Synthesis, Characterization and Thermal Study of New Transition Metall Complexes Derived from 3-Acetylcoumarine.

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Abstract

The synthesis, structure, physico-chemical and thermal investigation studies of some transition metal complexes ofCo(II),Ni(II) Cu(II) and Cd(II),withtwo ligands derived from 3-acetyl coumarine. The two ligands ligands(L^1 and L^2) were synthesized*vianucleophilic* substitution of 3-bromoacetylcoumar with potassium thiocyanateandethanolic solution of 1,2-phenlendiaminein respectively. The metal complexes of Co(II), Ni(II) Cu(II) and Cd(II),with $L^1$and L^2were prepared and isolated in the solid state then characterized by CHNM elemental spectral FT-IR, ^{1}H, ^{13}C NMR , Mass spectra,UV-Visible spectra. The thermal study (TG-DSC) of some complexes was carried out in nitrogen gas which assisted in determination the proper structure and formula of such complexes. The ligand acts as bidentate, through OO or NO, neutral in coordinating the metal ions under study. The results obtained from elemental analyses,magnetic susceptibility and electronic spectra suggested that all metal complexes were formed in 2:1 molar ratio of ligand to metal with octahedral structures. The complexes are found to be soluble in DMF and DMSO. The TG-DSC study revealed that the metal complexes were thermally stable with point decomposition over 350^0 C as well as the percent in loss of weight up on decomposition at inert conditions of nitrogen atmosphere has reported the proposed formula.

Key Words: nucleophilic substitution of 3-bromoacetylcoumarin, Transition metal complexes of Chromone-2-one and Ligationalbehaviour of Cumarine ligands.

Introduction

Transition metal complexes of cumarineligandshave been studied and attract attention against the antitumor activity [1-3].In particular metal *chelates* of cumarine have been known for some time to be antitumor agents [4,5].Because of their biological activity and analytical application,thiosemicarbazidesandthiosemicarbazones, as well as theirmetal complexes have been the subject of many studies [6,7]. The Schiff bases of coumarins comprise a very large class of Lewis bases that have interested in the field of coordination chemistry [8]. The antimicrobial activity of coumarin nucleus and related derivatives [9] has a great important effects like antibacterial, antithromboticandvasodilators[10].As it hasinvestigated in the literature the biological activity of some coumarinderivatives significantly enhances by binding to metal ions[11,12]. In continuation with this interest of cumarine chelates, we report the synthesis, characterization and thermal study of some first row transition metal complexes with two ligands derived from 3-bromoacetyl-cumarine-2-one.

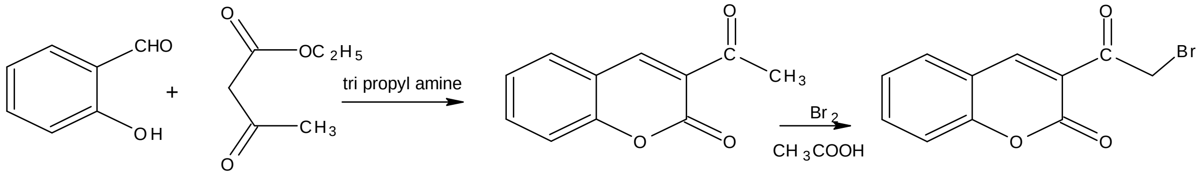
Experimental

All chemicals were of reagent grade, and solvents were dried and distilled before useaccording to the standard procedures. 3-Acetylcoumar-2one in was purchased from Sigma-Aldrich company and other starting materials like potassium thiocyanate and 1,2-phenylenediamine were supported from laboratories of chemistry department,college of science-Al-Mustansiriyauniversity. The hydrated chlorides$CoCl_2.6H_2O$,$NiCl_2.6H_2O$,$CuCl_2.2H_2O$,$CdCl_2.2H_2O$ and $Cd(CH_3COO)_2$were purchased from Alfa company, and were used without further purification as received .The measurements of molar conductivity were made on an Hanna conductivity bridge with cell constant 1.0 cm^{-1}. The magnetic susceptibilitymeasurements were made on a

Gouy balance at room temperature using Hg[Co(SCN)4]as calibrant on Sherewood magnetic balance. The vibration spectra were recorded in a KBr and CsI matrix using a Shimadzu FTIR spectrometer model 983 .The electronic spectra in the range (200–1000 nm) were done for all complexes and the free ligands complexes in DMF and ethanol solutions were scanned on aCarry 2390 instrument.1H and 13C-NMR spectra were determined on Burker DMX- 500 NMRSpectrophotometer on a 300 MHz, with TMS as standard and DMSO as solvent (Alalbayt University-Jordan).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 Baghdad university Abinhitham collage. 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, Ibn-CinaCenter, Ministry of Industry. Magnetic moment for prepared complexes 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.

2.2.Synthesisofω-bromo-3-acetylcoumarine

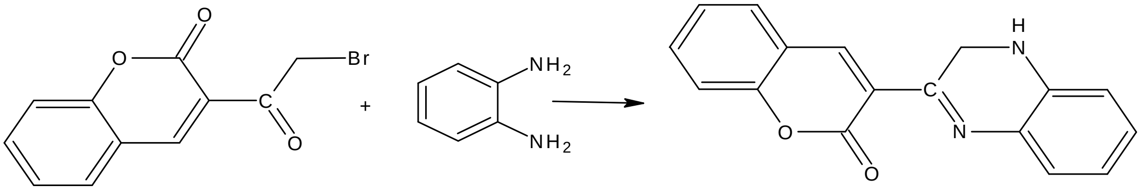
The bromination of (1) in acetic acid gave ω-bromo-8- 3-acetylcoumarin (2), [12] (Scheme 1) .



Scheme 1. Synthesisofω-bromo-3-acetylcoumarine.

2.3. Synthesis of 3-(quinoxalin-2-yl)-cumarine (3). [L^1]

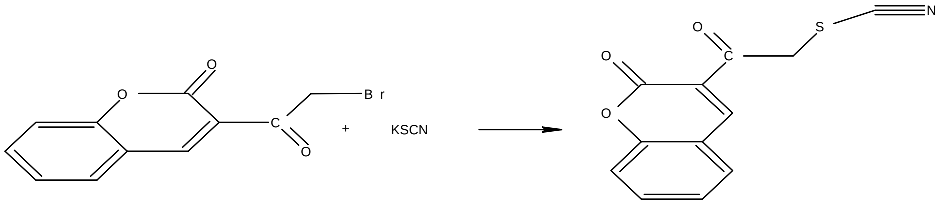
A solution of (2) (5 mmol) and 1,2-phenylenediamine (5 mmol) in absolute methanol (20 mL) was refluxed for 4hours. The solid obtained was filtered, washed with ethanol and dried under vacuum. The crude product was recrystallized from ethanol/benzene mixture to give compound 11 as pale brown crystals; yield 77%; m.p. 148 - 150°C, Scheme 2.



Scheme2 . Synthesis of .[L^1

2.4. Synthesis of 2-methylene-2H-chromene-3-(methyl carbonimidic)thioanhydride (5).[L^2]

A solution of compound (2) (10 mmol) in methanol(40 mL) was refluxed with potassium thiocyanate (10 mmol) for 3 hours. The solid formed on cooling filtered off, washed with ethanol and dried under vacuum. The product was then recrystallized from acetic acid to give 16 as brown needles; yield 90%; m.p.138 -–140 °C,Scheme 3.



Scheme 3.Synthesis of [L^2].

2.5.Synthesis of the Metal complexes

A mixture of L^1 and L^2 (2 mmol)in 50 mL.ethanol was added to an aqueous solution of Cadmium (II) Chloride dihydrate, nickel(II) chloride hexahydrate, Cobalt(II) Chloride hexahydrate and copper(II) chloride dihydrate (1 mmol, 10 ml). The mixture of reaction was refluxed for approximately2-3 hours and then excess solvent was distilled. The coloured complexes so obtained were filtered, washed with methanol and dried under vacuum over calcium chloride pellets.,Yield: 70-85%.

$$2L_1 + CdX_2.2H_2O \longrightarrow [\,Cd(L^1)_2]\,.X_2$$

$$X = CH_3COO \text{ or } Cl$$

Scheme 4. Synthesis of the Cd(II)complexes

Results & Discussion

Analyses and physical measurements

All the complexes are sparingly soluble in common organic solvents but highly soluble in DMF and DMSO. The analytical data (Table 1) indicate that the complexes are mononuclear with 2:1 molar ratio of ligand to metal ion. The molar conductance in DMF fall in the expected range for their non-electrolytic behaviour, indicating that the chloride ions are inside the coordination while the Cd(II) complexfall in the expected range for their electrolytic behaviour, indicating that the chloride ions are outside the coordination sphere and

Mass spectra

The figure(1) clearly exhibits the molecular ion peak m/e=188 which agree well with the formula $C_{11}H_8O_3$[13]. As well as the bromination of 3-acetyl cumarine (A) by Br_2 in chloroform solution leads to A2 derivative which it's mass spectra in figure(2) displays base peak at 267 that is consistent with $C_{10}H_7O_3Br$. However the other peaks at 186 and 88 are extremely attributed M-Br+ ion. The ring closure of 1,2-phenylenediamine with A2derivative,scheme(3) results in ligand L1 which shows molecular ion m/e=274 at relative intensity 100% then supports the proposed structure of L^1ligand.On the other hand the figure(3) represents the mass spectra of L2 ligand which shows absorptions at245, 244,192,160,128 and 81 that are assigned to $C_{12}H_7NSO_3$ and fragments of M-SCN,M-CH_2SCN and base peak of C_5H_5O+ respectively[14,15],figure(3).

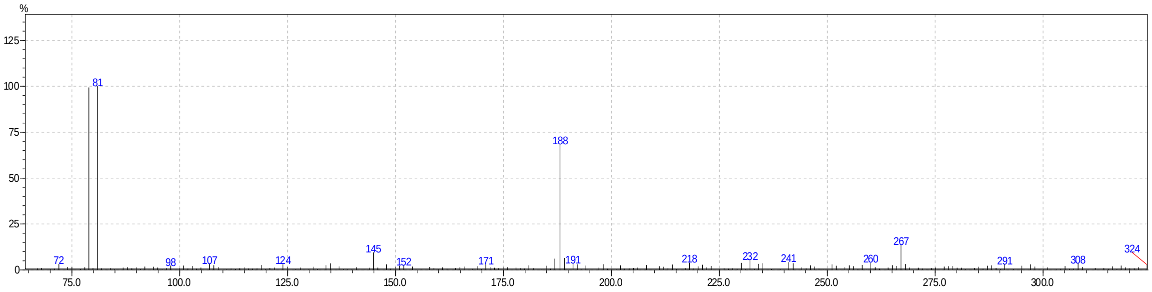


Figure 1. Mass of ω-bromo-3-acetylcoumarine

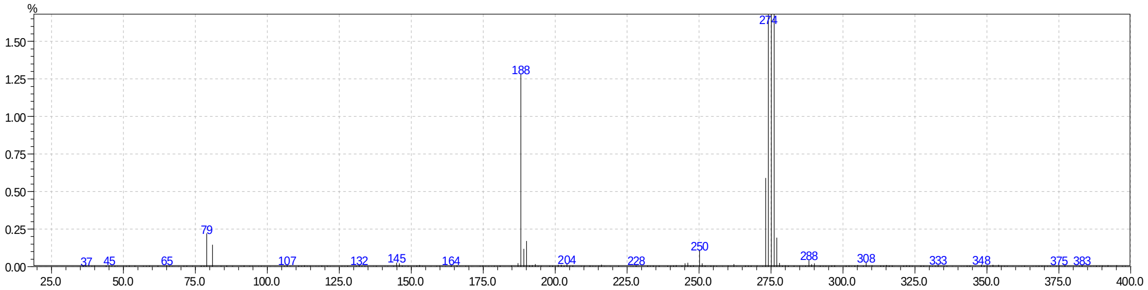


Figure 2 .Mass of L^{1}.

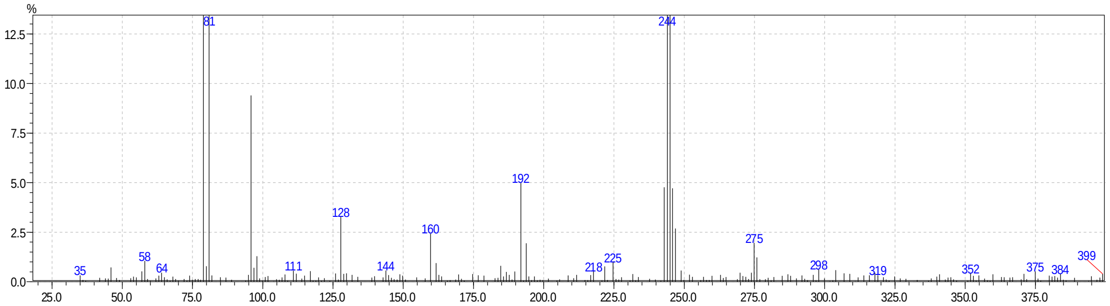


Figure 3 .Mass of L^{2}.

Infrared spectra

The bromination of 3-acetylcumarine have proved by the medium bands at 780 and 870 cm^{-1} that are attributed to H_2C-Br moiety[12].The distinct bands at 2962, 1710, and 1630 cm^{1-} in the IR spectra of L2 may be assigned to aliphatic –CH_2-,carbonyl of chromone and –C=C- moiety respectively [12]. As well as the spectra of ligand L^{1} formed from cyclo addition of A with 1,2-phenylenediamine was approved from appearance singlet absorption at 3370 cm-1 and strong absorptions at 1712 and 1630 cm-1 which are assigned to –C=O and –C=N- of quinoxaline moiety[13].Main characteristic infrared absorption bands of the 3-acetylcumarine A and their derived ligands L1 and L2 with their Ni(II), Co(II), Cu(II) and Cd(II) complexes, along with their assignments, are presented in Table 2. The free 3-acetylcoumarin) shows band at 1730cm-1 is attributed to (C=O) of the lactone ring [13]. The stretching vibration is observed at 2130 cm-1 with a shoulder on lower wave number side may be assigned to –S-CN moiety. The observed medium intensity band at 912 cm−1 in the free L^{2} ligand, which is ascribed to δ(CSC) of –SCN- moiety vibration [15], did not subject to remarkable changes in the spectra of solid complexes suggesting no involvement of the sulfur atom in the bonding with the metal's ions [15]. The medium intensity band observed at 1570 cm-1 is assigned to (C=C) of the chromoneringThe comparison of the positions of these bands with those observed in the infrared spectra of its Ni(II), Co(II), Cu(II) and Cd(II) complexes indicated that the band at 1670-1705 cm−1 showed a marked shift, this discussed that carbonyl group shared in the complexation toward Ni(II), Co(II), Cu(II) and Cd(II) ions, while that bands at 3328 and 3306 cm−1 which assigned to stretching vibration motions –O-H moiety is good proof for presence of coordinated water molecules[14]. This fact suggests the coordination of L2 through the nitrogen –S-CN and oxygen of lactone –C=O together and tending to form stable complexes. The observed medium intensity band at 912 cm−1 in the free HL ligand, which is ascribed to δ(CSC) of thiocyanato group attached directly to –CH2- moiety [15], shifted to lower values for the five HL complexes, suggesting the involvement of the sulfur atom in the bonding with the metal's ions. The band assigned to the stretching of v(C–S) is similarly shifted to lower frequencies. This also confirms that the sulfur atom is taking part in the complex formation [16]. On the other hand, the weak to medium intensity absorptions in the regions 400-470 and 490-544 cm1- are ascribed to M-O and M-N bonds [17].

Magnetic measurements

The magnetic susceptibilities of the complexes, recorded at room temperature (Table-3) show low magnetic moments indicating the presence of a spin exchange interactions between the metal ions. The values obtained of copper(II) complexes lie in the 1.73-1.85 BM range and corresponds to one unpaired electron. As well as the orbital contributions of cobalt (II) and nickel(II) complexes in the ranges 4.2-4.6 and 3.50-3.22 BM respectively indicated the high spin octahedral structures around Co(II) and Ni(II) ions[18,19].

Electronic spectral studies

Electronic spectral data of the complexes in DMSO solution are listed in Table(3). The ligands L^1 and L^2exhibited similar spectral features in the UV-Vis region with bands around 255, 310 and 440 nmrespectively. The first band below 310 nm is assigned to a ligand transition (n-π*) and(π-π*) [10,14] .The other two bands, 370 and 440 nm are attributed to charge transfer processes. The visible spectra of all the complexes are similar and show an intense absorption band near ~360 nm and moderately intense shoulder band near 395–415 nm and distinct band at ~656 nm. The separated weak energy bands of copper (II) complex in the range 550-871 nm could be attributed to $^2B_1g\longrightarrow{}^2B_2g$ and $^2B_1g\longrightarrow{}^2Eg$ transitions respectively and support the formation of distorted octahedral around Cu(II) ion [17]. The weak absorptions at 810,650 and 440 nm of cobalt(II) complex formed with L^1 ligand may be assigned to $^4T_1g\longrightarrow{}^4T_2g$,$^1T_1g \longrightarrow{}^4A_2g$ and $^4T_1g\longrightarrow{}^4T_1g(P)$ respectively [18]. The spectrum of the green complex of Co(II) formed with L2 ligand exhibited the following absorptions at 860 nm ,690 nm and 567 nm these peaks are characteristic of octahedral cobalt (II) complex respectively [12, 17].By the same way, the nickel(II) complex formed with L1 and L2 ligands showed two spin-allowed transitions at 410 , 395 nm and 840and550 nm that are remarkably belonged to $^3A_2g\longrightarrow{}^3T_2g$ and $^3A_2g\longrightarrow{}^3T_1g$ suggesting the octahedral geometry around Ni(II) ion respectively [18]. However, the cadmium(II) complexes formed with L1 showed only absorptions in the 393,361nm and 401,365 nm indicating the charge transfer and the benzenoid bands of coumarine ring[10,11].The absorptions in the regions 378,340 and 393,363nm attributed to the cadmium chloride and cadmium acetate(II) complexes formed with L2

NMR Spectra

The ^{1}H-NMR spectra of the L1 ligand in d6-DMSO solventTable.3 shows multiple signals at 6.5-7.90 ppm, corresponding to the eight protons aromatic ring protons of the phenyl and pyrazine moieties [15]. The singlet at 4.60 ppm was attributed to the two protons of the –CH2-Br group [10]. The signal of the –NH proton in the quinoxaline moiety was observed at 9.55 ppm, and the singlet peak at 8.77 ppm is attrinuted to H-C=C- in position 4 of coumarinering,figure (4). As well as the figure(5) shows the C^{13} NMR of L1 in d6-DMSO which displays resonance peaks related to aromatic –C=C- in the regions 113-125 ppm and 127-131 ppm are assigned to –C=O, -

C=N- and –C-N moieties respectively. The figures (5,6) show the^{1} H and ^{13}C nmr spectra of L2 in d6-DMSO where the absorptions in the region 6.2-7.80 ppm are ascribed to Ar-H protons and the chemical shift at 8.04-8.70 ppm is assigned to protons of annulated coumarine ring[12,13]. The singlet peak at 11.40-11.50 ppm may be attributed to H-C=C of coumarine ring in C4 position. However, the weak peak at 4.10 ppm could be assigned to CH2-Br due to effect of electron withdrawing effect of bromine and thiocyanato groups on the deshielding of aliphatic protons toward the weak magnetic field [20].

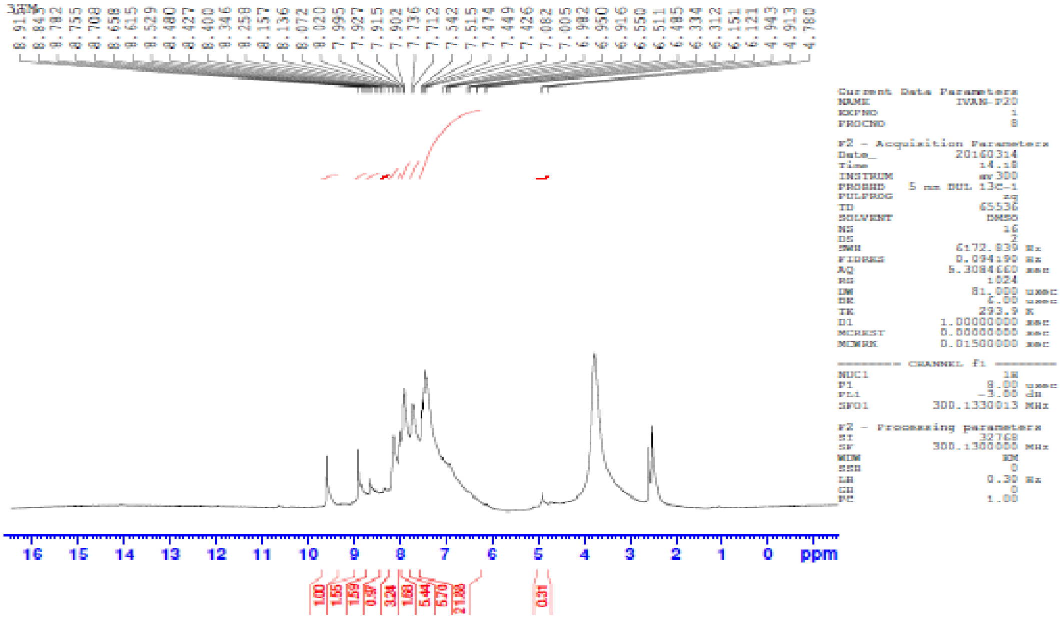


Figure 4 . H NMR spectra of L^{1} in DMSO- d6 solvent

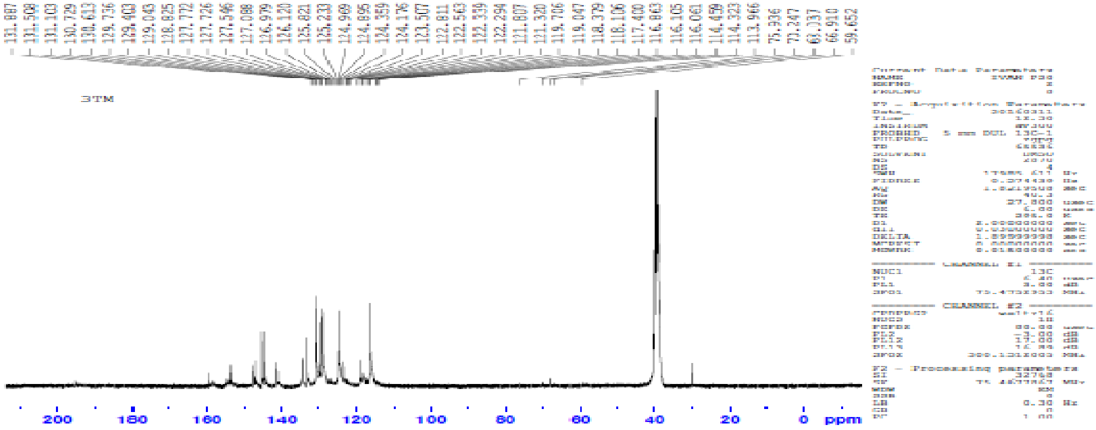


Figure 5.^{13} C NMR spectra of L^{1} in DMSO- d6 solvent.

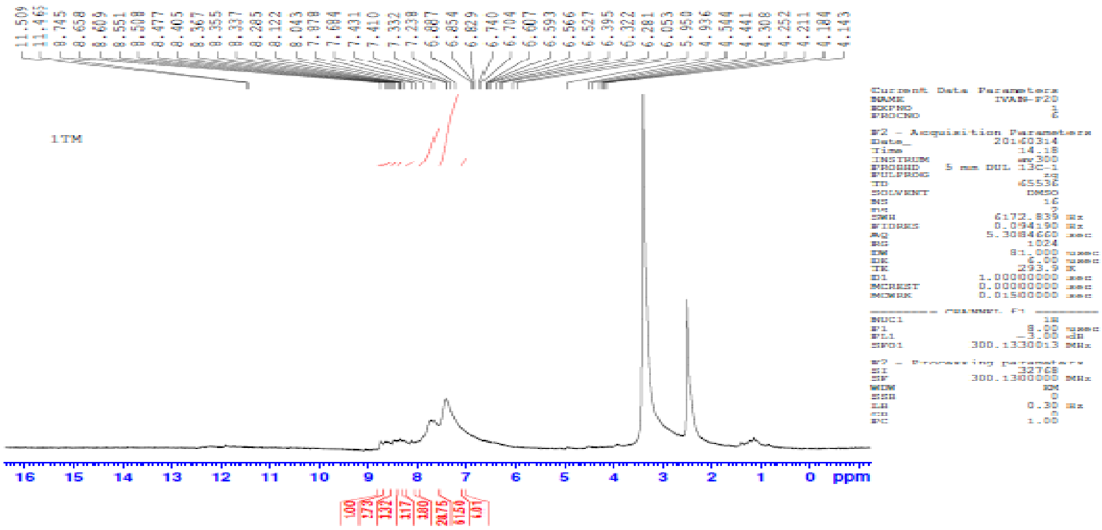


Figure 6.H NMR spectra of L^2 in DMSO d6 solvent.

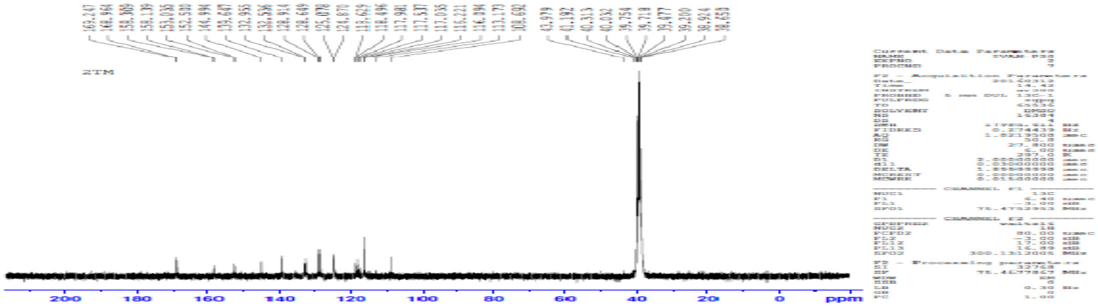


Figure 7.^{13} C NMR spectra of L^2 in DMSO- d6 solvent.

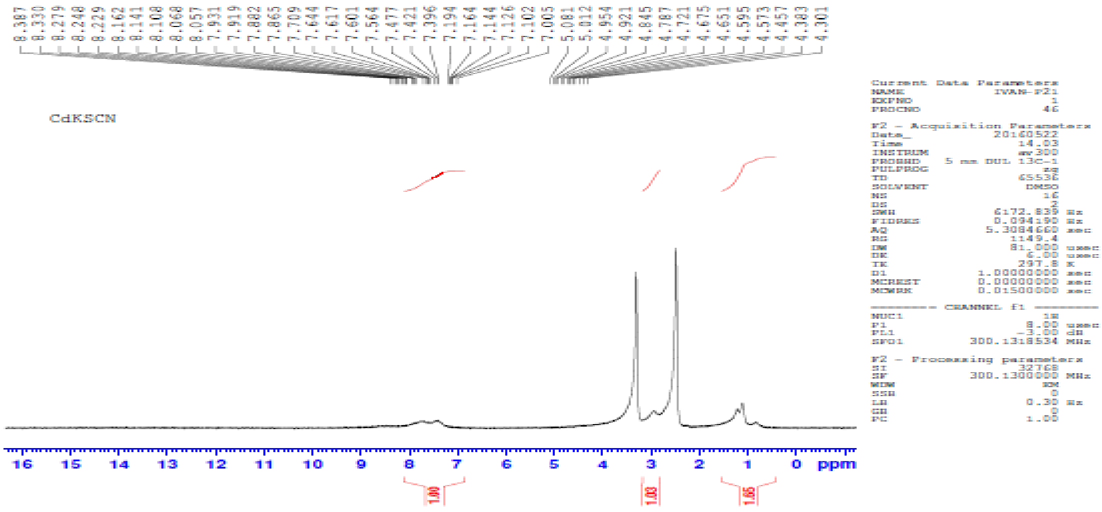


Figure 8.^{1}HNMR spectra of $[Cd L_2](OAC)_2]$ in DMSO d^6 solvent.

Thermal analysis

The thermal degradation of Co(II), Cu(II) and Cd(II)fig.9,10 complexes was studied using thermo gravimetric techniques and a temperature range of 25–360 °C. The thermal stability data are listed in Table 6. The data from the thermo gravimetric analysis clearly indicated that the decomposition of the complexes proceeds in three or four steps. Ethanol molecules were lost between 50-63.63^{0}C .All complexes were lost hydration water molecules between 100- 119 °C. The removal of water can proceed in one or two steps. Complex Cu(II) lost hydration water and ethanol molecules between 50 and 120 °C. The DSC analysis fig.11 of Cu(II) complex with L^1 ligand associated endothermic peaks have been detected over temperatures (122^{0}C) as indicated by DSC analysis . the corresponding values of entropy of activation Δs^* ,were in range -0.547 to -0.480 jmole^{-1} . the negative values of ΔH^* means that the decomposition processes are endothermic The degradation pathway for all complexes may be represented as follows:

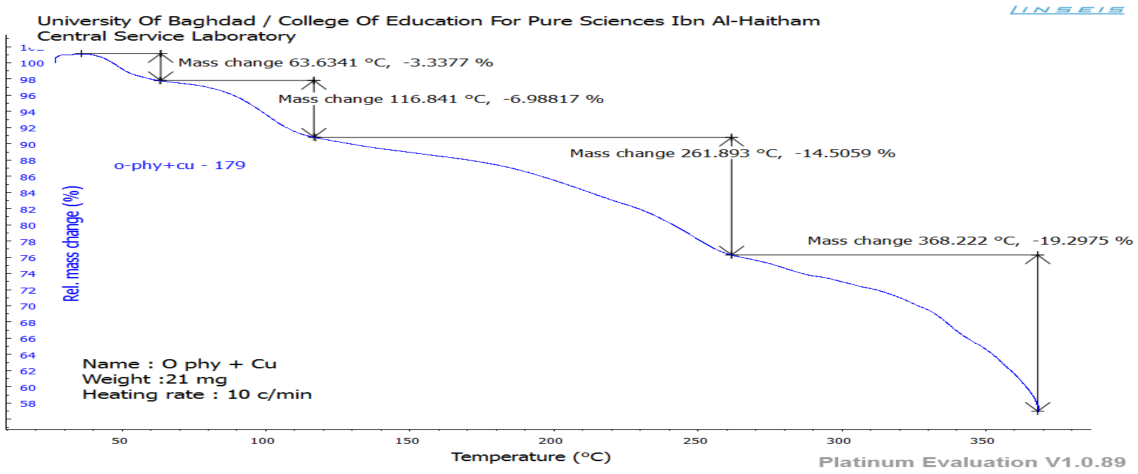


Figure 9.TG**Figure 5.**TG analysis of Cu(II) complex with L^1 ligand.

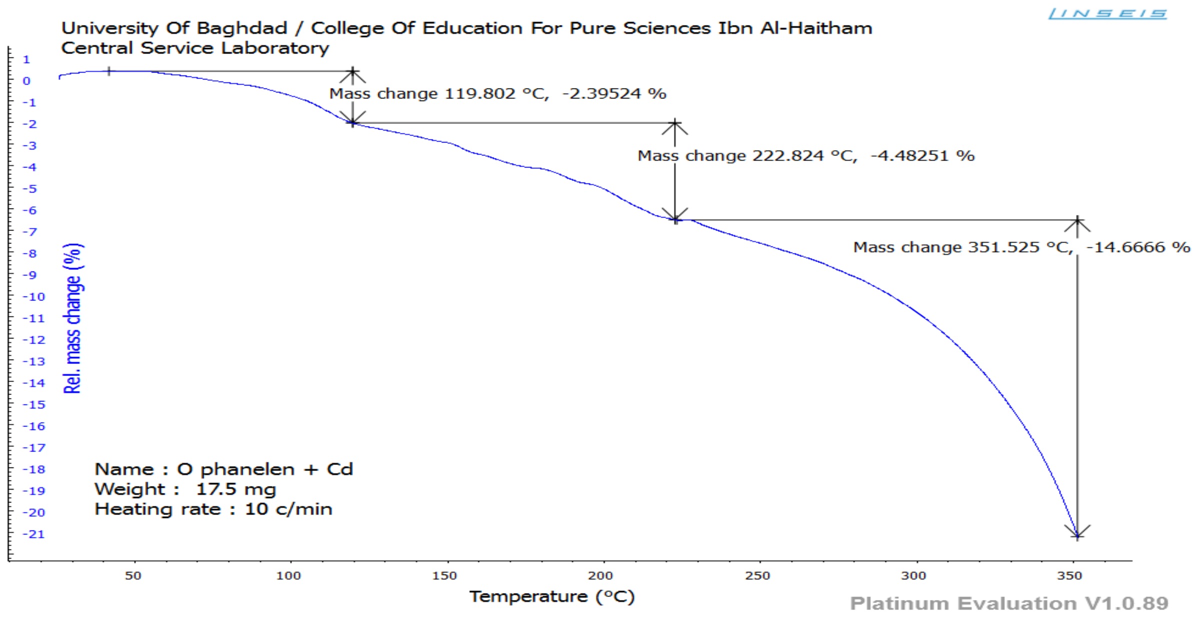


Figure 10.TGanalysis of Cd(II) complex with L^1 ligand.

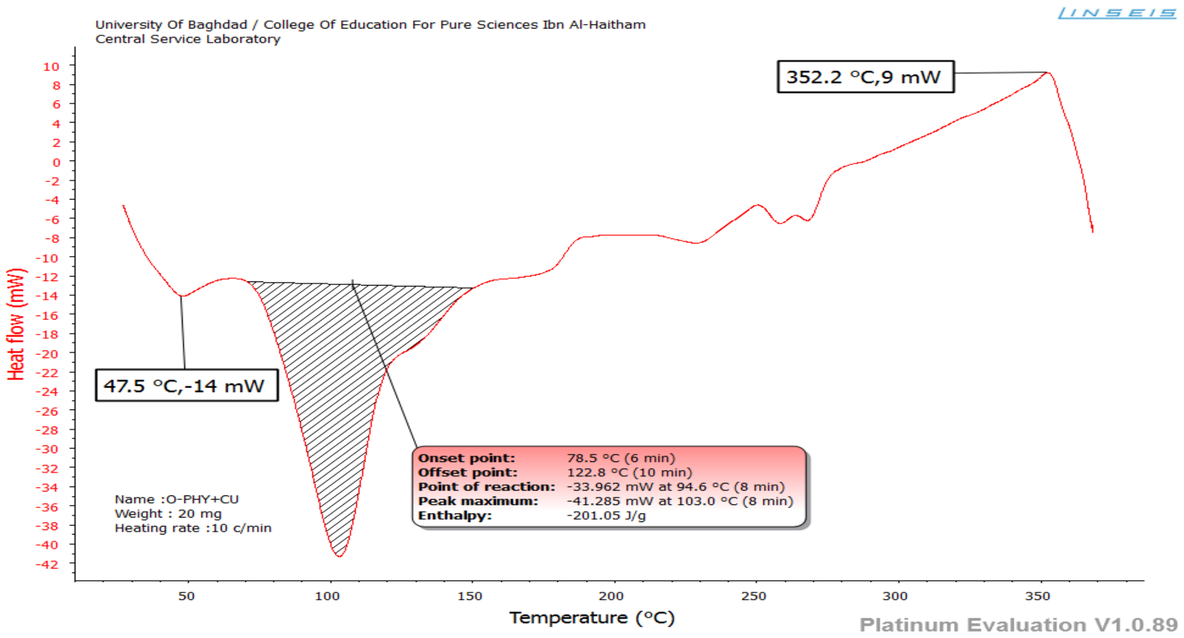
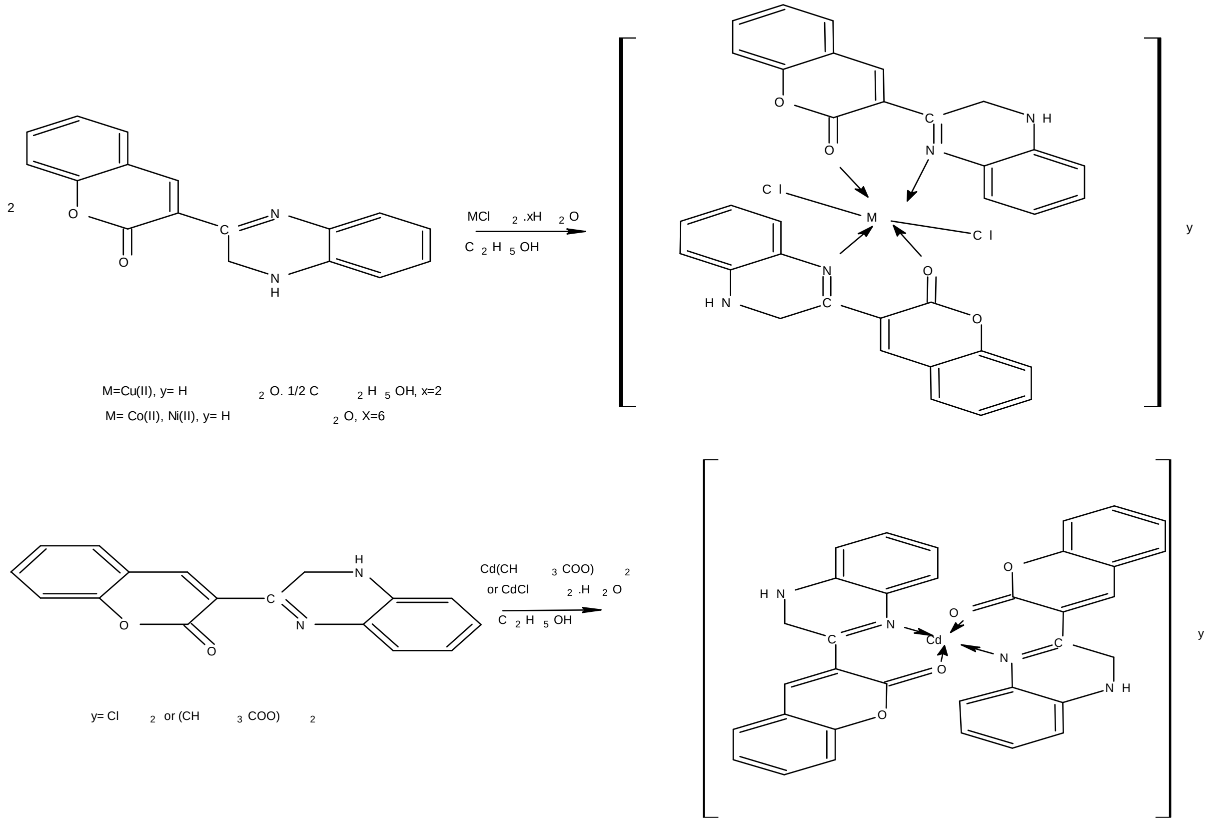
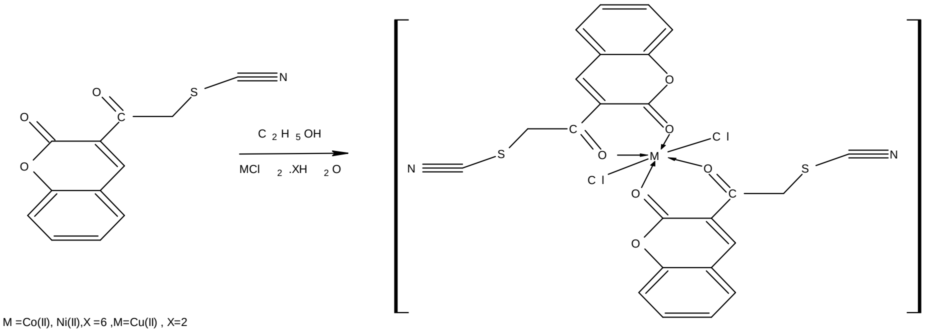


Figure 11.DSC analysis of Cu(II) complex with L^1 ligand.



Scheme 5.synthesis of complexes of L^1.



Scheme 6 .synthesis of complexes of L^2.

Table 1. The physical properties and elemental analysis of the prepared metal complexes.

Formula	Color	Mwt g/mol	M.p. (°C) [a]	C% Calc (Found)	H% Calc (Found)	N% Calc (Found)	S% Calc (Found)	M% [b] Calc (Found)	Cl% Calc (Found)
$C_{17}H_{12}O_2N_2$ [L^1]	Brown	276	148-150	73.90 (73.02)	4.38 (4.23)	10.14 (10.19)	-	-	
$[C_{34}H_{22}O_4N_4Cl_2Co].H_2O$	Brown	698.41	182 (Dec)	58.47 (58.02)	3.46 (3.16)	8.02 (8.27)	-	8.44 (8.17)	10.15
$[C_{34}H_{22}O_4N_4Cl_2Ni].H_2O$	Brown	698.14	161-163	58.49 (58.17)	3.46 (3.12)	8.79 (8.92)	-	8.02 (7.89)	10.16 9.96
$[C_{34}H_{24}O_4N_4Cl_2Cu].H_2O$	Purple	643.14	198 (Dec)	64.40 64.11	4.13 3.98	8.84 8.90	-	10.02 9.95	
$[C_{34}H_{26}O_5N_4Cd]OAC$ $[C_{36}H_{29}O_7N_4Cd]$	Beige	742.04	189-191	58.27	3.94	7.55	-	15.15 14.89	-
$[C_{34}H_{26}O_5N_4Cd]\ Cl_2$	Beigi Beige	717.45	192 (Dec)	56. 92 (56.55)	3.51 (3.17)	7.81 (7.67)	-	15.67 (14.22)	4.94 (4.69)
$C_{12}H_7O_3NS$ [L^2]	Yellow	245	138-139	58.77 (58.18)	2.88 (2.52)	5.71 (5.98)	13.07 (13.54)		
$C_{24}H_{14}O_6N_2S_2CoCl_2$	Brown	620.34	195-197	46.47 (46.09)	2.27 (2.11)	4.52 (4.63)	10.34 (10.22)	9.47 (9.13)	11.43 (11.09)
$C_{24}H_{18}O_8N_2S_2NiCl_2$	Dark green	656.13	oily	43.93 (43.12)	2.77 (2.09)	4.27 (4.50)	9.77 (9.22)	8.95 (8.21)	10.81 (10.51)
$C_{24}H_{14}O_6N_2S_2CuCl_2$	Silver	624.95	190-192	46.12 (45.91)	2.26 (2.19)	4.48 (4.66)	10.26 (10.01)	10.17 (9.98)	11.35 (11.12)
$[C_{24}H_{14}O_6N_2S_2Cd][OAC]$ $[C_{26}H_{22}O_{10}N_2S_2Cd]$	Brown	721.01	252-254 dec	46.64 (46.14)	2.80 (2.67)	3.89 (3.96)	8.89 (8.72)	15.59 (15.43)	-
$[C_{24}H_{14}O_6N_2S_2Cd]Cl_2$	Grey	673.82	260-262 dec	46.64 (46.13)	2.80 (2.43)	3.89 (3.98)	8.89 (8.67)	15.59 (15.33)	10.52 (10.21)

[a] Dec: Decomposed,calc :Calculated, [b] Content of metal was done by flame atomic absorption spectroscopy.

Table 2.FT-IR absorptions of the ligands L^1 and L^2 and theirmetal complexes in cm^{-1}.

Compound	**νOH**	**νNH**	**νC=O**	**νC=N**	**νC=C**	**νS-C,**	**νM–N**	**νM-O**	**Other band**
[L^1]	3455	3292	1649	1622 1580	1554	-			3088-CHAr
$Co\ [(L^1)\ _2Cl_2].H_2O$	3650(br)	-	1649	1593-1559	1556-1545	-	424-472	542	3023 2933
$Ni[(L^1)\ _2Cl_2].H_2O$	3440(br)	-	1664-1651	1622	1554	-	455	542	3088 2987
$Cu[(L^1)\ _2Cl_2]\ H_2O._.1/2C_2H_5OH_.$	3200-3600(br)	-	1645	1624,1585	1566,1533	-	434-489	511-599	3012 2901
$[CdL^1](CH_3COO)_2$		-	1654	1634	1568	-	445	523	3022
$[CdL^1]Cl_2$		-	1656	1611,1599	1579	-	434	546	3043 2926

L^2	3354	-	1714	1606	1556				3117
Co $[L^2]_2$		-	1716	1606	1550			620,754	3089
$Ni[L^2]_2.H2O$	3340, 3302		1714	1630,1606	1558	1292,1249		624,752	3120,932
$Cu[L^2]_2$			1728,1718	1635,1606	1560	1244, 1166		622,758	3148
$[C_{24}H_{14}O_6N_2S_2Cd][CH_3COO]_2$	3483		1712,1631	1606	1564	1327,1288		612,756	3182
$Cd[L^2]_2Cl_2$	-	-	1728,16	1606	1590	1367,1290		634,725	3128

* s: strong , m: medium ,br: Broad, w: Weak, sh :shoulder.

Table 3.The electronic spectra and molar conductance of the prepared complexes.

Complex	**UV-visible, λnm**	**νCm^{-1}**	**Tentative assignment**	**Dq**	**β** Nephelaxetic	**μ (B.M.)**	**$Λ_m$(S.mol^{-1}.cm^2)**	**Geometry**
L^1	310 255	32258 39215	n→π* π →π*			-		-
$[Co (L^1)_2Cl_2].H_2O$	656 401 368	15243 24937 27173	$^4T_{1g}\rightarrow{}^4T_{2g}$ $^4T_{1g}\rightarrow{}^4A_{2g(p}$ C.T	969.4	1.39	3.77	22	Octahedral
$[Ni (L^1)_2Cl_2].H_2O$	410 396	24096 25252	$^3A_2g\rightarrow{}^3T_2g$ $^3A_2g\rightarrow{}^3T_1g$	2409.6	2.33	2.6	27	Octahedral
$[Cu (L^1)_2Cl_2]$ $H_2O.$.1/2C_2H_5OH.	871 424 307	11481 23584 32578	$^2B_1g\rightarrow{}^2B_2g$ $^2B_1g\rightarrow{}^2E_2g$ LMCT	-	-	1.7	28	Octahedral
$[Cd(L^1)_2]Cl_2.H2O$	393 361	25445 27700	C.T n→π*	-	-	0.0	92	Tetrahedral
$[CdL^1](CH_3COO)_2$	401 365	24937 27397	C.T n→π*			0.0	101	Tetrahedral
L^2	366 330	27322 30303	C.T n→π*			0.0		
$[Co(L^2)_2Cl_2]$	848 357 293	11792 28011 34129	$^4T_{1g}\rightarrow{}^4T_{2g}$ $^4T_{1g}\rightarrow{}^4A_{2g(p}$ C.T	1621	1.66	3.4		octahedral
$[Ni(L^2)_2Cl2]$ H2O	840 550 293	11904 18181 34129	$^3A_2g\rightarrow{}^3T_2g$ $^3A_2g\rightarrow{}^3T_1g$ C.T	1190	1.15	2.8		octahedral
$[Cu(L^2)_2Cl_2]$	864 357	11574 28011	$^2B_1g\rightarrow{}^2B_2g$ $^2B_1g\rightarrow{}^2E_2g$			1.76		octahedral

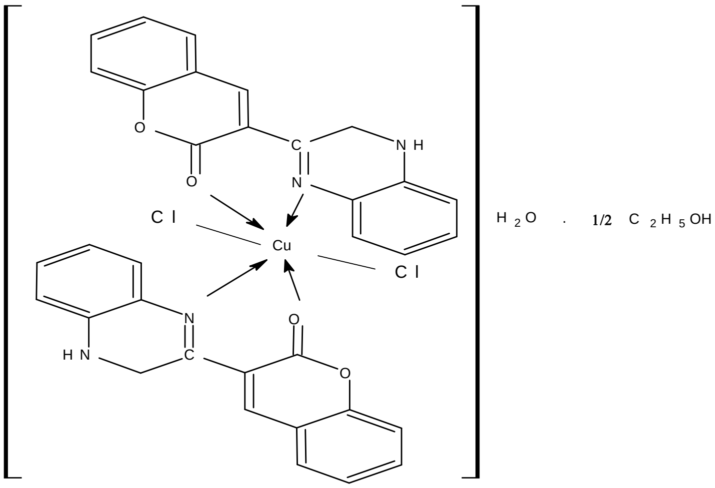
$Cd[L^2]_2Cl_2$	378 340	26455 29411	C.T n→π*	-	-	0.0	97	Tetrahedral
$[C_{24}H_{14}O_6N_2S_2Cd][CH_3CO O]_2$	393 336	25445 29761	C.T n→π*	-	-	0.0	109	Tetrahedral

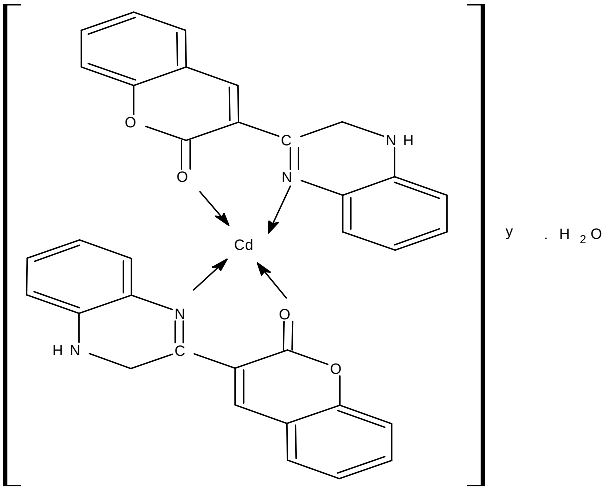
Table(4) . Decomposition steps with the temperature range and weight loss for some complexesof L^1.

Compound	Decomposition step	Temperature range (°C)	removes species	Weight loss % (Cald.)	Weight Loss%Found
$Co [L^1]_2$	1 st 2 nd 3 rth	147-181 181-247 247-352	H_2O Cl $(C_2H_6N_2Cl)$	2.64 5.4 16.72	2.04 4.4 16.63
$Cu[L^1]_2$	1 st 2 nd 3 rth 4rth	45- 63.63 63- 116.84 116 -261 261.8 -368	$1/2C_2H_5OH$ Cl, H_2O $C_2H_6N_2Cl$ C_8H_{10}	3.30 7.2 14.04 19.27	3.16 6.95 13.75 18.58
$Cd[L^1]_2$	1 st 2 nd 3 rd	45-119 119-222 222-351	H_2O 2Cl $C_2H_6N_2$	2.44 10.7 18.57	2.37 11.9 17.1

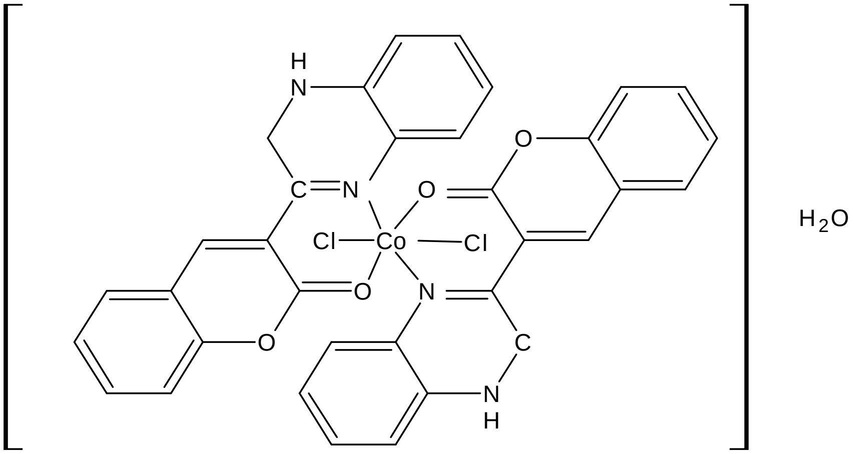
Conclusions

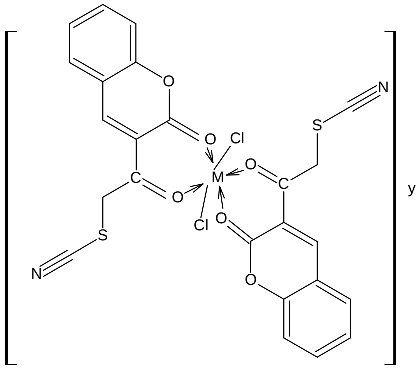
According to the results obtained from elemental analyses, spectral, magnetic susceptibility measurements and the TG-DSC analyses, the octahedral geometry around cobalt, nickel,copper and cadmium (II) ions were suggested and the IR dataadopted the chelation of the two ligands of coumarine derivative via nitrogen of quinoxalinemoiet and carbonyl of chromone ring, Scheme 7.





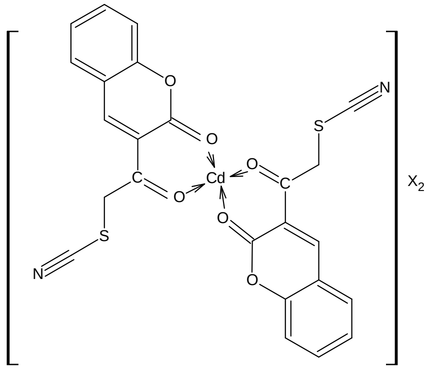
y = Cl_2 or $(OAC)_2$





M= Co(II), Cu(II) y=0

M= Ni(II), y= $2H_2O$



X= Cl_2 or $(OAC)_2$

Scheme 7. Octahedral configurations of the prepared complexes.

Conclusion

The complexes have the formula :-M [(L1) $2Cl_2$].H_2O where M= Co(II), Ni(II), Cu[(L1) $2Cl_2$] H_2O. 1/$2C_2H_5OH$.The thermal analyses of complexes shows significant weight losses corresponding to the elimination of ethanol and water molecules per mononuclear unit in the 650C and 100-120 ^{0}C ranges respectively. Therefore, onewater molecule are outside coordination sphere, whereas the Cd(II) are outside the coordination sphere for both it's chloride and acetate complexes.

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