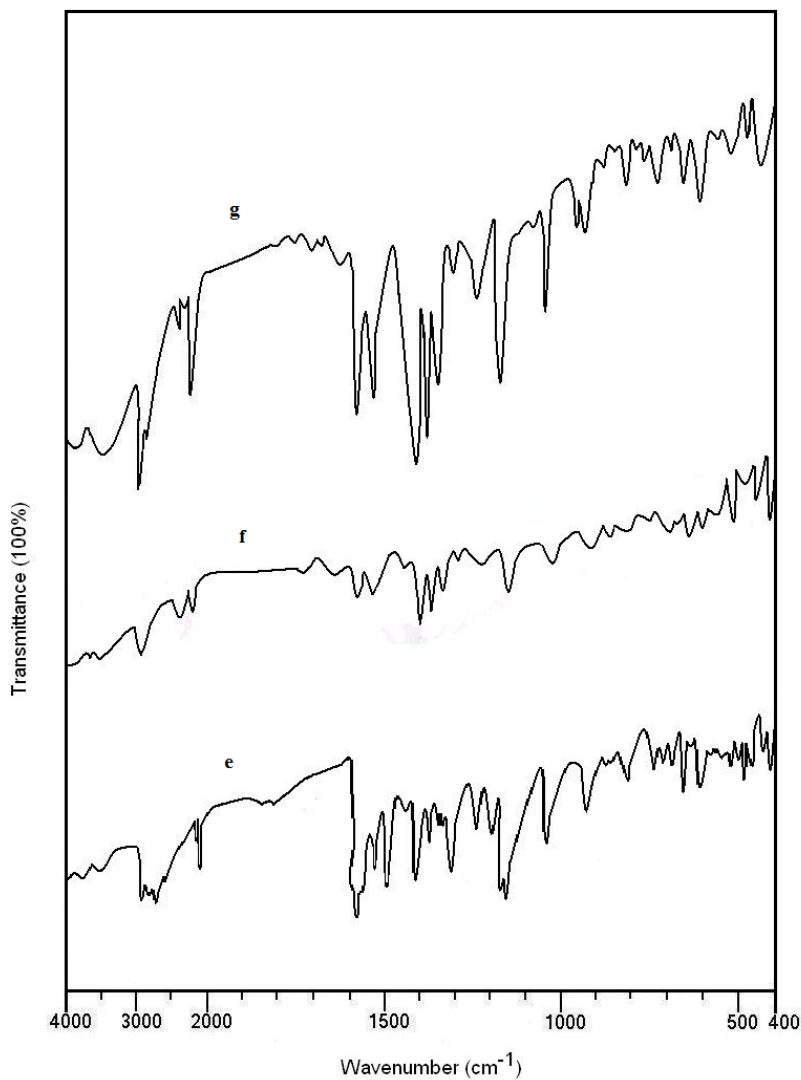
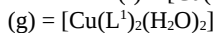
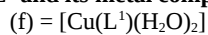
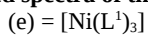


Fig. 2. Infrared spectra of the free ligand HL^1 and its metal complexes.



1.3 . ELECTRONIC SPECTRA AND MAGNETIC SUSCEPTIBILITY MEASUREMENTS.

The obtained spectral characteristic data (mainly ν_{max} in cm^{-1} and ϵ_{max} in $cm^2 mol^{-1}$) of the different band displayed by the free ligand and their binary complexes are given in (Tables 4, 5) and (Figs. 3-8).

The electronic spectra of the free ligand (HL^1) exhibit the band at 313 nm (31.948 cm^{-1}) assigned to $n \rightarrow \pi^*$ transitions of the non-bonding electrons and a medium intensity band at 412 nm (24.271 cm^{-1}) is attributed to $\pi \rightarrow \pi^*$ [18,19] transitions.

Three sets of bands could be recognized in electronic spectra of the obtained ligand complexes. The first set of bands with ν_{\max} in the range $28.089\text{--}32.258\text{ cm}^{-1}$, could be attributed to intra-ligand charge transfer transitions.

The second set includes bands having ν_{\max} in the range $25.000\text{--}27.624\text{ cm}^{-1}$. These bands are assigned to the ligand \rightarrow metal charge transfer transition ($L \rightarrow MCT$) type.

The third set of bands of the Iron (III) complexes $[Fe(L^1)_3]$ was found to have ν_{\max} at 21.186 cm^{-1} . This broad band is due to d-d transition and it is typical for distorted octahedral [20] Fe(III) complexes which may be attributed to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$.

The magnetic moment value of the complexes $[Fe(L^1)_3]$ at room temperature are diamagnetic.

Co(II) complexes display d-d transition bands at ν_{\max} 21.097 cm^{-1} and 21.276 cm^{-1} for $[Co(L^1)_3]$ and $[Co(L^2)_2]$ respectively. These bands could be attributed to (${}^4T_{1g} \rightarrow {}^4T_{1g}$) (P) transition, suggesting octahedral geometries [21,22].

At room temperature magnetic moment value of the Co(II) complexes are 4.16 and 2.10 expected for spin free octahedral Co(II) complexes [23,24,25].

The d-d bands of Ni(II) complexes $[Ni(L^1)_3]$ was found to have ν_{\max} at 21.276 cm^{-1} . This band could be assigned to the transition ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, suggesting octahedral geometry [26,27-31].

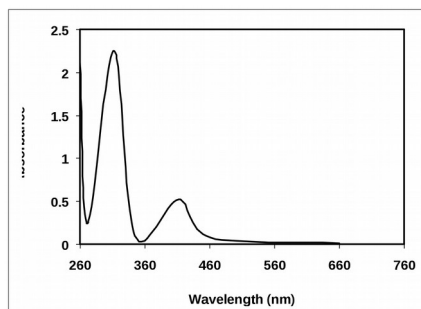
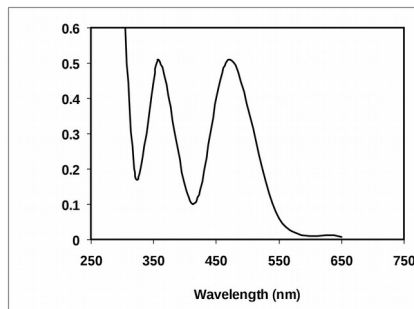
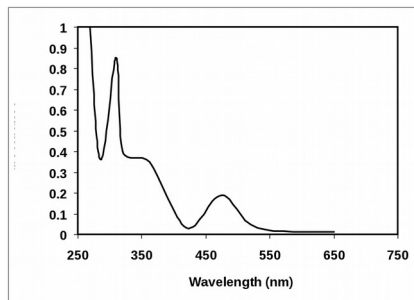
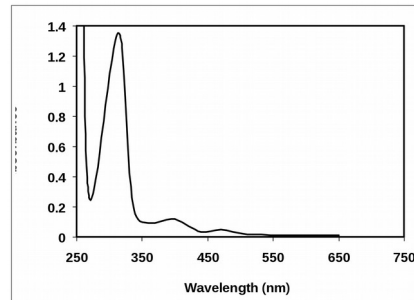
At room temperature magnetic moment of the Ni(II) complexes were found to be 2.03 B.M. respectively. Generally expected for spin free octahedral Ni(II) complexes [32,33].

The electronic spectra of the Cu(II) complexes display d-d bands ν_{\max} at 21.276 and 21.097 cm^{-1} for $[Cu(L^1)(H_2O)_2]$ and $[Cu(L^1)_2]$ respectively. This broad band is typical for distorted assignable to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, corresponding to a distorted octahedral geometry around the copper ion [34].

At room temperature magnetic moment value of the Cu(II) complexes are diamagnetic.

.Table 4 : Electronic spectral data of the complexes

Complexes	λ_{\max} (nm)	ν_{\max} (cm^{-1})	ϵ_{\max} ($\text{cm}^2 \text{mol}^{-1}$)	Assignment
HL ¹	412	24.271	5200	$n \rightarrow \pi^*$
	313	31.948	22500	$\pi \rightarrow \pi^*$
[Fe(L ¹) ₃]	472	21.186	5100	d-d
	356	28.089	5100	Intraligand
[Co(L ¹) ₃]	474	21.097	1900	d-d
	362	27.624	3500	CT
	310	32.258	8500	Intraligand
[Co(L ¹) ₂]	470	21.276	500	d-d
	400	25.000	1200	CT
	314	31.847	13500	Intraligand
[Ni(L ¹) ₃]	470	21.276	1900	d-d
	392	25.510	2600	CT
	315	31.746	12500	Intraligand
[Cu(L ¹)(H ₂ O) ₂]	470	21.276	4900	d-d
	334	29.940	11000	Intraligand
[Cu(L ¹) ₂]	474	21.097	4900	d-d
	335	29.850	10000	Intraligand

Fig. 3. Electronic Spectrum of HL¹Fig. 4. Electronic Spectrum of [Fe(L¹)₃]Fig. 5. Electronic Spectrum of [Co(L¹)₃]Fig. 6. Electronic Spectrum of [Co(L¹)₂]

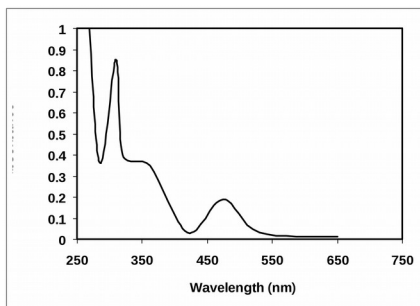
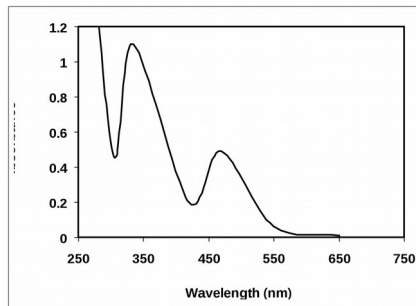
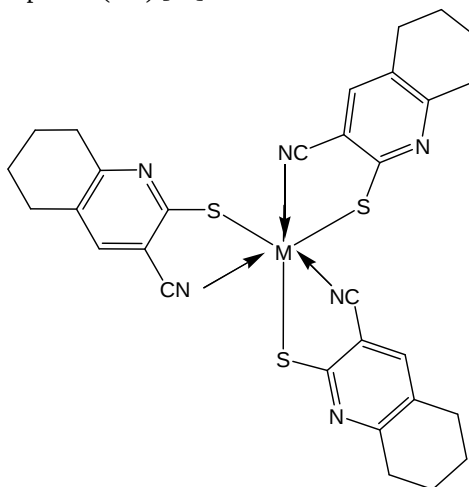
Fig. 7. Electronic Spectrum of $[\text{Ni}(\text{L}^2)_3]$ Fig. 8. Electronic Spectrum of $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})_2]$

Table 5 : The molar magnetic susceptibility (χ_g) and magnetic moment (μ_{eff}) of the complexes.

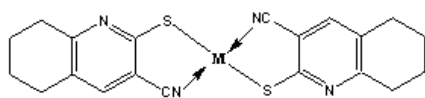
Complexes	χ_g	μ_{eff}
$[\text{Fe}(\text{L}^2)_3]$	0	D
$[\text{Co}(\text{L}^2)_3]$	0.02055	4.16
$[\text{Co}(\text{L}^2)_2]$	0.00388	2.10
$[\text{Ni}(\text{L}^2)_3]$	0.00518	2.03
$[\text{Cu}(\text{L}^2)(\text{H}_2\text{O})_2]$	0	D
$[\text{Cu}(\text{L}^2)_2]$	0	D

1.4. TENTATIVE STRUCTURES

Based on the above results gained from elemental analysis, IR, HNMR, and electronic spectra, the following tentative structures show the coordination sites of the ligands in the complexes (1-3) [11].



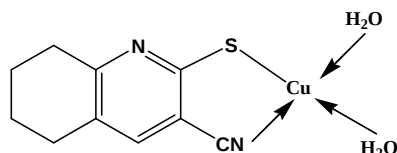
Where M = Fe
M = Co
M = Ni
(1)



Where M = Co

M = Cu

(2)



(3)

1.5. THERMAL STUDIES [35,36]

The TGA and DTA data are presented in (Table 6) and (Figs. 9-23). The anhydrous complex $[\text{Fe}(\text{L}^1)_3]$, $[\text{Co}(\text{L}^1)_3]$, and $[\text{Ni}(\text{L}^1)_3]$ was stable up to $t = 206^\circ\text{C}$, then it start decomposing.

The coordination water molecules of the complexes $[\text{Co}(\text{L}^1)_2(\text{H}_2\text{O})_2]$, $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{L}^1)_2(\text{H}_2\text{O})_2]$ decompose completely within a temperature range: $t = 210\text{-}385^\circ\text{C}$ as indicated by DTA and TGA curves, with a mass loss of 7.54-31.50%; (theoretical 7.54-31.97%) corresponding to loss of 1 or 2 water molecules only or and C_4H_8 , as shown in (fig. 43-52, 55-64) this confirms the results of elemental analysis and reveals that these water molecules are coordinately bonded to the metal ions in these complexes.

Kinetic data of the complexes

The coats-redfern and Horowitz-Metzger equations were used for evaluating the kinetic parameters [37,38].

(Table 7) reports the computed values of activation energy for the various decomposition steps which are given in (Table 6) .

Entropy (ΔS), enthalpy (ΔH) and free energy (ΔG) of activation [39-46] were computed using equations (1), (2), (3).

$$\Delta S = 2.303 (\log Zh/kT_s) R \quad \dots\dots\dots(1)$$

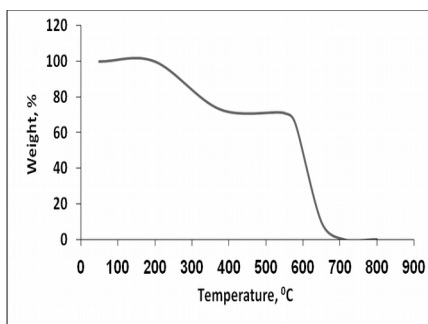
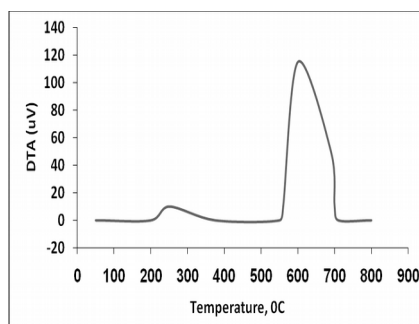
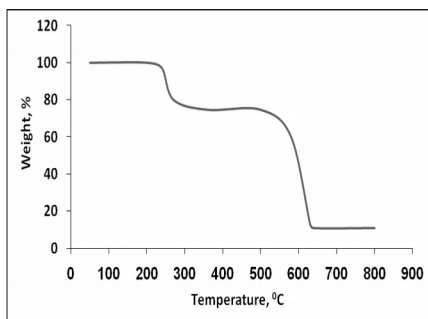
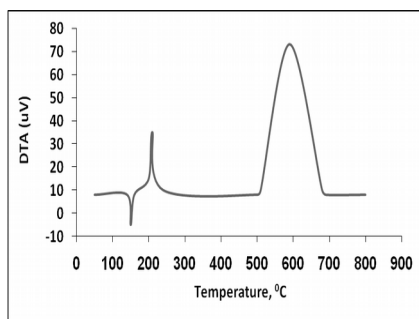
$$\Delta H = E - RT_s \quad \dots\dots\dots(2)$$

$$\Delta G = \Delta H - T_s \Delta S \quad \dots\dots\dots(3)$$

Where k and h are Boltzman and Plank constants, respectively. The data are compiled in (Table 8)

Table 6: TGA. data for binary complexes of the ligand (HL¹)

Compounds	M. wt.	Step	Decomp. Temp. °C	Lost of wt.		change
				% calc.	% found	
HL ¹	190.27	1 st 2 nd	200-375 550-710	29.49 70.51 -	29.00 71.00 -	Loss of C ₄ H ₈ Loss of C ₆ H ₂ N ₂ S No residue
[Fe(L ¹) ₃]	623.08	1 st 2 nd	206-387 420-700	30.34 60.68 8.98	29.23 61.54 9.23	Loss of L ² Loss of 2L ² Residue Fe
[Co(L ¹) ₃]	626.08	1 st 2 nd	280-350 500-620	30.20 50.18 19.62	29.85 51.49 18.66	Loss of L ² Loss of C ₂₀ H ₁₈ N ₄ Residue CoS ₂
[Co(L ¹) ₂]	473.49	1 st 2 nd	225-425 500-630	31.31 49.47 19.22	31.34 50.00 18.66	Loss of 2 C ₄ H ₈ Loss of 2C ₅ HN&2CN&S Residue CoS
[Ni(L ¹) ₃]	625.08	1 st 2 nd	260-330 400-700	30.24 50.26 19.50	30.00 50.00 20.00	Loss of L ² Loss of C ₂₀ H ₁₈ N ₄ Residue NiS ₂
[Cu(L ¹)(H ₂ O) ₂]	287.99	1 st 2 nd 3 rd	210-385 400-500 670-730	31.97 35.07 11.10 21.86	31.50 34.25 10.96 23.29	Loss of 2H ₂ O & C ₄ H ₈ Loss of C ₅ HN & CN Loss of S Residue Cu
[Cu(L ¹) ₂]	478.10	1 st 2 nd	355-400 660-735	54.87 10.88 26.71	54.79 10.96 26.71	Loss of 2C ₉ H ₉ N Loss of 2CN Residue Cu&2S

**Fig.9. TGA thermogram of HL¹****Fig.10. DTA thermogram of HL¹****Fig. 11. TGA thermogram of [Fe(L¹)₃]****Fig. 12. DTA thermogram of [Fe(L¹)₃]**

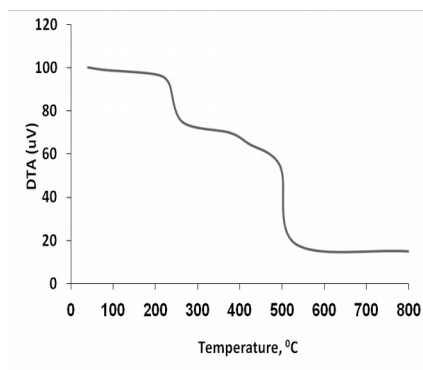
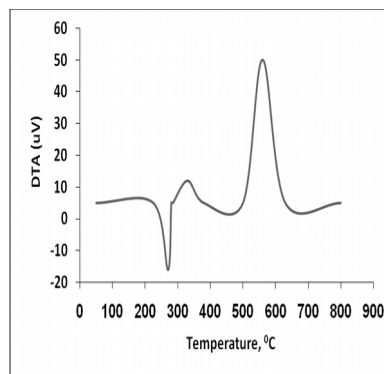
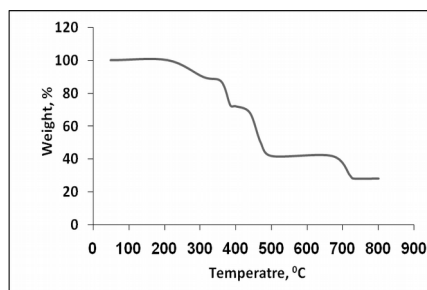
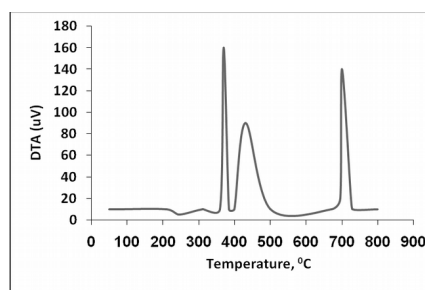
Fig. 13. TGA thermogram of [Co(L¹)₂]Fig. 14. DTA thermogram of [Co(L¹)₂]Fig. 15. TGA thermogram of [Cu(L¹)(H₂O)₂]Fig. 16. DTA thermogram of [Cu(L¹)(H₂O)₂]

Table 7: Kinetic parameters of the thermal decomposition of the Complexes.

Complexes	Coats-Redfern				Horowitz-Metzger		
	n	r	E	intercept	R	E	intercept
[Fe(L ²) ₃]	2.00	<u>0.9923</u>	4.56	0.830	<u>0.9913</u>	5.40	-15.0647
	2.00	<u>0.9518</u>	96.18	30.40	<u>0.9507</u>	98.35	-85.7042
[Co(L ²) ₂]	2.00	<u>1.0000</u>	10.16	2.9000	<u>0.9997</u>	11.28	-21.5295
	2.00	<u>0.9992</u>	38.60	9.5000	<u>0.9989</u>	40.92	-37.2220
[Cu(L ¹) ₂]	2.00	—	56.96	28.0000	<u>0.9996</u>	58.55	-77.9367
	0.00	<u>0.9998</u>	93.62	23.0000	<u>0.9917</u>	96.63	-71.6113

E (Kcal/mol)

Table 8: kinetic parameters of the thermal decomposition of the Complexes.

Complexes	Step	Coats-Redfern				Horowitz-Metzger			
		Z	ΔS	ΔH	ΔG	Z	ΔS	ΔH	ΔG
[Fe(L ²) ₃]	1 st	19.370×10 ²	-0.147	0.544	71.888	0.647	-0.214	1.380	104.868
	2 nd	64.750×10 ³²	0.431	89.002	-283.666	0.683	-0.218	91.179	279.865
[Co(L ²) ₂]	1 st	54.309×10 ⁴	-0.101	5.599	61.440	0.836	-0.213	6.718	123.541
	2 nd	82.179×10 ¹¹	0.032	31.675	4.960	0.935	-0.215	33.993	213.696
[Cu(L ¹) ₂]	1 nd	38.348×10 ³⁰	0.391	51.532	-204.117	0.969	-0.213	53.126	192.482
	2 rd	63.028×10 ²⁵	0.296	85.530	-203.060	0.646	-0.223	88.542	306.241

Z (s⁻¹), ΔH (kJmol⁻¹)

ΔG (kJmol⁻¹) ΔS (Jk⁻¹mol⁻¹)

1.6. MICROBIOLOGICAL SCREENING

Tests were directed towards bacteria. The tested bacteria species some of them are pathogenic, namely *Staphylococcus aureus* (Gram +ve) *Eicoli* and *Klebsilla*. These species were cultivated on nutrient agar (N.A) media. The synthesized compounds were dissolved in DMF. Sterilized filter paper discs were added to dissolve compounds until saturation. Then the saturated discs put on the surface of agar plates. The plates were incubated at 28 °C for 24 hours. The inhibition zones around the discs were measured in mm. (Table 9) indicates the antimicrobial activity of each compound.

Table 9: Microbiological screening of the complexes.

Complexes	Bacteria		
	<i>Staphylococcus Aureus</i> Gram +ve	<i>Eicoli</i>	<i>Klebsilla</i>
[Fe(L ¹) ₃]	+	-	-
[Co(L ¹) ₃]	-	+	-
[Co(L ¹) ₂ (H ₂ O) ₂]	+	-	-
[Ni(L ¹) ₃]	+	-	-
[Cu(L ¹)(H ₂ O) ₂]	-	-	-
[Cu(L ¹) ₂ (H ₂ O) ₂]	-	-	-

- No activity
+ Activity

References

- 1.F. J .Welcher, Organic Analytical Reagents, Vol.4, Van Nostrand, New York, (1948).
- 2.Yu. P. Aronson and S M Belen'Kll, Zashch. Met., 1, 125 (1965).
- 3.B. Donnelly. T. C. Downie, R. Grzeskowiak, H R Hamburg and D Dhorth, Corros. Sci., 18, 109 (1978).
- 4.S. Zen, M Hirooka. R. Nakajato and S. Koto, Kogyo kagku zasshi, 73, 2060 (1970).
- 5.Japanese Patent: JP7513318 (750203).
- 6.Japanese Patent: JP75126668 (751004).
- 7.Japanese Patent: SU929662 (820523).
- 8.W. O. Foye and J. R. Lo, J Pharm. Sci., 61, 1209 (1972).

9. Galal. E. H. Elgemeie and Badria A. W. Hussain, *Tetrahedron*, 50(1), 199-204 (1994).
10. Geary, W. J., *Coord. Chem. Rev.*, 7, 81 (1971).
11. Ragab R. Amin and Galal E. H. Elgemeie, *Synth. React. Inorg. Met. Org. Chem.*, 31(3), 431-440 (2001).
12. M. Abd-El-Mottalb, S. M. Abo-El-Wafa and Y. Z. Ahmed, *Egypt. J. Chem.*, 28 (5), 367-374 (1985).
13. Saxena S. B, Agarwal Y. K, Spectrophotometric Determination of the Stability Constant of 4-Substituted Thiosemicarbazides with Co^{2+} , Ni^{2+} and Cu^{2+} Systems. *J. Ind. Inst. Sci*, 66, 13-19 (1986).
14. Khalifa M. E, Rakha T. H, M. M. Bekheit, M. M. ligational Behaviour of 1-Picolinoyl-4-phenyl-3-thiosemicarbazid (H₂PTS) Towards some Transition Metal Ions, *Synth. React. Inorg. Met.-Org. Chem.*, 26(7), 1149-1161 (1996).
15. El-Asmy A. A, Al-Ansi T. Y, Amin R. R, Physicochemical Studies on Transition Metal Complexes of 1-Oxalylbis(4-phenylthiosemicarbazide). *Bull. Soc. Chim. Fr*, 127, 39-42 (1991).
16. El-Asmy A. A, Mabrouk H. E, Al-Ansi T. Y, Amin R. R, El-Shahat M. F, Binuclear Complexes of Some Transition Metal Ions with 1,1',3,3'-Propanetetra-carbohydrazide. *Synth. React. Inorg. Met.-Org. Chem.*, 23(10), 1709-1726 (1993).
17. Amin R. R, Coordination Compounds of Quadridentate Thiosemicarbazone: Their Preparation, Characterization and Structural Investigation, *Asian J. Chem.*, 12(2), 349-354 (2000).
18. Badiger B. M, Patil S. A, Kudari S. M, Kulkarni V. H, *Rev. Roum. Chim.*, 31, 849 (1986).
19. Patil S. A, Badiger, B. M, Kudari, S. M, Kulkarni, V. H, *Transition Met. Chem.*, 8, 238 (1983).
20. Sharam S, Chowdhary V, *J. Indian Chem.*, 28, 809-811 (1989).
21. Krishna C. H, Mahapatra C. M. and Dush K. C, *J. Inorg. Nucl. Chem.*, 39 1253 (1977).
22. N. RAMAN, S. RAVICHANDRAN and C. THANGARAJA, *J. Chem. Sci.*, Vol. 116, No. 4, July, pp. 215-219 (2004)
23. Deepak Shukla, Lokesh Kumar Gupta, Sulekh Chandra. *Spectrochimica Acta, Part A* 71, 746-750 (2008).
24. West D. X, Salberg M. M, Bain G. A, *Transition Met. Chem.*, 21, 206 (1996).
25. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry. The Elements of First Transition Series A*, Wiley-Interscience Publication, New York, 1988.
26. Kasim A. N. M, Venkappayya D and Prabhu G. V, *J. Indian Chem. Soc.*, 76, 67(1999).
27. E. Gao, S Bi, H. Sun, S. Liu, *Synth. React. Inorg. Met.-Org. Chem.*, 27, 1115 (1997).
28. L. K. Gupta and S. Chandra, *Trans. Met. Chem.*, 31, 368 (2006).

- 29.S. Djebbar-Sid, O. Benali-Baitich, M. A. Khan, G. Bouet, Synth. React. Inorg. Met.-Org. Chem., 27, 1219 (1997).
- 30.S. Rao and K. H. Reddy, Ind. J. Chem., 35A, 681(1996).
- 31.S. Chandra and L. K. Gupta, Trans. Met. Chem., 30, 630 (2005).
- 32.Cotton F. A. and Wilkinson G. Advanced inorganic chemistry (New York: Wiley Interscience) 1962.
- 33.Figgis B. N. An introduction to ligand fields (New Delhi: Wiley Eastern) 1976.
- 34.Khan T. A, Rather M. A, Vankey S. P, Inorg. Met.-Org. Chem., 27 (6), 843 (1997).
- 35.S. Goel, O. P. Pandey and S. K. Sengupta, Thermochim. Acta, 133, 359-364 (1988).
- 36.P. B. Maravalli and T. R. Goudar, Thermochim Acta, 325, 35-41 (1999).
- 37.A. W. Coats and J. P. Redfern, Nature, 20, 68 (1964).
- 38.H. H. Horowitz and G. Metzger, Anal. Chem., 35, 1464 (1963).
- 39.S. Glasston, Text Book of Physical Chemistry, 2nd ed., Macmillan, Indian, 1103 (1974).
- 40.R. K. Agrawal, S. C. Rastogi, Thermochim. Acta, 63, 363 (1983).
- 41.V. V. Savant, P. Ramamurthy, C. C. Patel, J. Less Common Metals, 22, 479 (1970).
- 42.A. K. Srivastava, S. Sharma, R. K. Agrawal, Inorg. Chim. Acta, 61, 235 (1982).
- 43.K. Arora, Asian J. Chem., 7, 508 (1995).
- 44.N. S. Bhave, V. S. Iyer, J. Therm. Anal., 32, 1369 (1987).
- 45.N. Calu, L. Odochian, G. L. Brinzan, N. Bilba, J. Therm. Anal., 30, 547 (1985).
- 46.H. S. Bhojya Naik, Siddaramaiah, P. G. Ramappa, Thermochim. Acta, 2998 (1996)

