Synthesis, Characterization and Thermal Study of Some Transition Metal Complexes Derived from Quinoxaline-2,3-Dione

Taghreed M. Musa
taghreedmohya@uomustansiriyah.edu.iq
taghreedmohya@yahoo.com

Mahmoud Najim A. Al-jibouri
mahmoud_inor71@uomustansiriyah.edu.iq
Bayader Fadhil Abbas
bayaderfadhil@gmail.com
Dept. of Chemistry/ College of Science/ University of Mustansiriyah

Abstract

The present paper describes the synthesis and structural studies of new transition metal complexes of cobalt(II), nickel(II), copper(II) and cadmium(II) with two bi dentate ligands derived from quinoxaline-2,3-dione. The two ligands were fully identified by elemental analyses, FT-IR, NMR and UV-Visible spectra. The metal complexes of Co(II), Ni(II), Cu(II) and Cd(II) were isolated in the solid state after reactions of their metal chlorides with the ligands in 2:1 mole ratio. The isolated solid metal complexes were characterized with the help of elemental analyses, NMR, FT-IR and UV-Visible spectra. As well as the thermal stability of the coordinated quinoxaline polymers were tested by TG-DSC analysis and it is found that cleavage of terminal moiety was investigated, the strong coordinated bonds between oxygen donor atoms in L1 while nitrogen donor atoms of quinoxaline ring in the L2 with the metal ions. Furthermore, the thermal stability of cobalt(II), nickel(II), copper(II) and Cd(II) complexes were screened by TG-DSC analysis and the results helped us in the investigation of the proposed structure of the prepared complexes in the formula $[M(L)_2Cl_2].XH_2O$ and $[Cd(L)_2]Cl_2$ where L= L^1 and L^2 ligands derived from quinoxaline-2,3-dione.

Keywords: Coordination polymers, transition metal copolymers, inorganic polymers of quinoxaline.

1. Introduction

Most of coordination polymers formed with heterocyclic derivatives [1-3] belongs to organic-inorganic hybrid materials. The variety of their structures leads to one of functional performances and thus the studies on them have aroused interest. The involvement of bridge ligands in the skeletal of metal complexes of pyrazine moiety may have affected on the physical properties of coordination polymers [4]. However, the polymers involving quinoxaline moiety have been interested in the field of diodes and semiconductors [5]. The Significant research efforts have been devoted to the synthesis of these new versions of conjugated polymers [6-8]. As well as the development of chelation of transition elements of the first row with poly dentate ligands of quinoxaline have introduced novel applications in the bioinorganic chemistry [10]. Recently, the introduction of secondary nitrogen-containing ligands into the metal-carboxylate system has been of interest not only because the use of mixed components can lead to novel structural features and interesting properties but also to make the construction process more controllable than with only a single ligand [11,12]. However, syntheses involving mixed ligands are more difficult due to the different solubility of mixed organic ligands and the competition between different organic ligands for the metal [13].

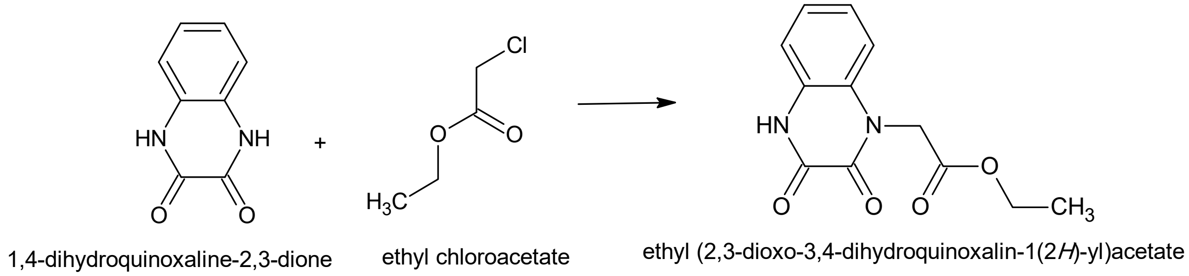
2. Experimental

Material and methods

Elemental microanalysis (C.H.N) was performed on, Euro vector E A 3000 A, Al al -Bayt University (Jordan). The FTIR spectra of the solid compounds were done on a (Shimadzu) FT-IR-8400S spectrophotometer. Solid samples were run at Al-Mustansiriyah University. The^{1}H -NMR was recorded in DMSO using a ultra-shield Bruker 300-MHz spectrometer at Al-Bayt University (Jordan). The mass spectra were done on GC MS –QP 2010 VLTRA at department of chemistry, College of science Al-Mustansiriyah University. The electronic spectra of the ligands and its complexes in various solvents (0.001M) were recorded on a Shimadzu UV-Vis spectrophotometer at Al-Mustansiriya University. The molar conductance of complexes was measured on Hana conductivity meter in DMSO. TG and DSC (Differential Scanning Colurimetry) thermo grams in different ranges were carried out at (R.T) heating rate = 10C^0/ min (Linseis STA PT-1000) were run in College of Education for Pure Science \Ibn-Haitham. The metal contents of the complexes were determined by atomic absorption measurements were performed by using the instrument Analytic Jena / A Spect LS /FL 1.3.0.0, A bnSina Center, Ministry of Industry. Magnetic moment for a prepared complex in the solid state at room temperature were measured according to Faraday's method using: Auto magnetic susceptibility Balance Sherwood Scientific. AL- Mustansiriyah University. The chloride content for complexes were determined by Mohr's method. Mass spectra were performed using the instrument: GC MS –QP 2010 VLTRA, AL- Mustansiriyah University. Purity of products was detected using T LC techniques using a mixture of chloroforms: methanol (4:1 v/v), and ethyl acetate: methanol (3:2 v/v), and Iodine chamber for spot location. The metal chloride $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$ and $CdCl_2.2H_2O$, were provided from Sigma-Aldrich company (UAE), 1, 4-phenylenediamine and solvents were supplied from Fluka company in 99% purity. All other chemicals used were of annular grade. The thermal analyses were scanned with differential scanning calorimetric (DSC) on STA PT-1000 Lenses Company/Germany. The measurement was conducted at a heating rate 100C /min. The samples were recorded at laboratories of College of Education for Pure Science\ Ibn-Al-Haitham, University of Baghdad.

Synthesis of the compound [diethyl 2,2'-(2,3-dioxo-2,3-dihydroquinoxaline-1,4-diyl) diacetate] [B]

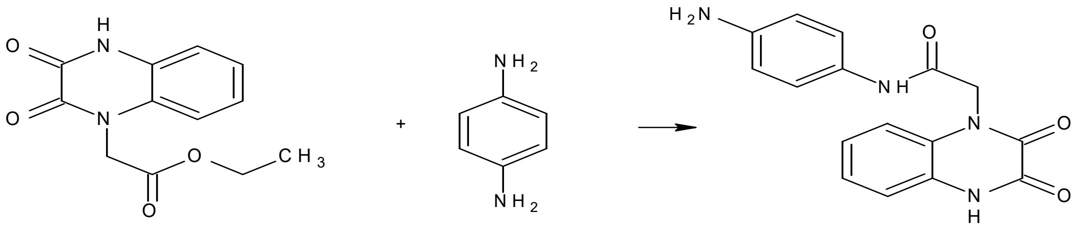
A solution of (1.6g, 0.0126 mole) 1,4 –di hydro quinoxaline in (20 ml) KOH (10%) [10gm KOH dissolved in 100ml ethanol] was added with stirring. Then (1.5g, 0.026 mole) ethyl chloro acetate was added drop wise. The reaction mixture was heating and stirring overnight on water bath, the grey precipitate washed several times with cold and derided to yielded 65% with melting point (122-124 ^{0}C), Scheme 1.



Scheme (1): Synthesis of [B].

Synthesis [4-aminophenyl 2,2$^-$ (2,3-dioxo-2,3-dihydroquinoxaline-1,4-diyl)diactemide]

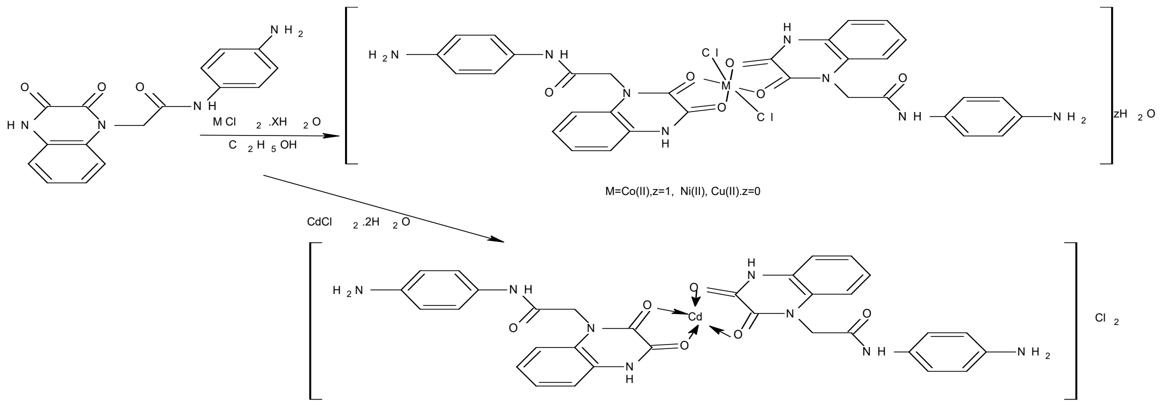
The mixture of Precursor [B] (1.3g, 0.0038mole) and (0.4g, 0.0038mole) 1,4 phenylendiamine in 25 ethanol were heated under reflux for 6 hours. The predicate was filtered, washed with water, dried and recrystallized from ethanol, Scheme 2.



Scheme (2): Synthesis of 4-aminophenyl 2,2$^-$ -(2,3-dioxo-2,3-dihydroquinoxaline-1,4-diyl) diactemide]

Synthesis of complexes

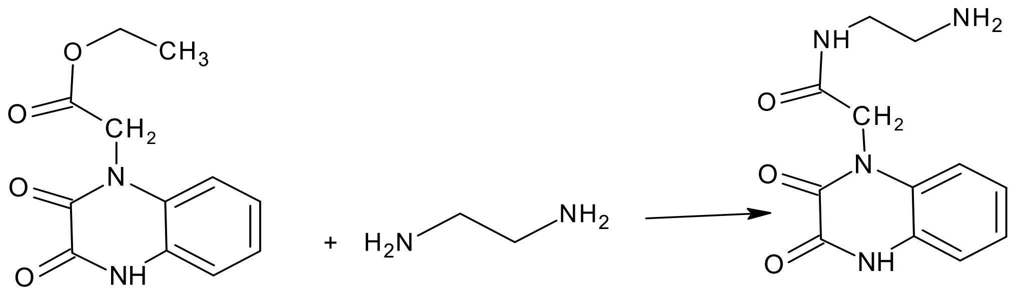
A solution of ligand (0.5g, 0.00109mole) in ethanol (25 ml). The added solution of [$CoCl_2.6H_2O$ (0.129 g, 0.00054 mole), $NiCl_2.6H_2O$ (0.129 g, 0.00054mole), $CuCl_2.2H_2O$ (0.093 g, 0.0019 mole), and $CdCl_2.2H_2O$ (0.82g, 0.00109mole] were stirring to refluxed at water bath for 2-3 hours. The isolated precipitates were filtered, dried recrystallized from ethanol and washing the complexes from di ethyl ether Scheme 3.



Scheme (3): Synthesis of metal complexes with L^1 ligand.

Synthesis of L^2 ligand

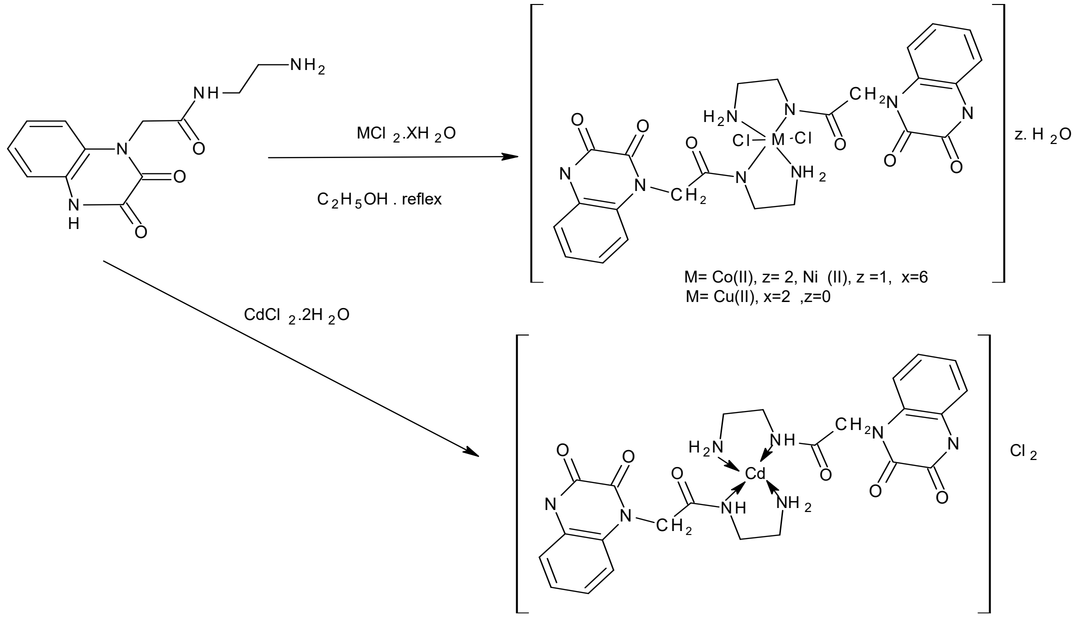
The ligand L^2 was prepared by refluxing 1 mmole of 1,2-diaminoethane with 1 mmole of diethyl 2,2'-(2,3-dioxo-2,3-dihydroquinoxaline-1,4-diyl) diacetate in absolute ethanol and after completion of reaction for 3 hours, the vaporization of half of original volume, the pale yellow crude was filtered off, washed several periods with ethanol and petroleum ether to afford pure precipitate of the ligand L^2, Scheme 4.



Scheme (4): Synthesis of L^2 ligand.

Synthesis of metal complexes with L^2 ligand:

The metal complexes with L2 ligand were prepared as the same method established in item 2.4 except the changing in the weights of ligand and metal salts, Scheme



Scheme (5): Synthesis of $[M(L^2)_2Cl_2]$ complexes

3. Results and Discussion

The physical properties and the elemental analyses of the prepared ligands and their metal complexes are listed in table (1). The founding presents of CHN values of the prepared compounds are in agreement with the theoretical values then confirm the expected structures. The metal complexes in DMSO solutions showed molar conductance in the region (19-73) $ohm^{-1}.cm^2.mol^{-1}$ indicating that all complexes were neutral except cadmium (II) complexes which were electrolytes due to the presence of chloride species as counter ions in the structure of their structures [16]. As well as the metal estimation measured via FAAS indicated formula of complexes and the molar ratio 2:1 (L:M) in all metal complexes. The results obtained from flame atomic absorption spectroscopy for all solid complexes formed with the two ligands of quinoxaline indicate the proper mole ratio 2:1.

FT-IR Spectra study

The FT-IR spectra of quinoxaline-2,3-dione derivatives (A) and (B) exhibited absorptions in the 1653-1734cm^{-1} and 1630-1590 cm^{-1} absorptions which are attributed to the esteric ν-C=O and ν-HC=CH-, ν-HC=N- of pyrazine ring, Table (2). The L1 exhibited strong bands around 1660 and 1600 cm^{-1} assigning to vibration modes of carbonyl and immine respectively [13,14]. As well as the appearance of medium absorptions around 3200-3300 cm-1 confirms the stretching of amino –NH2- moiety. The remarkable changes in these functional groups in the IR spectra of complexes to (1640-1654) and (1585-1610) cm^{-1} confirms the coordination of such active sites with the metal ions. In addition to the weak bands around 3074, 2960-2877 cm^{-1} and 780-900 cm^{-1} could be due to the vibration of -C-H and C-N- [17] of pyrazine moiety ring respectively. The appearance of new absorptions in the regions (1070-1093), (1330-1381), and (1616-1577) cm^{-1} assigning to ν-NH_2 , ν-C=O, and ν-C=N modes respectively thereby support the ring closure to afford the quinoxaline ring. The infra-red spectra of the metal complexes formed with the two ligands exhibited significant variations in the modes of –NH- and –C=O in the ranges 3200-3300 cm^{-1} and 1650-1640 cm^{-1} respectively. Furthermore, the new bands appeared around 400-460 and 477-590 cm^{-1} could be assigned to M-O and M-N bonds respectively.

NMR Study

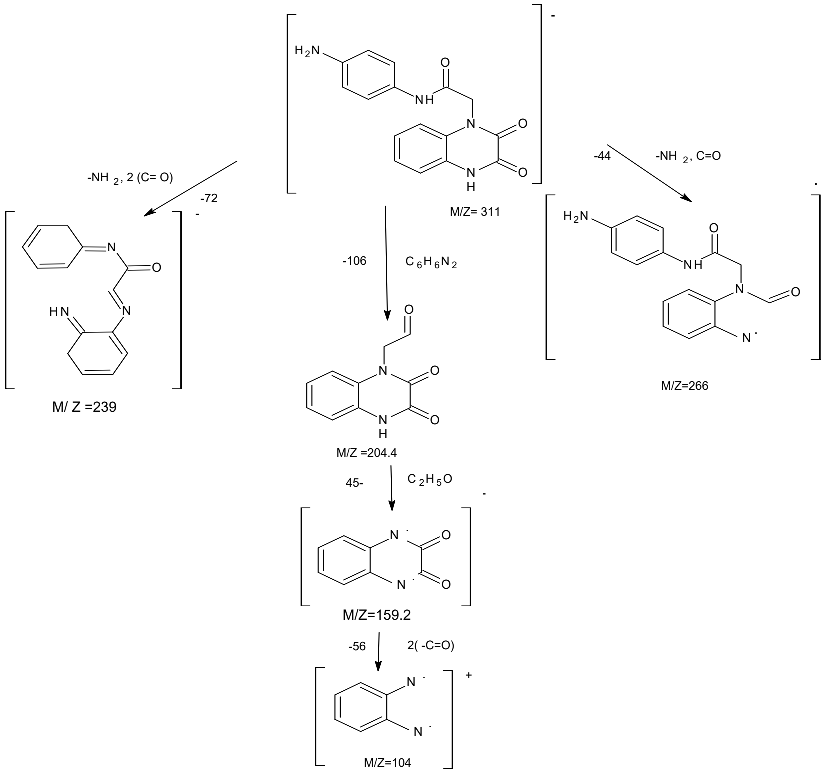
The ^{1}H NMR of the two ligands were shown in figures (1,2) where the variable peaks around (8.30.1-7.9), (8. 5-8.90) and (9.02-9.253) ppm were assigned to the resonance of aromatic and pyrazine protons in the structure of two ligand L^1. Furthermore, the absorptions around (2.20-3.74), (4.02-4.70) and (5.20-8.20) ppm may be ascribed to spin-coupling methylene –CH_2-CH_2- moiety, -NH- and the aromatic Ar-H protons respectively in the structure of L^2 ligand [13,18].

UV-Visible spectra

The electronic spectra of the ligands L^1, L^2 and their solution metal complexes were recorded in ethanol and DMSO solutions. The quinoxaline base ligand L^1 exhibits an absorption around and in the 220 nm region assigning to the $\pi \rightarrow \pi^*$ transition which is remained in the spectra of all complexes. The peaks around 290 and 350 nm are assigned to $n \rightarrow \pi^*$ transitions of (-C=N-, -C=C) groups and intra-ligand charge transfer[15].The electronic spectra of cobalt(II) complex in DMSO solution exhibited spin-allowed d-d transitions at 650 and 550nm assigning to the $^4T_1g \rightarrow {}^4T_2g$ and $^4T_1g \rightarrow {}^4T_1g(P)$ transitions respectively, indicating the octahedral geometry around cobalt(II) ion [19]. Moreover, the pale green solution of nickel(II) complexes in DMSO showed a spin-allowed peak around 700-670 nm and two intense peaks around 280 and 218 nm which are assigned to $^3A_2g \rightarrow {}^3T_2g$ and intra-ligand charge transfer which is overlapped with π-π^* respectively supporting an octahedral environment around nickel(II) ion. However, the brownish solution of copper (II) complexes displayed shoulder band in the visible region definitely around 790-835 nm that are assigned to $^2B_1g \rightarrow {}^2A_1g$ transition. As well as the high energy bands in the region 400-390 nm could be ascribed to the overlapping of the resolute d-d transition of the$^2B_1g \rightarrow {}^2Eg$ type with LMCT transition due to the Pi bonding of imine moiety of quinoxaline that has been bonded to the central metal ion. The solutions of cadmium (II) complexes in DMSO (10^{-3} M) recorded high intensity peaks around 390-310 and 210-244 nm which are concerning with the transitions of π-π^* , benzopyrazine bands and ligand to metal charge transfer respectively[17,19]. The magnetic moments of the solid complexes were measured by Farady's method at 300 K^0 and the values observed for copper(II) and nickel(II) complexes were (1.65-1.80) and (2.80-2.76) BM which fall in the expected of one and two odd electrons for d^9 and d^8 configurations [20]. However, the increased magnetic susceptibility of cobalt(II) complexes in the (4.75-4.85) BM region supporting the octahedral geometry around Co(II) ion due to orbital contribution, Table (3).

Mass spectra:

The figures (3,4) shows the mass spectra of the two ligands, hence, supports the molecular formula of their proposed structures. The mass spectra of the ligand (L^1), showed the parent ion peak at (M/Z =311) which corresponded to [M$^-$]. Other characteristic peaks were assigned to the fragments shown in scheme (6). The mass spectra of ligand L2 illustrates the parent ion peak at at M/Z= 262 as the most stable species detected the other peaks detected 236, 174, 120 correspond to $[C_{11}H_{14}N_3O_3]^+$,$[C_9H_7N_2O_2]^-$ and $[C_7H_8N_2]$ respectively. The proposed fragment ion pattern is out line in figure (4).



Scheme (6): Other Synthesis

Thermal analysis:

The thermal degradation of cobalt(II) of L^1 ligand and nickel(II) of L^2 complexes was studied by thermo gravimetric analysis (TG) from ambient temperature to 600 °C. while the thermal degradation of nickel(II) and copper(II) of ligand [L1] and Cobalt(II) of [L2] ligand at 355^0C. The data from the thermo gravimetric analysis clearly indicated that the decomposition of the complexes proceeds in four or five steps. The losing of hydrated water molecules was investigated from the exothermic peak around 50 - 250 °C temperature hence, the formation of copper oxide CuO was residue above 600 °C, figure (5,6). For these complexes, the removal of water can proceed in one or two steps [17,18]. All complexes lost hydration water between 50 and 120 °C, and then the coordinated water molecule was lost above ≥200°. The decomposition was complete at 350-600 °C for all complexes. Furthermore, the DSC analysis of nickel(II) complexes showed the stability of complexes in inert helium gas and the peaks as exothermic were very important to estimate some thermodynamic terms like entropy, enthalpy and Gibbs-Free energy [18,21]. The activation energy E* of the thermal behavior of the copper (II), and nickel (II) complexes, figures (5-9). The in the different stages is in the range of 31.14–333.95 kJmol^{-1} may agree with their stability in air and their spontaneous preparation in the solid state.

Table (1): Physical properties and elemental analysis of the prepared ligand L1and L2 and their metal complexes.

Compound	Mwt	colour	m.p. ^{0}C	Elemental analysis (found) calculate %					10^{-3}M DMSOΛ Ohm-^{1}cm^2 mol^{-1}
				C	H	N	M	Cl	
L^1 ($C_{16}H_{14}N_4O_3$)	310	Beige	198	(60.69) 61.93	(4.21) 4.55	(18.4) 18.06	-	-	-
[Co(L^1) Cl$_2$] H$_2$O ($C_{32}H_{30}N_8O_7Cl_2$ Co)	768	Red brown	>300dec	(49.53) 50.01	(3.78) 3.93	(14.69) 14.58	(8.72) 7.67	(8.56) 9.23	41
[Ni (L^1)$_2$Cl$_2$] ($C_{32}H_{28}N_8O_6Cl_2$ Ni)	768	Dark green	>272dec	(48.75) 51.23	(3.73) 3.76	(15.22) 14.94	(8.38) 7.82	(9.11) 9.45	36
[Cu (L^1)$_2$Cl$_2$] ($C_{32}H_{28}N_8O_6Cl_2$ Cu)	755	Dark red	>290 dec	(49.02) 50.90	(4.21) 3.74	(14.92) 14.84	(8.39) 8.42	(9.23) 9.39	22
[Cd (L^1)$_2$] Cl$_2$ ($C_{32}H_{28}N_8O_6$ Cl Cd)	803	Beige	>300 dec	(46.12) 47.81	(3.18) 3.51	(14.23) 13.94	(13.08) 13.98	(7.88) 8.82	73
L2 ($C_{12}H_{14}N_4O_3$)	262	brown	175-177	(53.32) 54.96	(4.89) 5.38	(22.91) 21.36	-	-	-
[Co (L^2)$_2$Cl$_2$]2H$_2$O	688	Red brown	>300	(43.44) 41.87	(4.02) 4.39	(17.85) 16.28	(8.24) 8.56	(9.19) 10.30	68
[Ni(L^2)$_2$Cl$_2$]H$_2$O ($C_{24}H_{26}N_8O_7Cl_2Ni$)	670	olive	298dec	(43.28) 43.02	(3.78) 4.21	(17.02) 16.72	(8.07) 8.76	(9.43) 10.58	29
[Cu(L^2)$_2$Cl$_2$] ($C_{24}H_{26}N_8O_8Cl_2Cu$)	656	pale Green	290dec	(43.09) 43.88	(3.99) 3.99	(17.29) 17.06	(8.32) 9.67	(9.78) 10.79	19
[Cd(L^2)$_2$] Cl$_2$ ($C_{24}H_{26}N_8O_8Cl_2Cd$)	705	beige	300dec	(39.74) 40.84	(3.25) 3.71	(15.98) 15.88	(14.28) 15.93	(9.58) 10.05	69

Table (2): IR **spectra of the ligands (L^1,L^2) and their metal complexes.**

Compound	νOH, ν(NH)	ν(C=O)	ν(C=N)	νAr-(C=C)	ν (C-N)	ν (M=O) ν (M-N)	νM-Cl
A	3392(sh), 3227(m)	1734 (s) 1653(s)	1630- 1590(sh.)	1685	1251(s)	-	--
L^1	3352(m), 3171	1660(s)	1600	1575	1302-1284(s)	-	---
$[Co(L_1)_2Cl_2]H_2O$	3553(br), 3184(sh)	1640	1615	1599	1310-1240(m)	510(w)	360(w)
$[NiL_1(H_2O)_2]Cl_2$	3454(br),3246 (sh)	1649	1600(sh)	1583	1298(m)	617(w)	280-320(w)
$[CuL_1Cl_2]$	3454(br), 3272(m)	1650	1585 (s)	1554	1294(m)	630(w)	376(m)
$[CdL^1]Cl_2$	3530 (br), 3302(m)	1654	1610(s)	1584	1294(s)	602(w)	359(w)
L^2	3302(sh)3213	1654, 1635		1554	1319	---	--
$[Co(L^2)_2Cl_2]2H_2O$	3530(br.) 3302	1633	1591	1562	1278	--- 639	
$[Ni(L^2)_2Cl_2]$ H_2O	3477(br), 3319 ---	1627	1597	1552	1261	--- 656	389
$[Cu(L^2)_2Cl_2]$ H_2O	3373(sh) 3209	1645	1593(sh)	1593sh	1280	-- 603	
$[CdL^2]Cl_2$	3522(br), 3522	1649	1597	1529	1298	626	-----

Br=broad, m=medium, sh.=shoulder,s=strong and w=weak.

Table (3) :UV-Visible absorptions, molar conductivity and magnetic moments of the prepared complexes

compounds	Band position λ max (nm)	Wave number υ cm^{-1}	Extinction coefficient dm^{3}mol^{-1}cm^{-1}	assignment	µ B.M.
L1	324 247	30864 40485	800 1300	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	-
$[Co(L^1)_2 Cl_2] H_2O$	672 420 354 238	14880 23809 28248 42016	90 120 820 600	$^4T_{2g}\rightarrow{}^4A_{2g}$ $^4T_{2g}\rightarrow{}^4A_{1g}$ LMCT	4.80
$[Ni(L^1)_2 Cl_2]$	760 420 320 277	13157 23809 31250 36101	120 200 450 1180	$^3A_1g\rightarrow{}^3T_1g$ $^3A_1g\rightarrow{}^3T_2g$ LMCT	2.80
$[Cu(L^1)_2 Cl_2]$	510 382 291	19607 26178 34364	500 800 2000	$^2A_1g\rightarrow{}^2B_2g$ $^2A_1g\rightarrow{}^2B_1g$ LMCT	1.80
$[Cd(L^1)_2] Cl_2$	428 370	23364 27027	210 700	LMCT LF	0.00
L2	346 266	28901 37593	900 1000	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	-
$[Co(L^2)_2 Cl_2]2H_2O$	610 460 386 276	16129 21739 25907 36231	190 200 400 1700	$^3A_1g\rightarrow{}^3T_1g$ $^3A_1g\rightarrow{}^3T_2g$ LMCT LF	4.70
$[Ni(L^2)_2 Cl_2] H_2O$	620 390 370	16129 25641 27027	200 280 600	$^3A_2g\rightarrow{}^3T_2g$ $^3A_2g\rightarrow{}^3T_1g$ LMCT	2.75
$[Cu(L^2)_2 Cl_2]$	580 370 290	16949 27027 34482	120 500 2000	$^2A_1g\rightarrow{}^2B_2g$ $^2A_1g\rightarrow{}^2B_1g$ LMCT	1.65.
$[Cd(L^2)_2] Cl_2$	405 380	24691 26315	1000 1200	LMCT LF	0.00

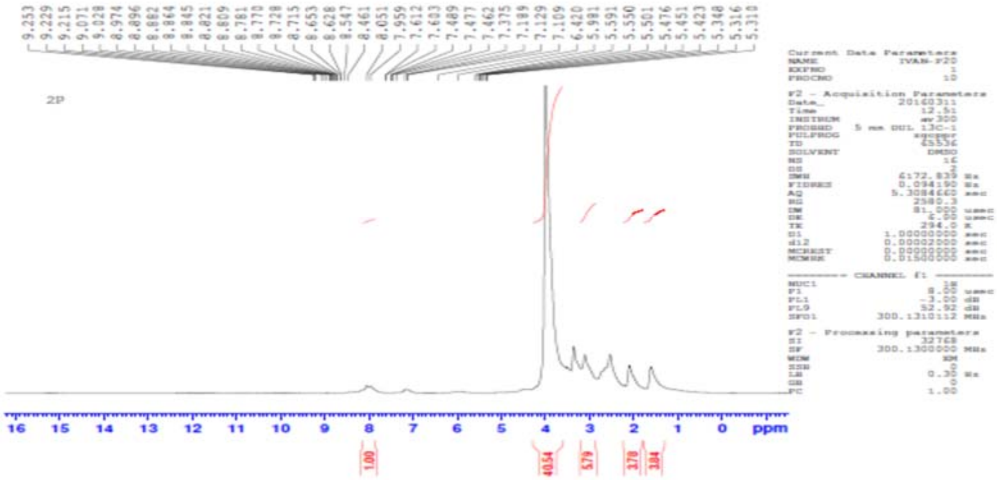


Figure (1): H NMR spectra of L^1 in DMSO-d^6 solvent.

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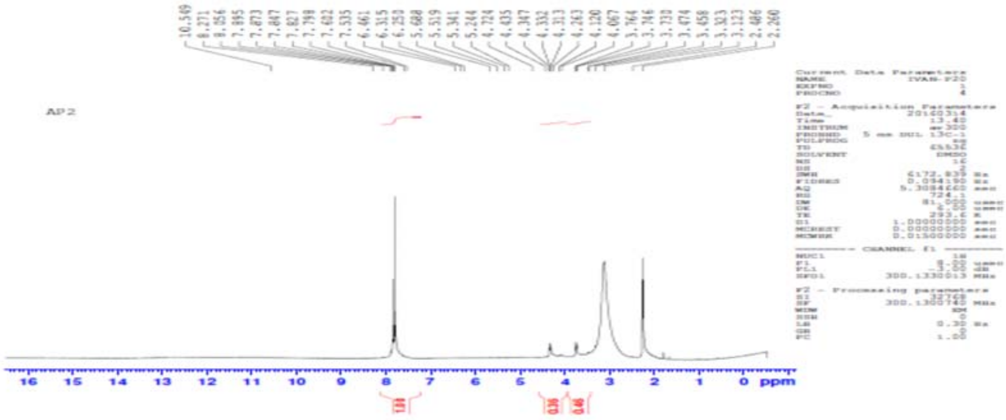
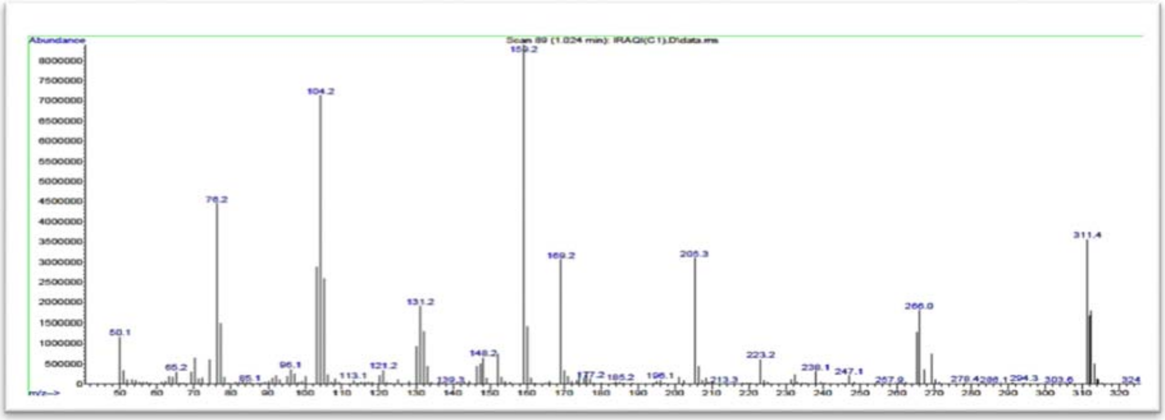


Figure (2): H NMR spectra of L^2 in DMSO-d^6 solvent.



Figure(3): Mass spectra of L^1 ligand.

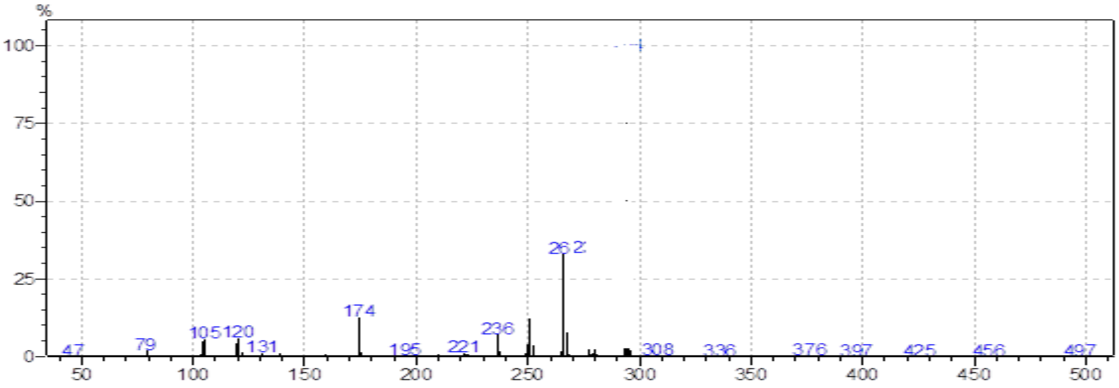


Figure (4): Mass of L^2 ligand.

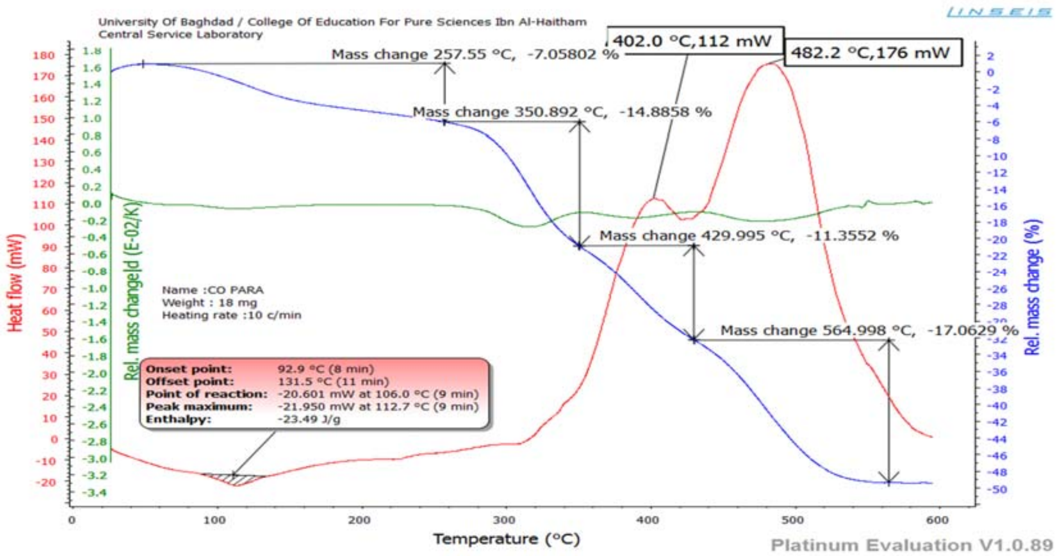


Figure (5): TG, DSC and DTG diagram of [Co(L^1)$_2$ Cl_2] H_2O.

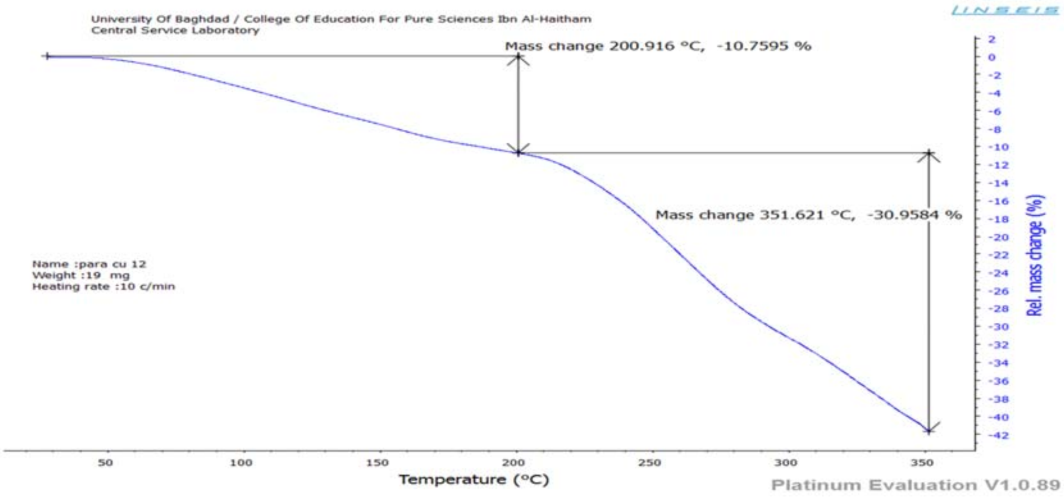


Figure (6): TG diagram of [Cu(L^1) $_2Cl_2$] H_2O

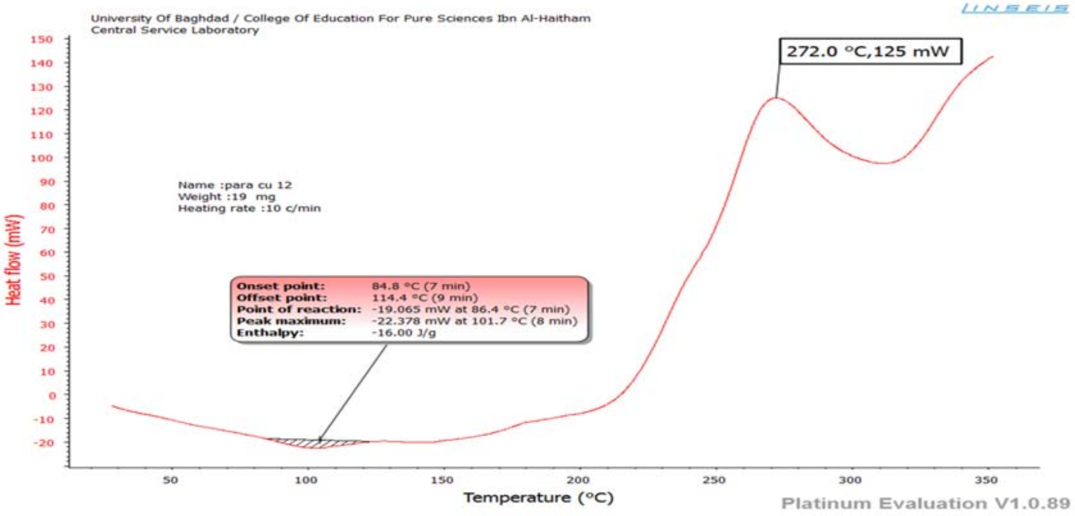


Figure (7): DSC diagram of [Cu$(L^1)_2$ Cl_2]

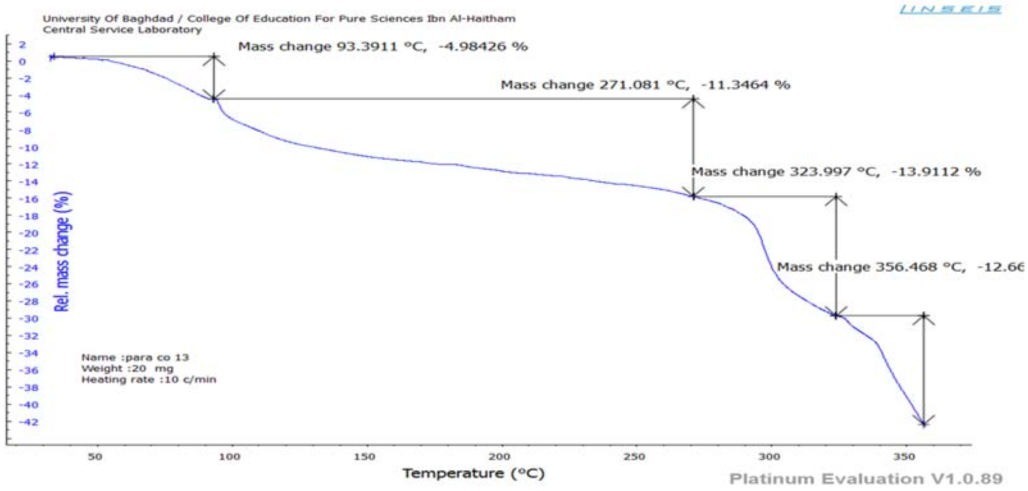


Figure (8): TG diagram of [Co$(L^2)_2Cl_2$]. H2O

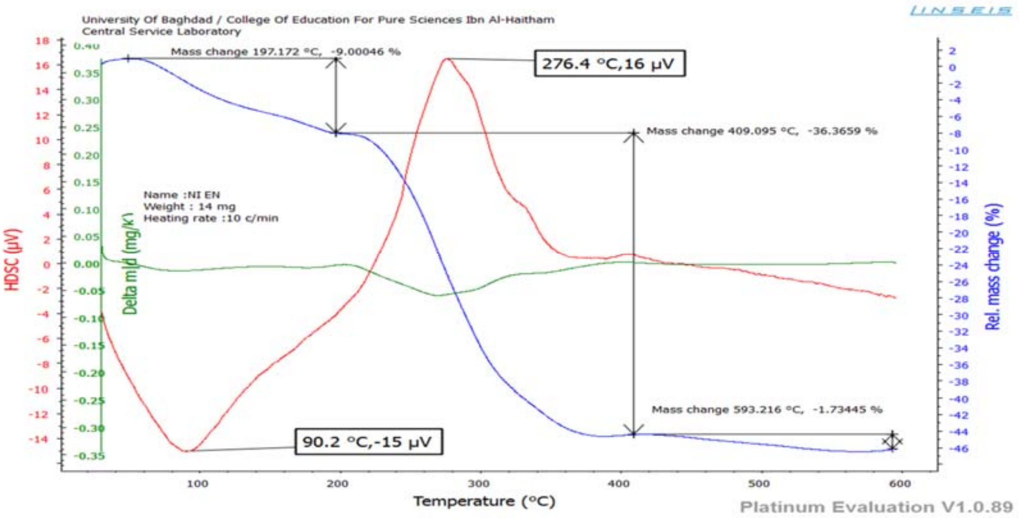


Figure (9): TG, DTG and DSC diagrams of $[Ni(L^2)_2Cl_2].H_2O$.

4. Conclusions

The results obtained from elemental analyses, FT-IR, NMR and UV-Visible spectra for the two ligands L1, L2 of quinoxaline-2,3-dione and their metal complexes with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) have confirmed their expected structures and the data observed for metal complexes through TG-DTG and DSC assigned the thermal stability in addition to support the molecular weights of the prepared compounds. The proposed geometry of the prepared complexes is shown in scheme 5.

Acknowledgement

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