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SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES ON SOME TRANSITION METAL COMPLEXES OF TETRAHYDRO-2-THIOXO-1H—CYCLOPENTA[b] PYRIDINE-3-CARBONITRILE.

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SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES ON SOME TRANSITION METAL COMPLEXES OF TETRAHYDRO-2-THIOXO-1H—CYCLOPENTA[b] PYRIDINE-3-CARBONITRILE.

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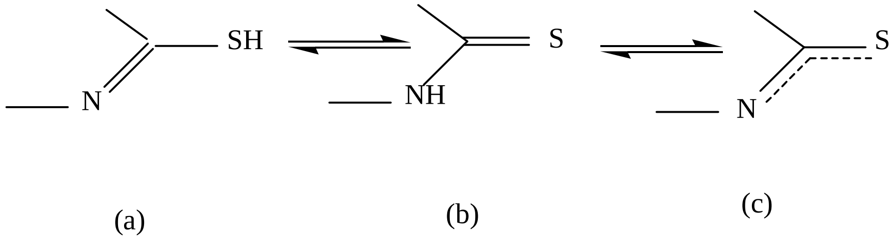
Abstract

A series of Cr(III), Co(II) , Cu(II) and Zn(II) complexes of two types (ML,ML) Where L is 2, 5, 6, 7 – tetrahydro – 2 –thioxo – 1H- cyclopenta[b] pyridine- 3-carbonitrile are synthesized and confirmed by their elemental microanalysis, IR, electronic absorption spectra, magnetic moment and HNMR spectra. 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. And biological effects were studied.

Introduction

Although many aspects of donor behavior of sulfur-containing ligands have been investigated [1-4], yet for heterocyclic systems attention has been mainly concentrated on nitrogen-containing ligand molecules [5,6]. Heterocyclic thiones are a group of ligands containing thioketonic (thiones) group directly attached to the carbon atoms of the heterocyclic molecules and thus, thione ligands possess donor behavior of both sulfur- containing systems as well as heterocyclic molecules. A common feature of all nitrogen-containing heterocyclic thiones is the thiol ↔ thione tautomerism (schems 1) where it has been established [7,8] that the thione dominates in the solid state.



Schems 1

Experimental

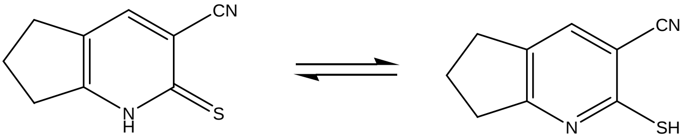
I- Materials

Metal salts: The metal salts $CrCl_3.6H_2O$, $CoSO_4.7H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ used for the preparation of complexes were of general grade reagents (prolabo chemicals).

II-Preparation Of The Ligand [9]:

Ligand (HL^1): 2,5,6,7-tetrahydro-2-thioxo-1H-cyclopenta[b]pyridine-3-carbonitri-le. The derived from heterocyclic compounds, which we are used, were prepared according to the literature procedure [9].

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



HL^1

Primary ligands

III-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 hour. The mixture (methanol) 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 P_4O_{10}. The binary complexes were analyzed for their carbon, hydrogen, nitrogen, sulfur, and metal contents.

IV-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 prper solvent.

V – IR spectra:

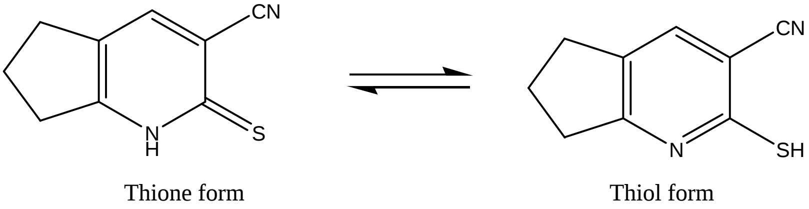
IR spectra of the ligand and its metal complexes were recorded on Shimadzu 140 Infrared Spectrophotometer (4000 - 400 cm) as KBr discs. The proton HNMR spectra DMSO –d6 on a Varian FT -200 Mhz spectrometer using TMS as internal standard at Assiut university. The electronic absorption spectra were recorded 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 thermogravimetic analysis were detrmined using Shimadzu analyzer 50 H For TGA and DTA in a dynamic nitrogen atmosphere (100 ml/min). The antimicrobile 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

I.1 The results of elemental analyses are show 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 dimethylformamide (DMF) solutions of Cr(III), Co(II), Cu(II) and Zn(II) complexes fall in the range 25.37-57.23 Ohm^{-1} Cm^{2} 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 Ohm^{-1} cm^{2} mol^{-1} [10]. On the other hand molar conductance values of Cr(III) complex (1:1) (metal : ligand) is 77.92 Ohm^{-1} Cm^{2} mol^{-1} indicate that this complex is 1:1 electrolyte [10].

1.2. IR SPECTRA

Infrared spectra of crystalline solid compounds have been investigated. The IR spectra of the free ligands 2,5,6,7-tetrahydro-2-thioxo 1*H*-cyclopenta[b]pyrindi-ne-3-carbonitrile (HL^{1}) exhibit thione-thiol (HN-C=S ↔ N=C-SH) tautomerism [11] as given in scheme **2**.



Thione form

Thiol form

Scheme 2

The IR spectra of the free ligands 2,5,6,7-tetrahydro-2-thioxo 1*H*-cyclopenta[b]pyrindi-ne-3-carbonitrile (HL^1) show the absorption band in the range 3600 - 3300 cm^{-1}, can be assigned to stretching vibration of (NH) group [12]. The appearance an absorption band at 2950 cm^{-1} in HL^1 attributed to **υ** aliphatic structure of cyclic. Also The presence of an absorption band at 2185 cm^{-1} attributed to stretching vibration of υ C≡N. The presence of an absorption band at 1240 cm^{-1} attributed to stretching vibration of υ C=S.

The IR spectra of investigated solid complexes shows disappearance the bands in the range 3500 - 3300 cm^{-1} due to stretching vibration of (NH) group in ligand . The disappearance of these band is due to the displacement of the hydrogen ion from the NH group [11,13,14] through the coordination moiety. This result confirmed by ^{1}H NMR data.

The band at 2185 cm^{-1} in HL^1 is att1ributed to stretching C≡N are shifted to lower frequencies due to coordination in all investigated complexes, in the range 2220-2200 cm^{-1} for HL^1 complexes.

The band at 1280 cm^{-1} in HL^1 which corresponding to stretching vibration of **C=S** are shifted tor lower frequencies due to coordination with metal ions [15] in the range 1150-1260 cm^{-1} for all complexes.

The appearance of a broad band in range 3450 - 3650 cm^{-1} is due to υOH of coordinated water complexes [14-16] .

Also the two new bands appear for all chelates at 500-540 cm^{-1} region corresponding to stretching [M-S] [16-17] metal-sulphur bond or M –O bond [17} and at 430-470 cm^{-1} due to stretching [M←N] [16] metal-nitrogen bond. The important IR bands are listed in (Tables 2) and (Figs 1,2)

1.3. ^{1}H NMR

The ^{1}H NMR spectrum of the ligand [9] HL^1 show characteristic signal at 2.2 ppm due to appearing the (–NH) proton and Moreover the appearance of the band located at 2.8 ppm may be assigned to the (–SH) proton. The band observed at 7.95 ppm may be assigned to (–CH–pyridine–) proton. The important ^{1}H NMR spectrum bands are listed in (Table 3) for ligand HL^1 and its complexes.

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

Compounds	Colour	Found (Calcd.%)					m.p. °C Decomp.	Conductance Ohm^{-1} cm^{2}mol^{-1}
		C	H	N	S	M		
HL^1 $C_9H_8N_2S$ M.Wt =176.24	Reddish brown	59.79 (61.34)	4.44 (4.57)	15.64 (15.89)	18.02 (18.19)	-	190	-
$[CrCl(L^1)(H_2O)_3]\cdot Cl\cdot 5H_2O$ $C_9H_{23}CrCl_2N_2O_8S$ M.Wt= 443.26	Dark brown	22.76 (24.36)	5.36 (5.18)	6.12 (6.31)	7.4 (7.2)	12.92 (11.73)	>330	77.92
$[CrCl(L^1)_2(H_2O)]\cdot 7H_2O$ $C_{18}H_{30}CrClN_4O_8S_2$ M.Wt= 584	Dark brown	35.09 (37.00)	5.17 (5.13)	9.49 (9.58)	11.05 (10.95)	8.50 (8.93)	>330	57.23
$[Co(SO_4)\ (L^1)(H_2O)_2]$ $C_9H_{11}CoN_2O_4S_{1.5}$ M.Wt= 318.23	Dark brown	3297 (33.96)	3.42 (3.48)	8.70 (8.80)	15.00 (15.12)	18.22 (18.52)	>330	30.24
$[Co(L^1)_2(H_2O)_2]$ $C_{18}H_{18}CoN_4O_2S_2$ M.Wt= 445.43	Dark brown	48.44 (48.54)	4.07 (4.07)	12.11 (12.58)	13.78 (14.40)	13.11 (13.23)	>330	28.45
$[Cu(SO_4)\ (L^1)]$ $C_9H_7CuN_2O_2S_{1.5}$ M.Wt=286.81	Dark Green	36.96 (37.69)	2.31 (2.46)	9.85 (9.77)	15.85 (16.77)	7.30 (22.16)	>330	25.37
$[Cu(L^1{}_2]\cdot 7H_2O$ C18H28CuN4O7S2 M.Wt=540.12	Dark Green	39.72 (40.03)	5.22 (5.23)	10.60 (10.37)	11.48 (11.87)	11.03 (11.77)	>330	32.33
$[Zn(L^1)_2(H_2O)_2]\cdot 2H_2O$ $C_{18}H_{22}ZnN_4O_4S_2$ M.Wt=487.92	Pale yellow	44.22 (44.31)	4.54 (4.55)	11.46 (11.48)	(12.98) (13.15)	(13.00) (13.40)	>330	37.79

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

Compounds	υ(H_2O)	Y NH	υ SH	υ alphatic St. of cyclic	Y C≡N	δ NH	δ (H_2O)	Y C=S	M-S	M← N
HL^1	-	3300	3200	2950	2185	1510	-	1240	-	-
$[CrCl(L^1)$	3500	-	-	2950	2220	-	1360	1260	510	460
$[CrCl(L^1)_2(H_2O)]\cdot 7H_2O$	3600	-	-	2950	2210	-	1360	1260	510	460
$[Co\ (L^1)(H_2O)_2]$	3550	-	-	2950	2205	-	1360	1250	510	470
[Co(L1)2(H2O)2]	3600	-	-	2950	2200	-	1360	1250	520	470
[Cu (L1)]	-	-	-	2950	2215	-	-	1250	500	450
[Cu(L1)2].7H2O	3600	-	-	2950	2200	-	1365	1250	510	450
[Zn(SO4) (L1)].3H2O	3600	-	-	2950	2205	-	1380	-	510	460
[Zn(L1)2(H2O)2].2H2	3550	-	-	2950	2190	-	1380	-	500	470

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

Complexes	m, 2H, CH_2	M, 4H, $2CH_2$	S, 1H, pyridine 4H	S, br, 1H, NH	S, br, 1H, SH	S, nH, H_2O
HL^1	1.91	2.61-2.95	7.95	2.2	2.8	-
$[Co\,(L^1)(H_2O)_2]$	0.6	2.6-2.8	8.4	-	-	3.6
$[Co(L^1)_2(H_2O)_2]$	0.9	2.5-2.85	8.4	-	-	4.4
$[Zn\,((L^1)]^{.}3H_2O$	1.8	2.7-3.05	8.4	-	-	4.2
$[Zn(L^1)_2(H_2O)_2]^{.}2H_2O$	1.8	2.4-2.7	8.5	-	-	5.6

1.4. Electronic Spectra And Magnetic Susceptibility Measurements.

The obtained spectral characteristic data (mainly υ_{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 (Fig. 3-8)

Cr(III) COMPLEXES

The electronic spectra of the Cr(III) complexes exhibits tow sets of bands. The first set of bands with υ_{max} at 30.581 cm^{-1} and 29.940 cm^{-1} could be attributed to intra-ligand charge transfer transitions in N----C----S moiety [18]. The second set having υ_{max} at 21.598 Cm^{-1} and 21.141 cm^{-1} attributed to the d-d electronic transition which may be assigned ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition. Octahedral geometry is proposed [19-21].

At room temperature magnetic moment value of the complexes $[CrCl(L^1)(H_2O)_3]^{.}Cl^{.}5H_2O$ and $[CrCl(L^1)_2(H_2O)]^{.}7H_2O$ are 3.82 and 3.97 B.M. respectively, indicating the presence of three unpaired electrons [21-24].

Co(II) COMPLEXES

The electronic spectrum of Co(III) complexes exhibits tow sets of bands. The first set of bands with υ_{max} at 30.674 and 30.120 cm^{-1}, could be attributed to intra-ligand charge transfer transitions. The second set include a shoulder bands having υ_{max} at 21.413 and 21.739 Cm^{-1} for $[Co((L^1)(H_2O)_2]$ and $[Co(L^1)_2(H_2O)_2]$ respectively attributed to the d-d electronic transition which may be attributed to $({}^4T_{1g} \rightarrow {}^4T_{1g})$ (P), suggesting octahedral geometries [25-26].

At room temperature magnetic moment value of the complexes $[Co(SO_4)_{0.5}(L^1)(H_2O)_2]$ is 3.74 indicating the presence of three unpaired electrons. And $[Co(L^1)_2(H_2O)_2]$ is 6.95 B.M., characteristic of high-spin octahedral [21,27,28] Co(II) complexes.

Cu(II) COMPLEXES

The electronic spectra of complex $[Cu(SO_4)_{0.5}(L^1)]$ display two sets of bands. The first set of band at υ_{max} 30.120 cm^{-1} could be attributed to intra-ligand charge transfer transitions. The second set having υ_{max} at band 21.881 cm^{-1} attributed to the d-d electronic transition which attributed to $^2B_{1g}\rightarrow{}^2A_{1g}$ transition, suggesting square planer geometries [29,30].

At room temperature magnetic moment value of the complex $[Cu(SO_4)\ (L^1)]$ is diamagnetic.

Zn(II) COMPLEXES

The electronic spectrum of Zn(II) complex exhibits two sets of bands. The first set of bands with υ_{max} at 33.670 cm^{-1} and 34.602cm^{-1} could be attributed to intra-ligand charge transfer transitions. The second set includes a shoulder bands having υ_{max} at 24.509 cm^{-1} and 26.178 cm^{-1} attributed to the L→MCT transition.

Zn(II) complex are found to be diamagnetic as expected for d^{10} configuration. On the basis of elemental analysis, infrared spectra, magnetic measured, thermal analysis and known coordination preferences, tetrahedral geometry [31,32] is suggested for $[Zn(SO_4)\ (L^1)]\cdot 3H_2O$, while octahedral structure [33,34] is suggested for $[Zn(L^1)_2(H_2O)_2]\cdot 2H_2O$.

Table 4 : Electronic spectral data of the complexes.

Complexes	λ_{max} (nm)	υ_{max} (cm^{-1})	ε_{max} ($cm^2\ mol^{-1}$)	Assignment
HL^1	400	25.000	1100	$n\rightarrow\pi^*$
	313	31.948	8400	$\pi\rightarrow\pi^*$
$[CrCl(L^1)(H_2O)_3]\cdot Cl\cdot 5H_2O$	463	21.598	150	d→d
	327	30.581	890	Intraligand transition
$[CrCl(L^1)_2(H_2O)]\cdot 7H_2O$	473	21.141	300	d→d
	334	29.940	2100	Intraligand transition
$[Co(SO_4)\,(L^1)(H_2O)_2]$	467	21.413	1700	d→d
	326	30.674	10900	Intraligand transition
$[Co(L^1)_2(H_2O)_2]$	460	21.739	150	d→d
	332	30.120	430	Intraligand transition
$[Cu(SO_4)\ (L^1)]$	457	21.881	500	d→d
	332	30.120	7400	Intraligand transition
$[Zn(SO_4)\ (L^1)]\cdot 3H_2O$	382	26.178	4800	CT
	297	33.670	10200	Intraligand transition
$[Zn(L^1)_2(H_2O)_2]\cdot 2H_2O$	408	24.509	7500	CT
	289	34.602	23500	Intraligand transition

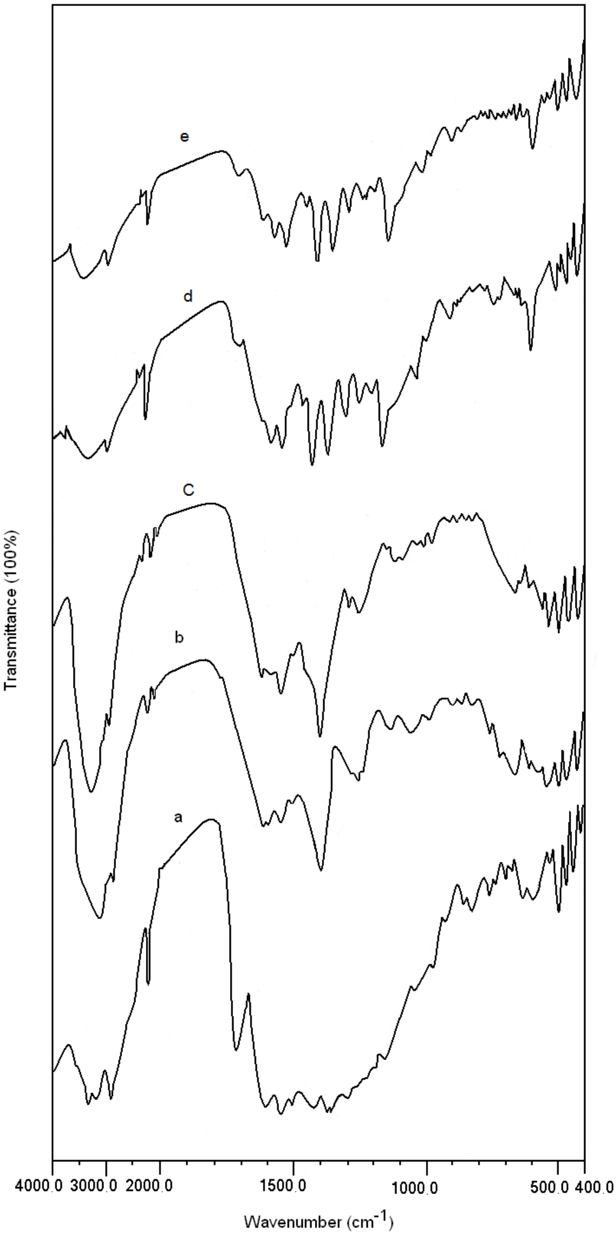


Fig. 1. Infrared spectra of the free ligand HL^1 and its metal complexes.

(a) = Free ligand
(b) = $[CrCl(L^1)(H_2O)_3]\cdot Cl\cdot 5H_2O$
(c) = $[CrCl(L^1)_2(H_2O)]\cdot 7H_2O$
(d) = $[Co(L^1)(H_2O)_2]$
(e) = $[Co(L^1)_2(H_2O)_2]$

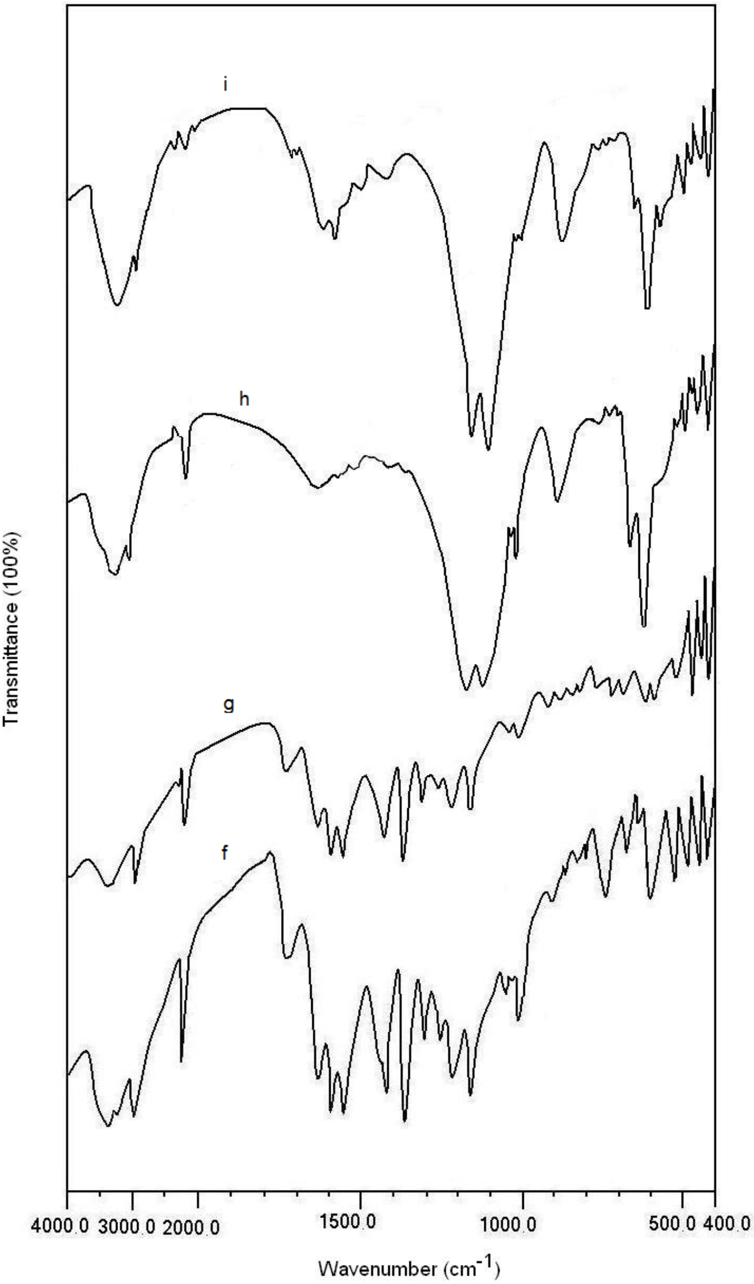


Fig. 2. Infrared spectra of the free ligand HL^1 and its metal complexes.

(f) = $[Cu((L^1)]$ (g) = $[Cu(L^1)_2]\cdot 7H_2O$

(h) = $[Zn(L^1)]\cdot 3H_2O$ (i) = $[Zn(L^1)_2(H_2O)_2]\cdot 2H_2O$

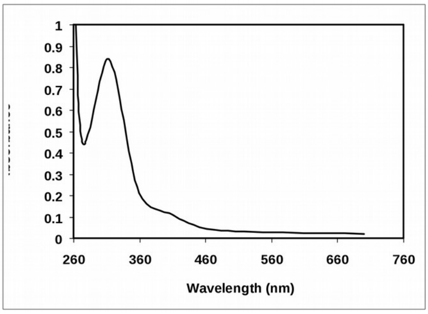


Fig. 3. Electronic Spectrum of HL^1

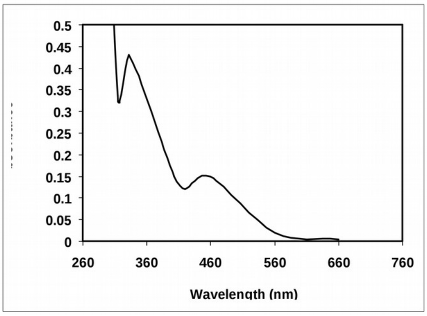


Fig.4. Electronic Spectrum of [Co(L^1)$_2$(H$_2$O)$_2$]

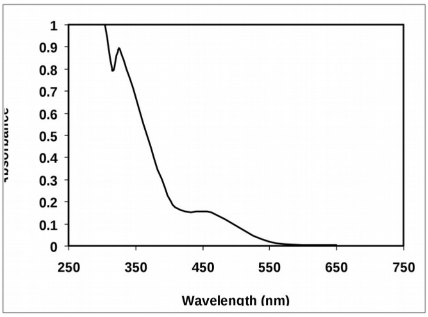


Fig. 5. Electronic Spectrum of [CrCl(L^1)(H$_2$O)$_3$]$^.$Cl$^.$5H$_2$O

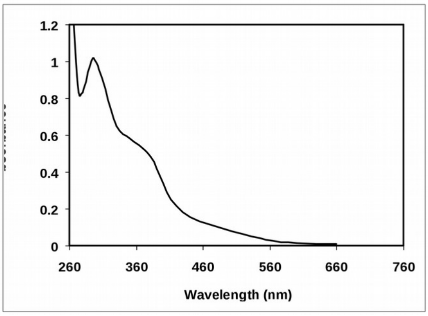


Fig. 6. Electronic Spectrum of [Zn(SO$_4$)$_{0.5}$(L^1)]$^.$3H$_2$O

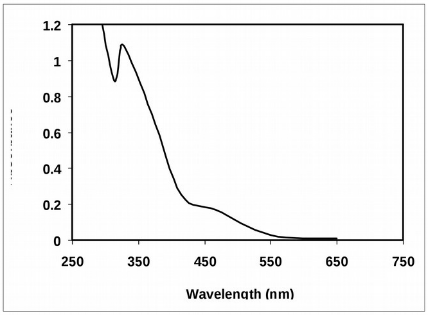


Fig. 7. Electronic Spectrum of [Co(SO4)(L^1)(H$_2$O)$_2$]

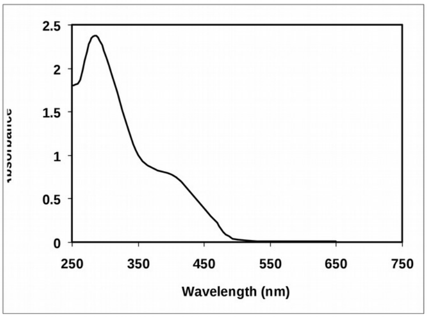


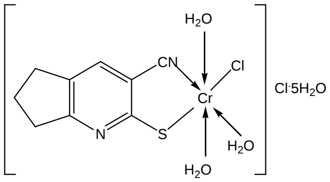
Fig. 8. Electronic Spectrum of [Zn(L^1)$_2$(H$_2$O)$_2$]$^.$2H$_2$O

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

Complexes	X_g	μ_{eff}
$[CrCl(L^1)(H_2O)_3]\cdot Cl\cdot 5H_2O$	0.01368	3.82
$[CrCl(L^1)_2(H_2O)]\cdot 7H_2O$	0.01128	3.97
$[Co(SO_4)_{0.5}(L^1)(H_2O)_2]$	0.01828	3.74
$[Co(L^1)_2(H_2O)_2]$	0.04507	6.95
$[Cu(SO_4)_{0.5}(L^1)]$	0	D
$[Zn(SO_4)_{0.5}(L^1)]\cdot 3H_2O$	0	D
$[Zn(L^1)_2(H_2O)_2]\cdot 2H_2O$	0	D

1.5. Tentative Structures

Based on the above results gained from elemental analysis, IR, ^{1}HNMR and electronic spectra, the following tentative structures show the coordination sites of the ligands in the complexes (1-8) [11].



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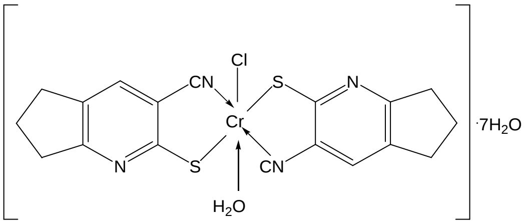

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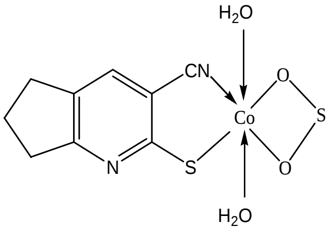

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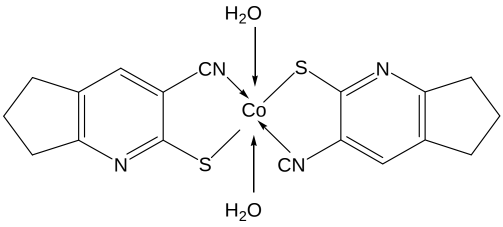

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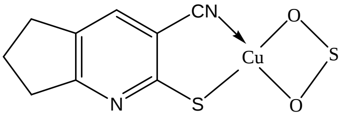

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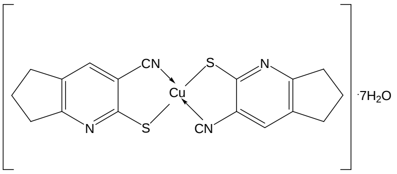

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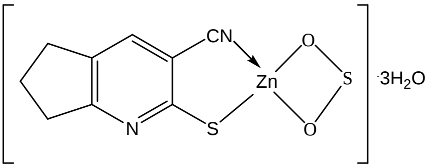

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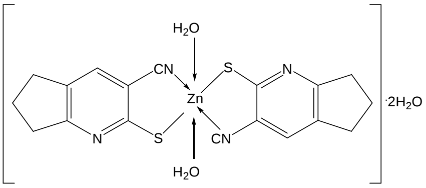


(8)

1.6. THERMAL STUDIES [35,36]

The complex of $[CrCl_2(L^1)(H_2O)_2]\cdot 6H_2O$, show the decomposition in three steps in the temperature range 40-267, 226-360 and 362-607°C. The first step corresponds to the evolution of 8 crystalline and coordinate water molecules, the second step corresponds to decomposition C_8H_7N with amount 26.47%. The third step amounted to 16.18%, attributed to the removal of 2Cl, while the final product is CrS and CN with amount 25%.

For the complex $[CrCl(L^1)_2(H_2O)].7H_2O$, the pyrolysis curves exhibit almost, the same TGA pattern, namely three decomposition steps in the range 40-120°C, 200-107°C and 350-700. The first step corresponds to the evolution of 8 crystalline and coordinate water molecules, the second step corresponds to decomposition $2C_8H_7N$ with amount 40.29%. The third step amounted to 14.93%, attributed to the removal of Cl and 2CN, while the final product is CrS_2 with amount 20.15%.

While the complex $[Co(SO_4)\ (L^1)(H_2O)_2]$ decompose in two step, the first step in the range 200-333°C which corresponds to the evolution of 2 coordinate water molecules. The second step corresponds decomposition C_5HN & (SO4), CN and S with amount 56.82%, while the final product is Co with amount 18.38%.

For the complex $[Co\ (L^1)_2(H_2O)_2]$ show the decomposition in two steps in the temperature range 226-333 and 400-616°C. The first step corresponds to the evolution of two coordinate water molecules, the second step corresponds to decomposition C_8H_7NS, CN and S with amount 45.76%, while the final product is CoS with amount 20.34%.

While the complex $[Cu(SO_4)\ (L^1)]$ decompose in three steps, the first step in the range 200-320°C which corresponds to the decomposition C_3H_6. The second step in the range 358-483°C corresponds decomposition C_5HN and CN with amount 35.07%, and the third step in the range 665-780°C corresponds decomposition (SO_4) with amount 16.42%, while the final product is CuS with amount 33.58%.

For the complex $[Cu (L^1)_2]^. 7H_2O$ show the decomposes in three steps in the temperature range 40-110, 200-341 and 645-729°C. The first step corresponds to the evolution of 7 crystalline water molecules, the second step corresponds to decomposition $2C_8H_7N$ with amount 43.19%, and the third step corresponds to decomposition 2CN with amount 9.85%, while the final product is CuS_2 with amount 23.48%.

While the complex $[Zn(So_4) (L^1)]^. 3H_2O$ decompose in three steps, the first step in the range 40-131°C which corresponds to the evolution of 3 crystalline water molecules. The second step in the range 223-360°C corresponds decomposition C_8H_7N with amount 34.33%, and the third step in the range 400-650°C corresponds decomposition CN, (SO_4) and S with amount 30.60%, while the final product is Zn with amount 19.40%.

For the complex $[Zn(L^1)_2(H_2O)_2]^. 2H_2O$ show decomposes in two steps in the temperature range 232-322 and 330-697°C. The first step corresponds to the evolution of 4 crystalline and coordinate water molecule, the second step corresponds to decomposition $2C_8H_7N$, 2CN and 2S with amount 71.64%, while the final product is Zn with amounts 13.61%.

The TGA and DTA data are presented in (Table 6) and (Figs. 9-11).

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).

$\Delta S = 2.303 (\log zh/kT_s) R$ ……………………………………………(1)

$\Delta H = E - RT_s$ ………..................……………….…..…...(2)

$\Delta G = \Delta H - T_s \Delta S$ …………………………………..……......(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 (HL^1).

Compounds	M. wt.	Step	Decomp. Temp. ºC	Lost of wt.		change
				% calc.	% found	
HL^1	176.24	1st 2nd	50-330 400-700	23.88 76.12 -	23.75 76.25 -	Loss of C_3H_6 Loss of $C_6H_2N_2S$ No residue
$[CrCl(L^1)(H_2O)_3]^{\cdot}Cl^{\cdot}5H_2O$	442.26	1st 2nd 3rd	40-167 226-360 362-607	32.59 26.49 16.03 24,89	32.35 26.47 16.18 25.00	Loss of $8H_2O$ Loss of C_8H_7N Loss of 2Cl Residue Cr&S&CN
$[CrCl(L^1)_2(H_2O)]^{\cdot}7H_2O$	582.04	1st 2nd 3rd	40-120 200-307 350-700	24.63 40.29 14.93 20.15	24.63 40.29 14.93 20.15	Loss of $8H_2O$ Loss of $2(C_8H_7N)$ Loss of Cl&2CN Residue CrS_2
$[Co(SO_4)\ (L^1)(H_2O)_2]$	318.23	1st 2nd	200-333 335-533	24.55 56.93 18.52	25.00 56.82 18.38	Loss of $2H_2O$&C_3H_6 Loss of C_5HN&0.5(SO4) & CN&S Residue Co
$[Co\ (L^1)_2(H_2O)_2]$	445.43	1st 2nd	226-333 400-616	34.39 45.18 20.42	33.90 45.76 20.34	Loss of $2H_2O$&C_8H_7N Loss of C_8H_7NS&CN&S Residue CoS
$[Cu(SO_4)\ (L^1)]$	286.81	1st 2nd 3rd	246-320 358-483 665-780	14.69 35.25 16.75 33.33	14.93 35.07 16.42 33.58	Loss of C_3H_6 Loss of C_5HN&CN Loss of 0.5(SO4) & Residue CuS
$[Cu(L^1)_2]^{\cdot}7H_2O$	540.12	1st 2nd	40-110 200-341 645-729	23.35 43.38 9.63 23.64	23.48 43.19 9.85 23.48	Loss of $7H_2O$ Loss of $2C_8H_7N$ Loss of 2CN Residue CuS_2
$[Zn(SO_4\ (L^1)]^{\cdot}3\ H_2\ O$	342.07	1st 2nd 3rd	40-131 223-360 400-650	15.77 34.18 30.97 19.08	15.87 34.33 30.60 19.40	Loss of $3H_2O$ Loss of C_8H_7N Loss of CN&0.5(SO_4)&S Residue Zn
$[Zn(L^1)_2(H_2O)_2]^{\cdot}2H_2O$	487.92	1st 2nd	232-322 330-697	14.77 71.83 13.40	14.75 71.64 13.61	Loss of $4H_2O$ Loss of $2C_8H_7N$&2CN&2S Residue Zn

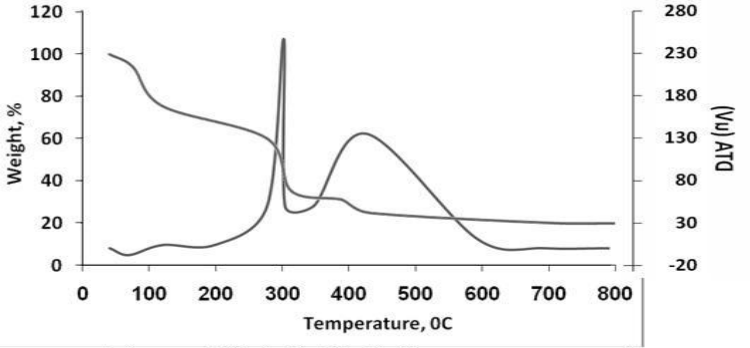
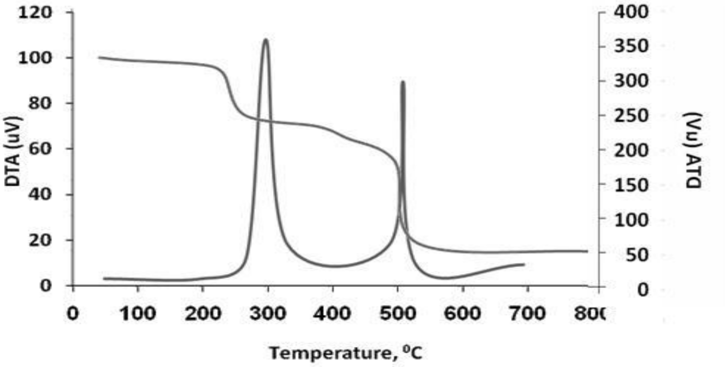
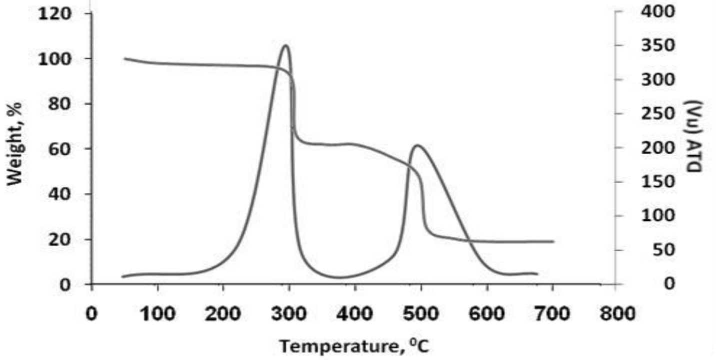


Fig (9) TGA & DTA thermogram of {CrCl $(L1)_2$ (H_2O) $_7$}



Fig(10) TGA & DTA thermogram of {Co(SO_4) (L1)2(H_2O)}



Fig(11) TGA & DTA thermogram of {Co $(L1)_2$ (H_2O) $_2$}

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

Complexes	Step	Coats-Redfern				Horowitz-Metzger		
		n	r	E	intercept	r	E	intercept
$[CrCl(L^1)(H_2O)_3]^{\cdot}Cl^{\cdot}5H_2O$	1st	2.00	0.9893	0.35	3.5616	0.9938	0.75	-4.6080
	2nd	2.00	1.0000	13.38	3.9000	0.9999	14.70	-23.9193
	3rd	1.00	0.9992	8.37	2.0000	0.9996	12.65	-14.4863
$[CrCl(L^1)_2(H_2O)]^{\cdot}7H_2O$	1st	2.00	1.0000	0.58	2.3075	0.9979	0.87	-7.3312
	2nd	2.00	0.9981	19.76	10.000	0.9970	20.97	-35.4631
	3rd	2.00	0.9796	21.21	5.5000	0.9799	22.92	-27.0653
$[Co(L^1)_2(H_2O)_2]$	1st	2.00	0.9949	35.54	21.2000	0.9942	36.76	-59.6167
	2nd	0.33	1.0000	15.99	1.3000	1.0000	21.15	-20.4503
$[Cu(L^1)_2]^{\cdot}7H_2O$	1st	0.33	1.0000	0.21	3.2913	1.0000	0.73	-4.9692
	2nd	0.50	0.9999	4.64	1.7000	1.0000	5.89	-9.3257
	3rd	1.00	0.9999	39.24	6.2000	0.9998	42.11	-30.4590
$[Zn(L^1)_2(H_2O)_2]^{\cdot}2H_2O$	1st	2.00	0.9460	5.42	0.1000	0.9817	1.60	-3.2475
	2nd	2.00	0.9684	8.53	0.3000	0.9911	2.67	-3.9457

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
$[CrCl(L^1)(H_2O)_3]^{\cdot}Cl^{\cdot}5H_2O$	1st	86.941×10^3	-0.113	-2.746	39.749	0.858	-0.209	-2.348	75.892
	2nd	71.558×10^5	-0.081	8.450	56.555	0.856	-0.213	9.769	136.457
	3rd	56.341×10^3	-0.123	2.274	92.550	0.898	-0.215	6.558	164.153
$[CrCl(L^1)_2(H_2O)]^{\cdot}7H_2O$	1st	7.891×10^3	-0.133	-2.274	43.409	0.787	-0.209	-1.982	699.720
	2nd	13.303×10^{12}	0.039	15.037	-7.262	1.112	-0.211	16.247	136.152
	3rd	45.146×10^7	-0.048	15.360	49.153	0.969	-0.214	17.073	-133.383
$[Co(L^1)_2(H_2O)_2]$	1st	33.917×10^{23}	0.258	30.730	-118.631	1.415	-0.209	31.958	152.899
	2nd	21.478×10^3	-0.131	9.396	113.937	1.017	-0.214	14.554	184.748
$[Cu(L^1)_2]^{\cdot}7H_2O$	1st	27.657×10^3	-0.122	-2.683	40.078	0.988	-0.208	-2.163	70.224
	2nd	15.670×10^3	-0.234	-0.244	137.841	1.023	-0.212	1.005	125.714
	3rd	41.865×10^8	-0.032	31.146	62.535	0.985	-0.216	34.016	244.759
$[Zn(L^1)_2(H_2O)_2]^{\cdot}2H_2O$	1st	459.793	-0.160	0.868	88.943	0.955	-0.212	-2.954	113.266
	2nd	11.46×10^2	-0.154	3.146	103.275	0.949	-0.213	-2.714	135.646

Z (s^{-1}),
ΔS ($Jk^{-1}mol^{-1}$)
ΔH ($kJmol^{-1}$)
ΔG ($kJmol^{-1}$)

1.7. 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 antmicrobiological activity of each compound.

Table 9: Microbiological screening of the complexes.

Complexes	Bacteria		
	Staphylococcus A ureus Gram +ve	*Eicoli*	*Klebsilla*
$[CrCl(L^1)(H_2O)_3]^{.}Cl^{.}5H_2O$	-	-	+
$[CrCl(L^1)_2(H_2O)]^{.}7H_2O$	+	-	-
$[Co(SO_4)_{0.5}(L^1)(H_2O)_2]$	+	-	+
$[Co(L^1)_2(H_2O)_2]$	+	-	-
$[Cu(SO_4)_{0.5}(L^1)]$	+	-	-
$[Cu(L^1)_2]^{.}7H_2O$	+	+	-
$[Zn(SO_4)_{0.5}(L^1)]^{.}3\ H_2O$	+	-	+
$[Zn(L^1)_2(H_2O)_2]^{.}2H_2O$	+	+	-

- No activity
+ Activity

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