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Preparation and Characterization of New Mixed Ligand Complexes of (p-Methyl Anilino)-p-Chloro Phenyl Acetonitrile and Ethylene Diamine

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Abstract

New mixed ligand complexes of some metal ions Zn(II), Cd(II) and Hg(II) were prepared by reacting with mixture of two bidentate ligands [HL = (P-methyl anilino) –P– chloro phenyl acetonitrile and en = ethylene diamine] in a molar ratio of 1:1:1[M : HL : en] in ethanol . The ligand HL was previously prepared by Strecker’s procedure which includes the reaction of p- toluidine with P-chlorobenzaldehyde in the presence of KCN in acidic medium. The structures of new compounds were identified by elemental analyses, atomic absorption and thermal analyses TG/DTG in addition to FTIR and U.V-VIS. Spectra. The electrical conductivity measurements of metal complexes were also determined. From the obtained data the octahedral structure was suggested for all prepared complexes.

Keywords: veterinary drugs complexes of mixed ligand; (α – Aminonitrile & en) complexes; Zn (II), Cd(II)) and Hg complexes.

تحضير وتشخيص معقدات فلزية جديدة لخليط الليكاندين (بارا مثيل انيلينو)– باراكلوروفنيل اسيتونتريل واثيلين ثنائي امين

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الخلاصة

حضرت معقدات فلزية جديدة لخليط ليكاندين مختلفين لبعض ايونات العناصر الفلزية Zn(II) ، Cd(II) و Hg(II) من تفاعلها مع خليط الليكاندين ثنائي السن احدهما HL = (بارا مثيل انيلينو) – بارا– كلوروفنيل اسيتونتريل والثاني en = اثيلين ثنائي الامين بنسبة مولية (1: 1: 1 لكل من الايون الفلزي :HL : en). حضر الليكاند HL المحضر مسبقا بطريقة ستريكر من مفاعلة بارا– تولودين مع بارا–كلورو بنزالديهايد بوجود سيانيد البوتاسيوم وفي وسط حامضي. شخصت تراكيب المعقدات الفلزية الجديدة من خلال التحليل الدقيق للعناصر ومطيافية الامتصاص الذري اللهبي والتحاليل الحرارية DTG/TG بالاضافة الى اطياف الأشعة تحت الحمراء البعيدة والأشعة فوق البنفسجية – المرئية فضلاً عن قياسات التوصيلية الكهربائية للمعقدات الفلزية . من النتائج المستحصلة تم اقتراح الشكل الهندسي للمعقدات المحضرة انها ثمانية السطوح.

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Introduction

α-Amino nitriles are very important compounds for the preparation of amino acids and heterocycles containing nitrogen such as imidazoles, thiadiazoles [1] and other pharmacologically useful molecules [2]. Beside that they were used as synthetic activating transcription for the explanation of biological reaction and identified as biologically inhibitors [3, 4], herbicides [5]. Adolph Strecker was the first to prepare α -amino nitriles in 1850, by treating aldehydes with ammonia and hydrogen cyanide [6] .The nucleophilic addition of cyanide ion to imines (Schiff bases) provides a direct route for the synthesis of α-amino nitriles [7]. α-Aminonitriles are potentially a bidentate ligands through two nitrogen atoms in the coordination chemistry [3,8]. Their complexes have an area of increasing interest, because these complexes have numerous applications, such as veterinary drugs [9-12].The ligand ethylene diamine (en) is used as a bidentate chelating agent. It is used in manufacture of chelating agents such as ethylene diamine tetraacetic acid (EDTA) [13]. Ethylene diamine is useful to prepare template model and macrocyclic complexes [14]. In addition, several articles have been reported on the coordination chemistry of mixed ligand complexes for en [13, 15, 16].

This work presents the synthesis and characterization of new metal complexes of metal ions Zn(II), Cd (II) and Hg(II) of mixed ligands{∝-aminonitrile HL which was previously prepared [17] and ethylene diamine}. We developed these complexes to be more active as veterinary drugs than the previously prepared which were tested as "synthetic chemical prophylactic agent against *E.coli* infection during production period in layers" [9-12].

HL ligand and en were coordinated with metal ions by the nitrogen atoms of ∝-amino group (C≡N group) and the two nitrogen atoms of en; the coordination chemistry of mixed ligands with metal ions was studied.

Experimental

1. Instruments:

Melting points were obtained by using Gallenkamp MF-600-010 F melting point apparatus. Infrared spectra of metal complexes were recorded as CsI discs by SHIMADZU FTIR-8400S, Spectrophotometer. Electronic Spectra of the ligand HL and its metal complexes in DMF were recorded by U.V – visible Spectrophotometer (Shimadzu U.V-1800 Double puma). Thermal analyses of TG and DTG were obtained by using Thermo gravimetric analyzer Perkin- Elmer TGA 4000. The curves of TG and DTG were recorded from 30 ^{0}C up to 900^{0}C with heating rate of 20^0 C/min. The helium was used as inert gas in rate 20 ml/min. Elemental analyses for CHN were performed by using Euro- EA3000 (Italy). Metal contents were determined by using Perkin – Elmer 5000 atomic absorption Spectrophotometer. Electrical conductivities of metal complexes at room temperature were measured by using Hunts Capacitors Trade Mark British.

2. Chemicals:

The chemicals, Zinc Chloride 98.8%, Cadmium Chloride monohydrate 99.9%, Mercury Chloride 98% (Merck), ethylene diamine 99% and ethanol absolute 99% (Fluka) were used in this study. Dimethyl formamide (DMF) was dried and distilled prior to use [18].

3. Preparation of ligand α-aminonitrile (HL):

The aldehyde (p-chlorobenzaldehyde) (7.028 g, 0.05mol) was dissolved in 50 mL of glacial acetic acid. A small portion of p-toluene sulfonic acid was added to the mixture to reach the pH to 2. The amine, p- toluidine (5.358g, 0.05mole) was added to the mixture followed by additions of concentrated H_2SO_4 drop wise to adjust the pH of the mixture to 3-4. KCN (0.05mole) was added to the mixture with continuous stirring. The end of the reaction was checked by thin layer chromatography (TLC) using chloroform: ethyl acetate (1.5: 0.5) as eluent. The reaction mixture was poured on ice and the ammonia was added to make the mixture slightly alkaline. The obtained yellow precipitate was filtered, washed several times with water and dried. The solvent of recrystallization was a mixture of ethanol and water.

4. Preparation of metal complexes:

An ethanolic solution of metal salts (1m mole) containing (0.136g) $ZnCl_2$, (0.201g) $CdCl_2.H_2O$ and (0.271g) $HgCl_2$ were added with continuous stirring to a hot mixture of HL ligand (0.256g, 1mmole) and en (0.067mL, 1mmole) in absolute ethanol. The precipitation took place. Each mixture was heated under reflux for one hour to complete precipitation. The products were filtered off, washed with ethanol and dried under vacuum. The purity of all complexes was tested by TLC. The mixture of chloroform and acetone in different ratios was used as eluent.

Results and Discussion

a) Physical data and atomic absorption:

Table -1 describes the physical properties of metal complexes. The suggested molecular formula was supported by elemental analysis, atomic absorption, thermal analyses spectral studies and electrical conductivity measurements. Atomic absorption of some complexes showed less agreeable results because of instrumental errors

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Table 1- Molecular formula, physical properties, elemental analysis and atomic absorption of HL and mixed ligand complexes

symbol molecular formula M.wt.(gm/mole)	colour	M.P°C	Yield %	C % Found (calc.)	H % Found (calc.)	N% Found (calc.)	Cl% Found (calc.)	M% Found (calc.)
HL $C_{15}H_{13}N_2Cl$ 256.50	Yellow	86-87	92.00	69.63 (70.17)	5.59 (5.06)	11.23 (10.91)	14.35 (13.84)	-
C1 [Zn HL (en)Cl_2]$2H_2O$ 1.5 C_2H_5OH 557.89	white	> 260 decomp.	81.32	42.81 (43.01)	6.71 (6.09)	10.23 (10.03)	18.95 (19.08)	12.52 (11.70)
C2 [CdHL(en)Cl_2] $0.35H_2O$ 506.22	Off White	250	79.45	40.51 (40.29)	4.63 (4.28)	11.15 (11.06)	20.72 (21.03)	21.96 (22.21)
C3 [Hg L(en) $(H_2O)_2$] 0.25 H_2O 555.60	Gray	> 260 decomp.	70.25	36.54 (36.71)	4.11 (4.22)	9.23 (10.07)	5.91 (6.38)	37.00 (36.09)

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b) Infrared spectra:

Important characteristic stretching frequencies of the ligand HL and mixed ligand complexes are listed in Table-2. Their spectra are shown in Figure -1, 2. The most important stretching modes exhibited by HL is represented by ∝-amino and nitrile group. The bands related to nitrile (C≡N) stretching vibrations of free ligand HL appeared at (2220) cm^{-1} [3, 8, 17]. These bands were splitted in C1 and C2 complexes as a result of linkage with metal ions through nitrogen atom [3, 8, 19]. The spectra of C3 complex showed shifts in C≡N stretching vibrations to lower frequencies which indicate the linkage of C≡N. The decreases are attributed to metal dπ to ligand pπ* back-bonding [3, 8, 20]. The I.R spectra of mixed ligand complexes C1 and C2 showed shifts in stretching vibrations of υ_{N-H} for HL. The C3 complex showed disappearance in bands related to υ_{N-H} for the same ligand. In both cases the ligand HL coordinated with metal ions through the nitrogen atom of α-amino group [3, 8, 21]. The bands which related to stretching vibrations of aromatic C-H and δ_{CH3} vibrations were appeared at (3060-2975) and (1350-1327) cm^{-1} respectively [21,22].Additional bands were observed at (1161-1009), (1485-1467) and (2950-2777) cm^{-1} and were assigned υ_{N-c}, δ_{CH2} and υ_{CH2} vibrations respectively[23]. The bands of complexes C1- C3 shown in (3390-3288) cm^{-1} and (3300-3228) cm^{-1} were assigned to the asymmetric and symmetric υ_{NH2} of en ligand which coordinated with Zn (II), Cd (II) and Hg (II) [23]. The complexes bands of C1, C2 and C3 appeared at 1595, 1616 and 1572 cm^{-1} respectively. The bands were attributed to δ_{N-H} which was present in both ligands (HL & en) [23]. The disappearances and shifting of υ_{NH} were reliance as indicator to the coordination between ligands and metal ions through the N atoms of ∝-aminonitrile group and NH_2 of en. The bands appeared at low frequencies refer to $\upsilon_{M-N\equiv C}$, υ_{M-N}, υ_{M-NH}, υ_{M-NH2} and υ_{M-OH2} stretching vibration [3, 8, 23]. Beside that the complexes C1 and C2 showed stretching mode of M-Cl [23]. The complexes C1, C2 and C3 spectra gave additional bands belonging to lattice and coordinated water vibrations [3, 8, 21, 23]. The complex C1 spectrum showed bands related to lattice ethanol (appeared at 3892-3722, 1649 and (1150 cm^{-1})which were attributed to υ_{OH}, δ_{OH} and υ_{C-O} respectively [3, 8, 22]. Generally, the shifts of C≡N and N-H stretching frequencies of the ligands in the metal complexes showed that chelating of the metal ions with two ligands occurs through the nitrogen atoms of HL(∝-aminonitrile) and the nitrogen atoms of en.

Table 2- Characteristics stretching vibrations υ (cm^{-1}) of FTIR spectra for HL and mixed ligand complexes

Symbol	**υ_{N-H} of α-aminonitrile (υ_{N-H2} of en)**	**$\upsilon_{C\equiv N}$**	**υ_{OH} H_2O Lattice (H_2O) coord. EtOH***	**δ_{N-H}**	**$\upsilon_{M-N\equiv C}$**	**HL**	**en**	**υ_{M-Cl} $\upsilon(_{M-OH2})$**
						υ_{M-N} υ ($_{M-NH)}$	**υ $_{M-NH2}$ υ $_{(M-NH)}$**	
HL	3360	2220	-	1500 m	-	-	-	-
C1 Zn(II)	3165 (3390-3335) Asym (3300-3252) Sym.	2357 2131	3481-3892 3722*	1595	376	(368)	511	326
C2 Cd(II)	3174 (3288)Asm. (3265)Sym.	2233 2156 2057	3834-3452	1616	361	(332)	542	300
C3 Hg(II)	(3359)Asm. (3228)Sym.	2119	3415 (696) (629)	1572	370	3614	420 (586)	(488)

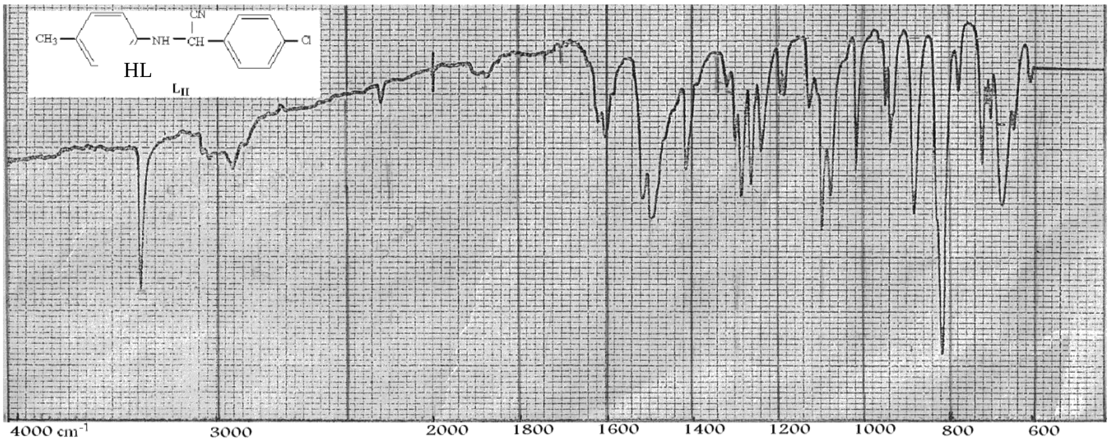


Figure 1- The I.R spectrum of HL ligand.

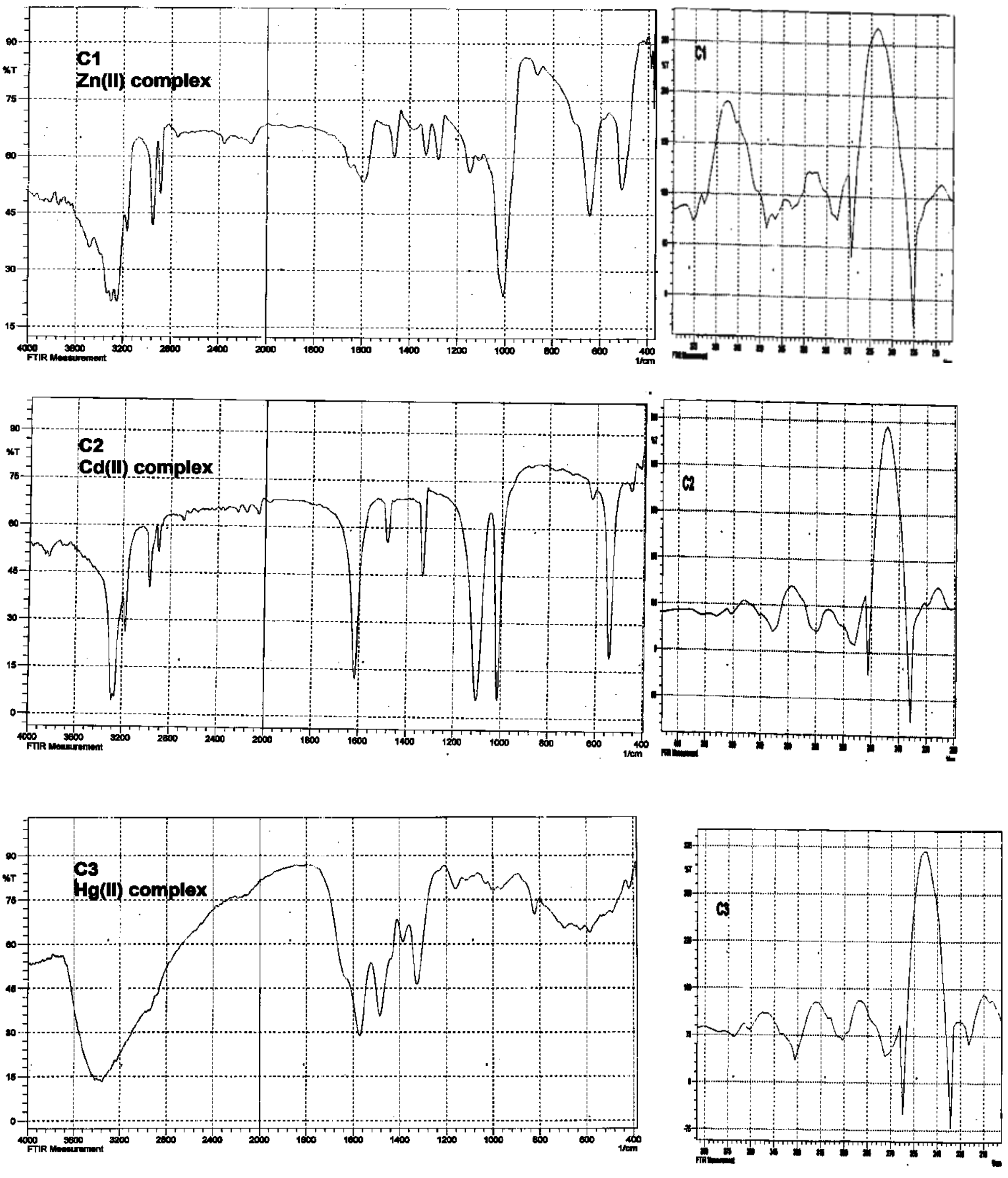


Figure 2- FTIR spectra of mixed ligand complexes; C1 of Zn (II), C2 of Cd(II) and C3 of Hg(II)

c) Electronic Spectra, Magnetic Moment Susceptibility and Conductivity Measurements:

Table -3 and Figure -3 describe the electronic spectra of ligand HL and mixed ligands complexes in DMF and magnetic moment susceptibility and conductivity measurements. The ligand HL showed two bands; high intensity band appeared at 36231cm^{-1} attributed to $\pi \rightarrow \pi^*$ transitions of aromatic ring and the conjugated of π -system of the nitrile group [3,8,20,22]; the second band was of lower intensity appeared at 30769 cm^{-1} assigned to $n \rightarrow \pi^*$ transition (as they might be masked by $\pi \rightarrow \pi^*$ band) [3,8,22].Complexation of mixed ligands (HL and en) with metal ions Zn(II),Cd(II) and Hg(II) caused shifts of wavelengths due to coordination of N atoms of mixed ligands with metal ions. These bands are attributed to L- M charge transfer and Intra-ligand transitions [3, 8, 22, 24]. Figure (2) shows bands of maximum absorptions of HL and mixed ligand complexes. The spectra of complexes

C1, C2 and C3 showed no bands in the visible region which is quite familiar with d^{10} - system where no d-d electronic transition is occurred [3, 8, 22, 24].

The solid complexes of Zn (II), Cd (II) and Hg (II) are diamagnetic because of filled-d orbital. The conductivity measurements of complexes in DMF (10^{-3}M) showed low values indicating they were non-electrolytes [25].

Table 3- Electronic spectral data, electrical conductivities in (DMF 10^{-3}M) and suggested geometries for HL and mixed ligand complexes.

Symbol	**λ max (nm)**	**Maximum absorption υ max(cm^{-1})**	**Band assignment**	**Molar conductivity in DMF at 18 °C μs.cm^{-1}**	**μ_{eff} B.M**	**Suggested structure**
HL	276 325	36231 30769	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
C1 Zn(II)	294 366	34014 27322	$\pi \rightarrow \pi^*$(Intraligand) L → M (C.T)	16	Dia.	Octahedral
C2 Cd(II)	265 371	37736 26954	$\pi \rightarrow \pi^*$(Intraligand) L → M (C.T)	13	Dia.	Octahedral
C3 Hg(II)	266 288	37594 34722	$\pi \rightarrow \pi^*$(Intraligand) L → M (C.T)	12	Dia.	Octahedral

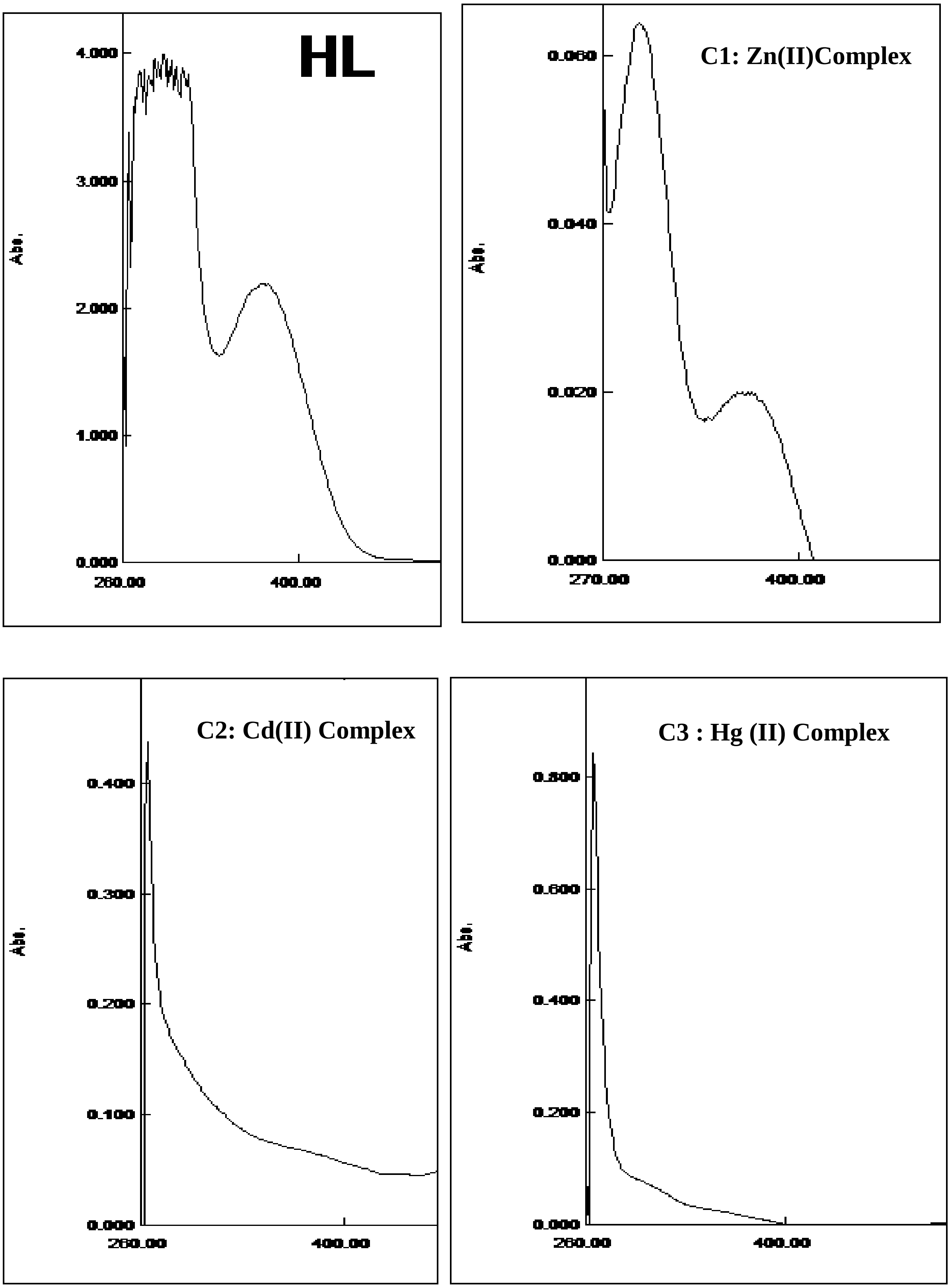


Figure 3- Electronic spectra of HL and their mixed ligand complexes; C1 of Zn (II), C2 of Cd(II) and C3 of Hg(II)

d) Thermal analyses of complexes:

The thermal properties of the complexes were studied by TG and DTG in temperature ranging from 30 to 900 °C at a rate of 20°C /min. using helium as inert gas in rate of 20 ml /min. Thermal decomposition of complexes are described in Table -4 and their thermographs are shown in

Figure -4 .The results were in agreement with those obtained by elemental analysis, atomic absorption and FTIR spectroscopy. The TG/DTG thermograms of these complexes lead to the following:

1. The presence of more than one peak in the TG/ DTG thermograms of three complexes indicates that the analysis happens in several steps [26].
2. The first step loss of lattice water molecules [27].
3. The next step loss of coordination water of crystallization [27].
4. Fragments which are not directly bonded to metal ion were found to leave at lower temperature than those directly bonded [28].
5. The final step of thermal decomposition of complexes gave free metal of C1 [27], metal chloride of C2 [29], but from the weight loss of C2 we can suggest that the corresponding transition process may be attributed to the sublimation of part of the $CdCl_2$ [29, 30] and no residue (volatilization) of C3 [29, 31, 32].
6. The difference in the thermal behavior of the complexes may be attributed to the strength of the chelating and affinity between the ligands and the metal ion (M-L) [26].

Table 4- Stages of thermal decomposition of mixed ligand complexes.

Stable phase	**Temp. range of decomp. ^oC**	**Peak temp. at DTG ^oC**	**Weight loss % found (calc.)**
C1: [Zn HL (en)Cl_2]$2H_2O$ $1.5C_2H_5OH$			
↓ - $0.5C_2H_5OH$	23 -126	*	4.21 (4.12)
↓ - C_2H_5OH ↓ -$2H_2O$ ↓ - en ↓ - Cl-Ph	126-326	166.23	45.82 (45.35)
↓ - Cl_2	326-385	355.21	12.50 (12.76)
↓ - CH_3-ph-NH – ↓ - C=N ↓ - CH	385-485	450.59	24.99 (25.98)
Zn (residue)			12.40 (11.72)
C2: [Cd HL (en)Cl_2]$0.35H_2O$			
↓ - $0.35H_2O$	23 -270	*	1.21 (1.24)
↓ - Cl-Ph-CH	270 - 520	299.73	24.65 (24.59)
↓ -en – ↓ -C=N ↓-HN-Ph-CH_3 ↓- $0.7CdCl_2$ (volatilization)	520 - 650	598.78	62.50 (63.41)
0.3 $CdCl_2$ (residue)			10.00 (10.89)
C3: [Hg L(en)$(H_2O)_2$]0.25 H_2O			
↓ - $0.25H_2O$	85-140	137.80	0.79 (0.81)
↓ - $2H_2O$	140-210	*	5.00 (6.48)
↓ - L ↓ - en ↓ -Hg	210-370	224.70	93.60 (92.71)
No residue [No metal remained (volatilization)]			….......

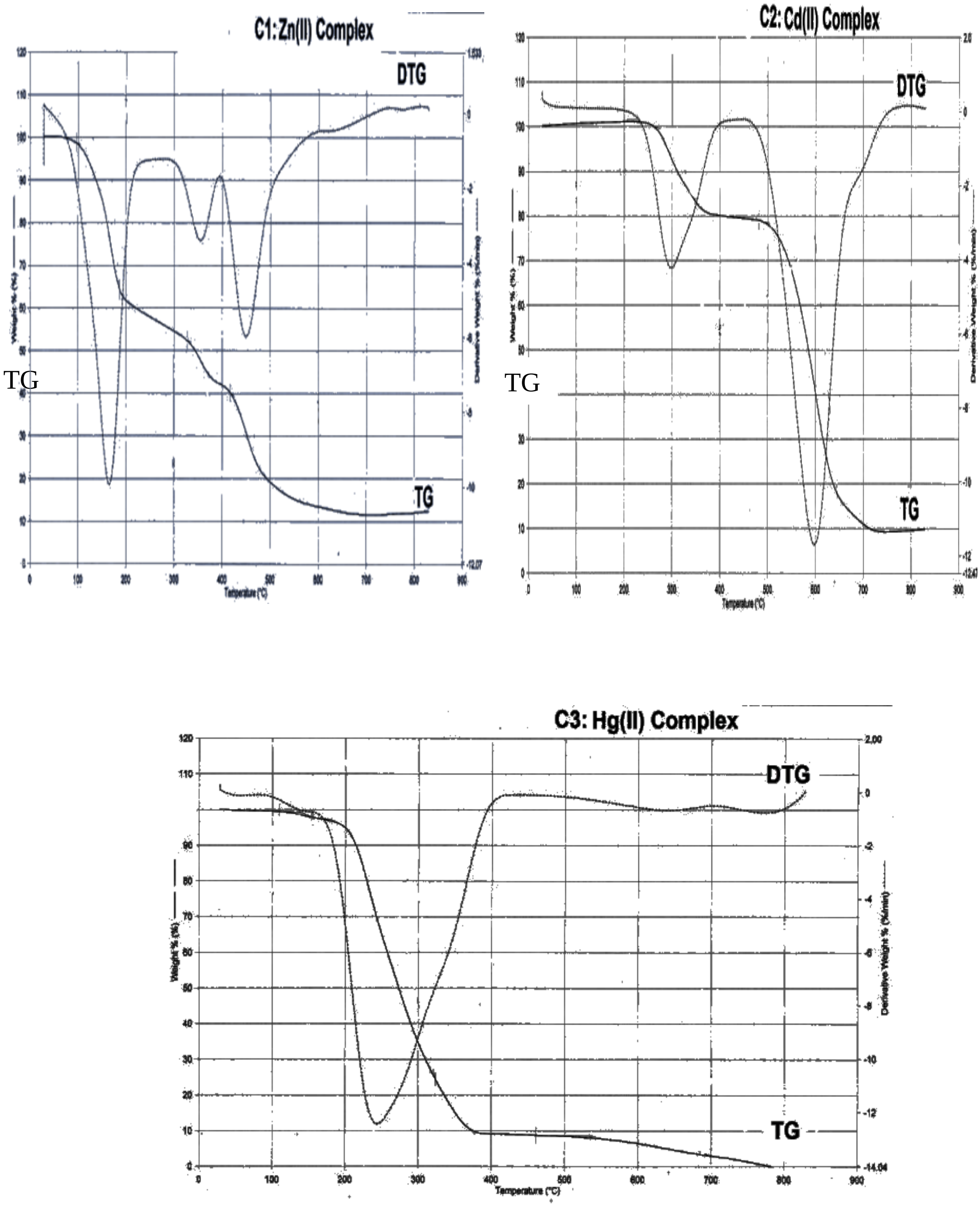
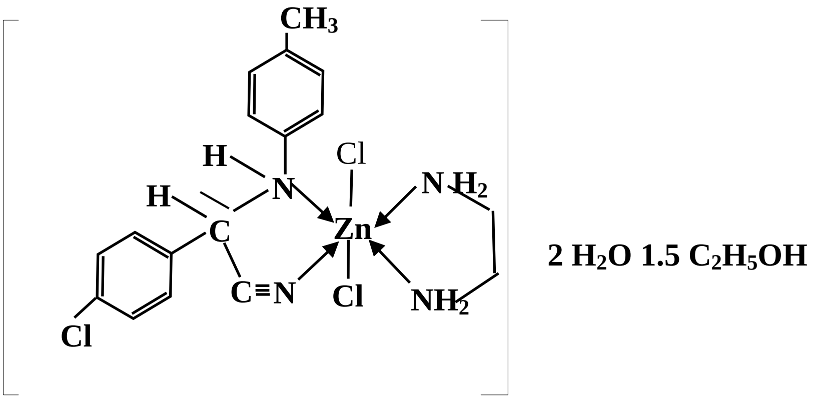


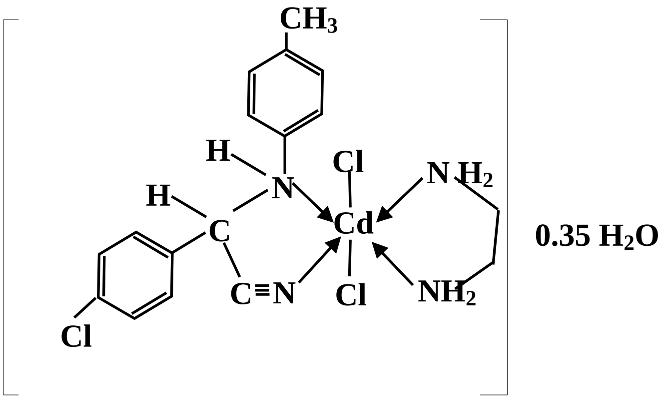
Figure 4- The thermograms of mixed ligand complexes; C1 of Zn (II), C2 of Cd(II) and C3 of Hg(II) by TG & DTG

According to the above-mentioned data the structures of metal complexes can be suggested as instated in scheme **1**

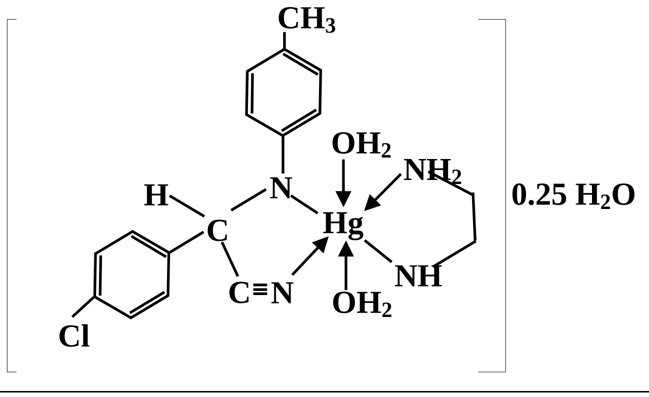
C1 : [Dichloro – ethylene diamino - {(P-methyl anilino) –P– chloro phenyl acetonitrile} Zinc (II)] (2) Hydrate (1.5) Ethanol.



C2 :[Dichloro – ethylene diamino - {(P-methyl anilino) –P– chloro phenyl acetonitrile} Cadmium (II)] (0.25) Hydrate.



C3 : [Diaqua – ethylene amido amino - {(P-methyl anilino) –P– chloro phenyl acetonitrile} Mercury (II)] (0.25) Hydrat.



Scheme1- The suggested stereochemistry structures and names for metal complexes of mixed ligand.

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