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Synthsis and Structural Characterization of New Metal Complexes and Mixed Ligand Complexes of 2-N-(3, 4-DIHYDROXY BENZYLIDENE) BENZOTHIAZOLE

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Abstract

The new Schiff base 2-N-(3,4-dihyroxy benzylidene) benzothiazole (H2L1) was prepeared from reaction of 2-aminobenzothiazol (2-ABT)and 3,4- dihdroxy benzaldehyde. Metal complexes of the new ligand with metal ions Co(II), Ni(II), Cu(II), Pd(II), Pt(IV), and Ru(III) were prepared by reacting H_2L_1. (2 mmole) with the metal ions (1mmole) in presence and absence of triethylamine (Et_3N,2mmole) in ethanol . Mixed ligand complexes ($ML'L_I$) were synthesised by reacting H_2L_I and other ligands L' acetylacetone, (acac). ethylene diamine (en), 2,2- bipyridyl (bipy), and the Schiff base HL_{II} that has been already prepared from 2-ABT and salicylaldehyde, with metal ions and ET_3N in a molar ratio of 1:1:1:2, respectively in ethanol. Structures of the new compounds were characterised by elemental and thermal analyses as well as i.r and u.v- visible spectra. The magnetic properties and electrical conductivities of metal complexes were also determined . Some complexes exhibted biological activities against two types of pathogenic bacteria.

الخلاصة

حضرت قاعدة شيف الجديدة 2-N-(3و4- ثنائي هيدروكسي بنزايلدين) بنزوثايازول (H2L1) من مفاعلة 2-أمينوبنزوثايازول (2-ABT) مع 3و4- ثنائي هيدروكسي بنزالديهيد. حضرت معقدات الليكاند مع ايونات الفلزات :. الكوبلت (II) والنيكل (II) والنحاس (II) والبلاديوم(II) والروثينيوم (III) بمفاعلة (2ملمول) H_2L_I مع 1 ملمول من الايون باضافة او بدون اضافة ثلاثي اثيل امين (Et_3N) في الايثانول حضرت معقدات فلزية جديدة (ML_IL') لخليط من HL_I مع ليكندات اخرى L' (L' = استيل اسيتون (acac) واثيلين ثنائي الامين (en) و 2و2- ثنائي البريديل (bipy) وقاعدة شيف HL_{II} المحضرة سابقا من مفاعلة 2-ABT مع ساليسيل الديهيد).

شخصت التراكيب الكيميائية للمركبات الجديدة باعتماد التحليل الدقيق للعناصر والتحاليل الحرارية فضلا عن اطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية – المرئية. كما حددت الخصائص المغناطيسية والتوصيلية الكهربائية للمعقدات الفلزية . اظهرت بعض المعقدات فعالية بيولوجية ضد نوعين من البكتريا المرضية.

Introduction

The synthesis of Schiff bases from condensation of 2-ABT with different aldehydes have been reported earlier [1-3]. Some of these bases exhibited antimicrobial and anticancer activities[1,2,4]. The biological activities were attributed mainly to azomethin group as well as to the biologically active thiazole ring [5-7]. Some complexes of Schiff bases were found more active than the parent ligands against bacteria and fungi [2,3] and as herbicides [8]. Complexes containing more than one metal centre represent synthetic models of ferromagnetic interaction between metal centres which can explain oxidation-reduction processes in biological systems in addition to their catalytic and biological activities [9-11]. This gave us motives to synthesise new metal complexes of a new Schiff base 2-N-(3,4-dihydroxybenzylidene) benzothiazole (H_2L_1) and other complexes from a mixture of H_2L_1 and other ligands (acac, en, 2,2-bipy, and the previously prepared Schiff base HL_{II})[3] to offer more binding sites that allow for binuclear, trinuclear complexation or more with metal ions.

Experimental

Melting points (uncorrected) were obtained by using Gallenkamp MF-600- 010F melting point apparatus. Elemental analyses were performed by using Elmental analyses-Perkin Elmer 240 B. Infrared spectra of H_2L_1 and its metal complexes were recored as KBr and CsI discs respectively on Perkin Elmer 983. GIP Pye Unicam SP_3-300 i.r. Spectrophotometer. Electronic spectra were recorded on u.v- visble Spectrophotometer Shimadzu u.v. –160 A. Thermal analyses by TG and DTG were obtaned by using Thermogravimetric analyser (TGA). A Du-Pont Thermobalance Model 951. Electrical conductivities of metal complexes at room temperature were measured by using Capacitor Analyser and Resistance Bridge type CRB_3. Magnetic susceptibility ($\mu_{eff.}$B.M) of metal complexes were measured at room temperature by following Faraday's method using Bruker Magnet B.M.G. Metal contents were determined by using Schimadzu –680G atomic obsorption flame emission Spectrophotometer.

b) Materials and methods

Metal salts $RuCl_3$ $3H_2O$ 98%, H_2PtCl_6. $6H_2O$, 83%, $Ni(CH_3COO)_2$. $4H_2O$ (Purum), $PdCl_2$ 60% (Fluka); $CuCl_2$. $2H_2O$. 98.5% (Hopkins):$CoCl_2$. $6H_2O$ (extra pure). (Merck) were used as received from suppliers. 3,4-Dihydroxy benzaldehyde 98%, benzonitrile (Puriss) (Fluka) and triethyl amine Et_3N, 99.5% (BDH) were used without further purification. Dimethyl formamide (DMF) and ethanol were dried and distilled prior to use[12,13]. 2-ABT was purified by crystallisation from boiling water[14]. 2-Chlorobenzonitrile palladium (II) was prepared according to a previously published method[15].

Preparation of H_2L_1 and HL_{11}: A solution of 2-ABT (1 mmole) in dry ethanol was added to 3,4-dihydroxy benzaldehyde or salicylaldehyde (1 mmole) dissolved in a minimum amount of dry ethanol. 3-4 drops of piperidine were added and the solution was heated in a water bath for 30 min. with continueous stirring at 70°C. A precipitate was formed after cooling the mixture to room temperature. The product was filtered off, and washed with cold ethanol, followed by ether, crystallized from ethanol and then dried under vacuum.

Preparation of metal complexes of H_2L_1 (C_1-C_7):

A solution of a metal salt of Co(II), Ni(II), $Cu_{(II)}$, $Pd_{(II)}$, $Pt_{(IV)}$, and $Ru_{(III)}$ respectively in ethanol was added to a solution mixture of (H_2L_1) and Et_3N in absolute ethanol in a molar ratio of 1:2:2 respectively with continuous stirring.. Precipitation of C_3 and C_4 took place immediately, while precipitation of other complexes required heating under reflux for 1-1.5 hr. The products were filtered off, washed with cold ethanol, followed by ether and dried under vacuum.

Preparation of complexes of H_2L_1 (C_8-C_{11}):

These complexes were prepared following the same previously mentioned method without the addition of Et_3N. Precipitates were formed immediately. Each mixture was heated for 30 min to allow complete precipitation. The products were purified by the same previous manner.

Preparation of mixed ligand complexes (C_{12}-C_{16}):

An ethanolic solution of metal salts of the ions Co(II), Cu(II), Pd(II), Pt(IV), and Ru(III) was added to a mixture of (H_2L_1) and Et_3N and L' (acac, en, bipy, and $HL_{(11)}$) in absolute ethanol, with continueous stirring. The molar ratio of reactants was 2:1:1 except for C_{16} in which it was 3:3:1 respectively. Precipitation took place immediately. Each mixture was heated under reflux for 30 min to allow complete precipitation. The products were purified in the same previous manner.

Results and Discussions

a) Physical data and elemental analyses

Table (1) describes the physical properties of H_2L_1 and its metal complexes in absence and presence of other ligands, together with the elemental analyses. The suggested molecular formulae were further supported by thermal analyses and spectral studies.

Elemental analyses of few complexes showed less agreeable results in nitrogen contents. This may be attributed to incomplete combustion as well as instrumental errors. The suggested molecular formulae were further supported by thermal analysis and spectral studies.

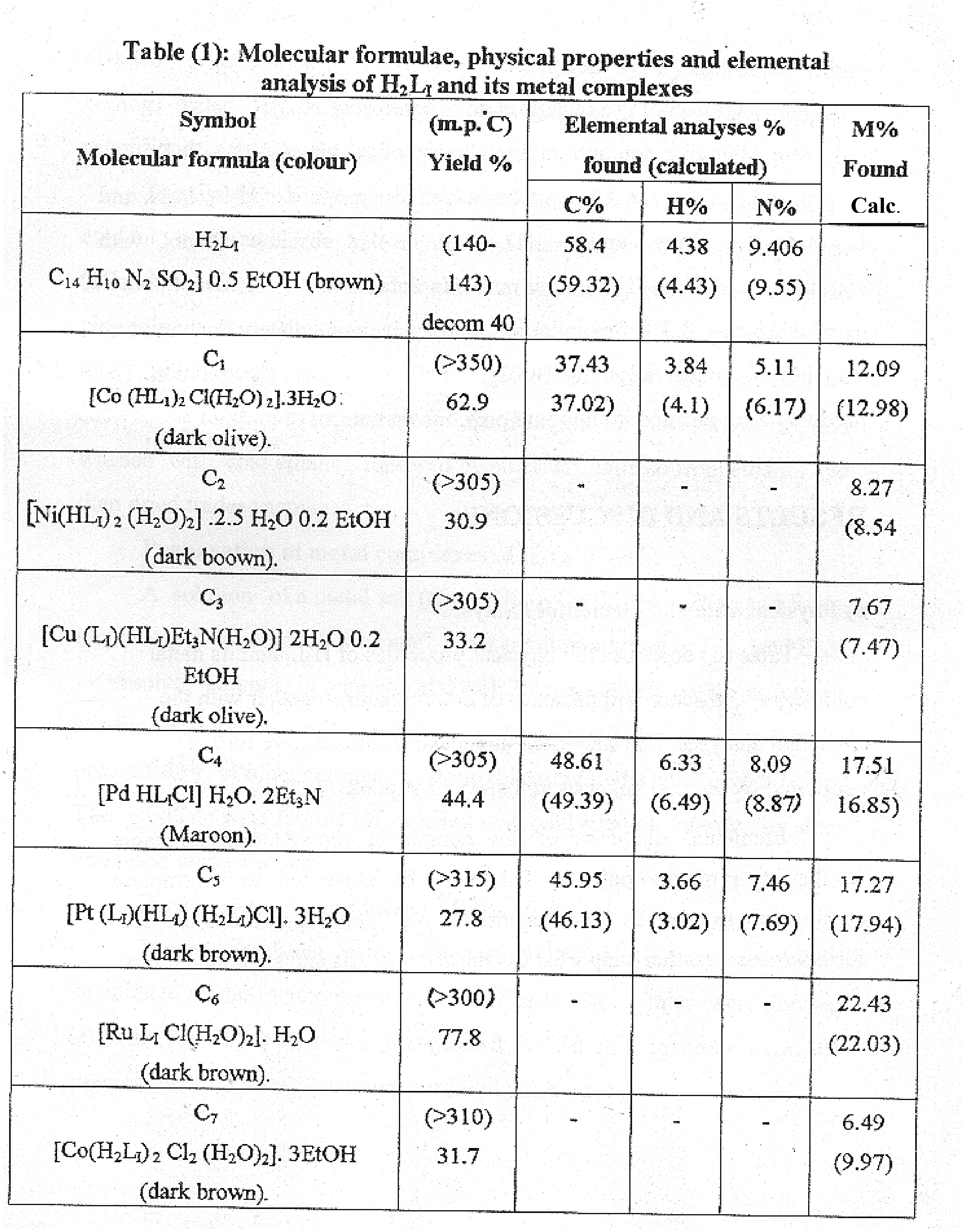


Table (1): Molecular formulae, physical properties and elemental analysis of H_2L_I and its metal complexes

Symbol Molecular formula (colour)	(m.p.°C) Yield %	Elemental analyses % found (calculated)			M% Found Calc.
		C%	H%	N%	
H_2L_1 $C_{14} H_{10} N_2 SO_2]$ 0.5 EtOH (brown)	(140- 143) decom 40	58.4 (59.32)	4.38 (4.43)	9.406 (9.55)	
C_1 $[Co (HL_1)_2 Cl(H_2O)_2].3H_2O$ (dark olive).	(>350) 62.9	37.43 37.02)	3.84 (4.1)	5.11 (6.17)	12.09 (12.98)
C_2 $[Ni(HL_I)_2 (H_2O)_2]$ .2.5 H_2O 0.2 EtOH (dark boown).	(>305) 30.9	-	-	-	8.27 (8.54
C_3 $[Cu (L_I)(HL_I)Et_3N(H_2O)]$ $2H_2O$ 0.2 EtOH (dark olive).	(>305) 33.2	-	-	-	7.67 (7.47)
C_4 $[Pd HL_ICl] H_2O. 2Et_3N$ (Maroon).	(>305) 44.4	48.61 (49.39)	6.33 (6.49)	8.09 (8.87)	17.51 16.85)
C_5 $[Pt (L_I)(HL_I) (H_2L_I)Cl]. 3H_2O$ (dark brown).	(>315) 27.8	45.95 (46.13)	3.66 (3.02)	7.46 (7.69)	17.27 (17.94)
C_6 $[Ru L_I Cl(H_2O)_2]. H_2O$ (dark brown).	(>300) 77.8	-	-	-	22.43 (22.03)
C_7 $[Co(H_2L_I)_2 Cl_2 (H_2O)_2]$. 3EtOH (dark brown).	(>310) 31.7	-	-	-	6.49 (9.97)

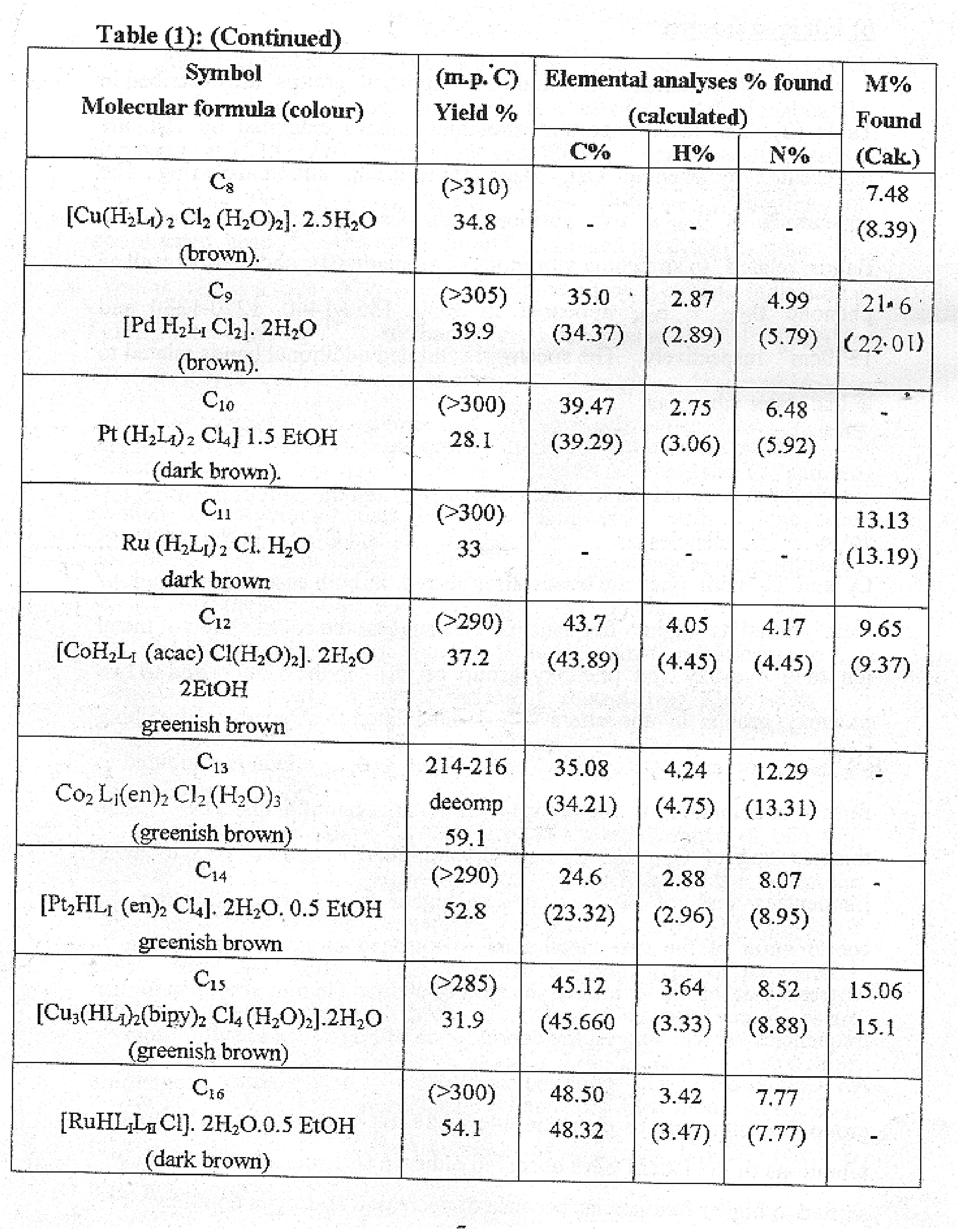


Table (1): (Continued)

Symbol Molecular formula (colour)	(m.p.°C) Yield %	Elemental analyses % found (calculated)			M% Found (Calc.)
		C%	H%	N%	
C_8 $[Cu(H_2L_I)_2Cl_2(H_2O)_2].2.5H_2O$ (brown).	(>310) 34.8	-	-	-	7.48 (8.39)
C_9 $[PdH_2L_ICl_2].2H_2O$ (brown).	(>305) 39.9	35.0 (34.37)	2.87 (2.89)	4.99 (5.79)	21•6 (22·01)
C_{10} $Pt(H_2L_I)_2Cl_4]$ 1.5 EtOH (dark brown).	(>300) 28.1	39.47 (39.29)	2.75 (3.06)	6.48 (5.92)	-
C_{11} $Ru(H_2L_I)_2Cl.H_2O$ dark brown	(>300) 33	-	-	-	13.13 (13.19)
C_{12} $[CoH_2L_I(acac)Cl(H_2O)_2].2H_2O$ 2EtOH greenish brown	(>290) 37.2	43.7 (43.89)	4.05 (4.45)	4.17 (4.45)	9.65 (9.37)
C_{13} $Co_2L_I(en)_2Cl_2(H_2O)_3$ (greenish brown)	214-216 deeomp 59.1	35.08 (34.21)	4.24 (4.75)	12.29 (13.31)	-
C_{14} $[Pt_2HL_I(en)_2Cl_4].2H_2O.0.5$ EtOH greenish brown	(>290) 52.8	24.6 (23.32)	2.88 (2.96)	8.07 (8.95)	-
C_{15} $[Cu_3(HL_I)_2(bipy)_2Cl_4(H_2O)_2].2H_2O$ (greenish brown)	(>285) 31.9	45.12 (45.660	3.64 (3.33)	8.52 (8.88)	15.06 15.1
C_{16} $[RuHL_IL_{II}Cl].2H_2O.0.5$ EtOH (dark brown)	(>300) 54.1	48.50 48.32	3.42 (3.47)	7.77 (7.77)	-

b) Infrared spectra

The characteristic vibrations of important groups are described in Table (2). The most important stretching modes exhibited by H_2L_I are represented by phenolic OH, azomethine group and thiazole ring. The appearance of υ_{OH} at two positions indicates different environments [1,3]. Bands related to stretching vibrations of aromatic CH, and C=C as well as phenolic $\upsilon_{C-O} + \delta_{OH}$ appeared at 3020, 1550-1440, 1270-1230 and 1370 cm^{-1} respectively.

The spectrum exhibited additional bands related to lattice ethanol vibrations[16].

The i.r spectra of H_2L_1 complexes (C_1-C_{11}) showed the disappearance of one band related to υ_{OH} of H_2L_1 and the shift of the other to lower frequencies as in C_1, C_2, C_4 and C5. In the spectra of C_3 and C_6 both phenolic bands disappeared. In both cases υ_{C-O} vibrations were shifted to higher frequencies. This suggest the coordination of metal ion to a hydroxy and phenoxy group of H_2L_1 in the formers and two phenoxy group in the latters [10,17]. Bands related to azomethine stretching vibrations of H_2L_1 were shifted in C_1, C_3, C_4, and C_6. Which is attributed to further coordination of metal ions to imino nitrogen of Schiff base [3,18] . The thiazole ring of C_3, C_5, C_8 and C_{11} exhibited a shift of υ C=N to lower frequencies and of υ_{C-N} and υ_{C-S} to higher frequencies indicating the coordination of the two metal ions to nitrogen atom of thiazole ring[21]. Whereas that of C_9 exhibted the shift of all thiazole ring groups to higher frequencies which suggest the coordination of Pd(II) ion to sulfer atom[21]. All Complexes C_7-C_{11} exhibited coordination of metal ions to azomethine group. Coordination to phenolic OH were excluded as the stretching vibrations of the latters were observed either in their positions or slightly shifted to higher frequencies because of decreased hydrogen bonding [21].

As far as mixed ligand complexes (C_{12}-C_{16}) are concerned, the Co(II) complex C_{12} showed similar behaviour to that of C_1. Additional bands appeared at 1535, 1270, 1260, 1195 and 430 cm^{-1} and were attributed to $\upsilon_{C=C} + \upsilon_{C=O}, \delta_{C-H} + \upsilon_{C=C}, \upsilon_{C-CH3} +$ $\upsilon_{C=C}$ and υ_{Co-O} vibrations of coordinated acac [21]. The spectrum of C_{13} showed the disappearance of υ_{OH} as well as a shift of $\upsilon_{C=N}$ of azomethine nitrogen of H_2L_1 indicating a bridge type bonding [18]. New bands were observed at 1050, 1480, 2950-2840 and 490 cm^{-1} and were assigned to $\upsilon_{C-N}, \delta_{CH2}, \upsilon_{CH2}$ $and\ M-NH_2$ vibrations respectively together with assymmetric symmetric stretching vibrations and δNH_2 of coordinated en[21]. The Pt(IV) complex C_{14} showed similar behaviors to that of C_5 towards H_2L_1 with bridge type, coordination by azomethine group [18,19] . Vibrational modes of coordinated (en) showed the formation of Pt-NH2 and Pt-NH bonds [21].

The Cu(II) complex, C_{15} showed similar coordination behaviour to C_{14} towards C=N groups of Schiff base and thiazole ring. New peaks appeared at 1595, 1480 and 270 cm^{-1} were assigned to $\upsilon_{C=N}$. $\upsilon_{C=C}$ and υ_{Cu-} of coordinated bipy [21].

The Ru(III) complex, C_{16} exhibted the disappearance of one υ_{OH} band of H_2L_1 and, the disappearance of υ_{OH} of HL_{II} and the shift of the other υ_{OH} band of H_2L_1 to lower frequencies. The positions of $\upsilon_{C=N}$ of both Schiff bases were also shifted. This indicates a bridge type of polynuclear complexes. Bands related to M-N, M-O, M-S of all metal complexes are also given in table (2). The complexes C_1, and C_4-C_{16} showed stretching modes of M-Cl. The position of those bands and their modes in C_7, C_{9-11} refer to cis[21, 18, 31], while those of C_{10} and C_{13}-C_{15} refer to trans configurations [21, 22].

C) Electronic Spectra, Magnetic Susceptibility and Conductivity Measurements.

The ligand H_2L_1 exhibited two high intensity bands in both ethanol and DMF. The first band appeared at 36364 and 38610 cm^{-1} respectively (ε max=18683 and 27961 $\ell\ mol^{-1}\ cm^{-1}$ respectively) and the second band appeared at 33333 and 31640 cm^{-1} (ε max=15714 and 16191 $\ell\ mol^{-1}\ cm^{-1}$ respectively). The two bands were attributed to $\pi \rightarrow \pi^*$ transitions of the aromatic rings [16, 23] and to conjugated Schiff base system respectively. Bands related to $n \rightarrow \pi^*$ transition may be masked by the extended second band [16]. Complexation of H_2L_1 with metal ions caused bathochromic shifts with the appearance of new bands in the visible and near i.r regions. These bands were attributed to M-L charge transfer and to ligand field transitions. Table (3) describes bands of maximum absorption of complexes in DMF with their assignments. All complexes exhibted spectral behaviours of octahedral geometries [24-28] except palladium (II) complexes which showed square planar behaviours [24, 25]. Magnetic moments (μ_{eff} *BM*) of Co(II), Ni(II) and Cu(II) complexes showed high spin paramagnetic character, and complexes of Pd(II) and Pt(IV) ions were diamagnetic, whereas Ru(III) complexes were low spin paramagenetic. Crystal field parametrers B',10Dq, 10Dq/B' and β) in Co(II), Ni(II) complexes and positions of absent bands were calculated by applying band ratios and energies of absorption bands on Tanaba Saugano diagrams [24,25,27,28].

Copper (II) complexes exhibited behaviours of Jahn Teller distrotion[21]. Bands observed in Ru(III) complexes were referred mainly to Ligand → metal charge transfer which lie near intraligand $n \rightarrow \pi^*$ transition bands[24].

Conductivity mesurements in DMF (10^{-3}M) showed that complexes were non electrolytes.

According to the above mentioned observations together with results obtained from CHN, atomic absorption, and thermal analyses and i.r spectra the stereochemical structures of the complexes were suggested as illustrated in scheme (1).

C) Thermal Analyses

Thermal decomposition stages and weight losses by TG and DTG techniques for some complexes of H_2L_1 and mixed ligand complexes are described in Table (4). Thermograms of some other complexes are shown in Figure (1). Results came in agreement with those obtained from elemental analyses. Complexes in which the metal ion is covalently bonded to phenoxy groups gave mainly metal oxides [29,30] as final products, while those bonded to azomethine groups only gave metal halides [29].

d) Antibacterial activity

A preliminary study on biological activity of the prepared compounds in DMF (1mg/ml) on gram (-) E.Coli and gram (+) B.Subt was carried out using plate agar method[31]. No antibacterial action was exhibited by H_2L_1. In contrast, complexes C_6, C_{10} exhibited growth inhibition against E.Coli of 10-12 mm diameter. The Co(II) complex C_{13} showed the same inhibition zone against both types. C_3, C_5 and C_{14} showed growth inhibition diameter of > 12 mm and C_{15} 19mm against B.subtluse.

Table (2): Characterterstic stretching vibrations υ (cm^{-1}) of i.r spectra for Schiff bases H_2L_I and metal complexes

Symbol	**Azome thine**	*Thiazole vibrations*			υ_{OH}	υ_{H2O}				
	$\upsilon_{C=N}$	$\upsilon_{C=N}$	υ_{C-N}	$\upsilon_{C=S}$	**Phenolic (EtOH)**	**Lattice (coordinate)**	$\upsilon_{C=N}$	υ_{M-O}	υ_{M-Cl}	υ_{C-O} **(Others)**
H_2L_I	1590	1520	1105	740	2910,2830* (3580-3180)	-	-	-	-	1270 -1230
C_1	1610	1520	1105	740	2815	3100-3620 (800 pr) (660pw)	(460sh)^a	(440)^d (290)^e (118)^f (415)^g	345	1290
C_2	1595	1520	1110	740	2890 (3500)	3380,3270 3140 H.b (660)	-	(460)^d (280)^e (920)^f (370)^g	-	1285
C_3	1555	1485	1170	745	(3660-3500)	3500-3100 (865 pr) (805 pw)	(525)^a (250)^b (325)^c	(460)^d (385)^b	-	1300
C_4	1610	1520	1105	740	2900 (3620-3500)	3500-3030	(480)^a	(410)^d (295)^e (1180)^f	370	1290
C_5	1590	1510	1115	745	2800	3660-3300	(240)^b	(400)^d (280)^e (1170)^f	330	1300
C_6	1600-1560	1520	1105	740	-	3660-3160 (800p)(660w)	(480)^a	(405)^d (395)^g	330	1310
C_7	1550	1520	1105	740	2910,2830 (3580-3080)		(500)^a	(400)^g	360 330	-
C_8	1630-1580	1505	1170	747	2910,2830	3660-3100 (850 pr) (665 pw)	(495)^a	(370)^g	350 330	-
C_9	1590-1560	1535 1518	1115	755	2920,2850	3340-3160	(460)^a	-	360 330	(380) υ_{M-S}

Table (2): (Continued)

Symbol	Azome thine	*Thiazole vibrations*			υ_{OH} Phenolic (EtOH)	υ_{H2O} Lattice (coordinate)	$\upsilon_{C=N}$	υ_{M-O}	υ_{M-Cl}	υ_{C-O} (Others)
	$\upsilon_{C=N}$	$\upsilon_{C=N}$	υ_{C-N}	$\upsilon_{C=S}$						
C_{10}	1610	1520	1105	745	2920,2830 (3580-3220)	-	(450)^{a} (260)^{b}	-	355sh 330	-
C_{11}	1620	1500	1180	755	2930,2870	(660)	(440)^{a} (280)^{b}	(410)^{g}	360 330 300	-
C_{12}	1560	1515	1105	740	2910,2830 (3640-3400)	3400-3150 (690 pr) (600 pw)	500^{a}	(360)^{j} (430)^{k}	290	(610) MO. Ring deform
C_{13}	1620-1610	1520	1110	740	-	(690 pr) (600 pw)	(545)^{a} (490)^{e}	(510)^{g} (460)^{j}	360	
C_{14}	1630	1480	1125	765	2780 3580-3380	3380-3300	(540)^{a} (230)^{b} (420)^{d} (580)^{e}	(470)^{g} (360)^{h} (1180)^{I} (420)^{j}	330	
C_{15}	1650	1480	1150	750	2900,2840	3540-3140 (650)	(550)^{a} (220)^{b} (270)^{f}	(440)^{g} (225)^{h} (1050)^{I} (1090)^{I} (410)^{j}		
C_{16}	1590-1550	1510	1115	740	2900 (3500-2840)	3500-3140 (880)	(570)^{a}	(490)^{g} (260)^{h} (1160)^{i} (460)^{j}	345	

υ_{M-N} of: (a) Sciff base; (b) thiazole ring; (c) Et_3N; (d) NH_2 of en; (e) NH (en); (f) bipy

υ_{M-O} of: (g) H_2L_I; (h) OH; (i) δ_{MOH}; (j) coord. H_2O; (k) acac ;(*) affected by hydrogen bonding.

Table (3): Electronic Spectral data electrical conductivities (DMF 10^{-3}), Magnetic susceptibilities (μeff, B.M) and suggested geometries for metal complexes of H_2L_1 and Mixed ligands complexes.

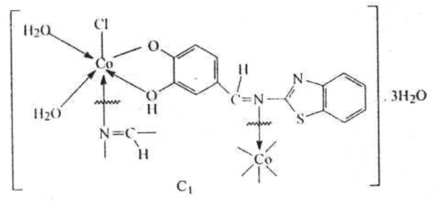
Symbol	Maximum absorrption υ max(cm^{-1})	Band assignment	Dq/B′	B′ (cm^{-1})	β	10Dq (cm^{-1})	υ_2/υ_1	Conductivity Scm^2mo^{-1}	μeff BM	Suggested geometry
C_1 (Co(II))	υ_1 5876(cal) υ_2 12821 υ_3 17680	$^4Tig\rightarrow{}^4T_2g$(F) $^4Tig\rightarrow{}^4A_2g$(F) $^4Tig\rightarrow{}^4T_1g$(P)	0.76	858	0.88	6527	2.18	11.6	4.44	Octahedral
C_2 (Ni(II))	υ_1 8207(cal) υ_2 13333 υ_3 22222	$^3A_2g\rightarrow{}^3T_2g$(F) $^3A_2g\rightarrow{}^3T_2g$(F) $^3A_2g\rightarrow{}^3T_1g$(P)	1.15		0.71	8384	1.62	11.9	4.04	Octahedral
C_3 (Cu(II))	υ_1 13295 υ_2 16666 υ_3 21000	$^2B_1g\rightarrow{}^2A_1g$ $^2B_1g\rightarrow{}^2B_2g$ C.T., $\pi \rightarrow \pi$ *	-	-	-	-	-	9.2	2.70	Octahedral
C_4 (Pd(II))	υ_1 20492 υ_2 25842	$^1A_1g\rightarrow{}^1B_1g$ $^1A_1g\rightarrow{}^1Eg$	-	-	-	20492	-	10.9	Diamagnetie	Square planar
C_5 (Pt(IV))	υ_1 22989 υ_2 26525	$^1A_1g\rightarrow{}^3T_1g$ $^1A_1g\rightarrow{}^1T_1g$	-	-	-	-	-	30.4	Diamagnetie	Octahedral
C_6 (Ru(III))	υ_1 12346 υ_2 18254	$^2T_2g\rightarrow{}^4T_1g$ $^2T_2g\rightarrow{}^2A_2g$, ^2T_1g	-	-	-	-	-	15.5	1.39	Octahedral

Table (3): (Continued)

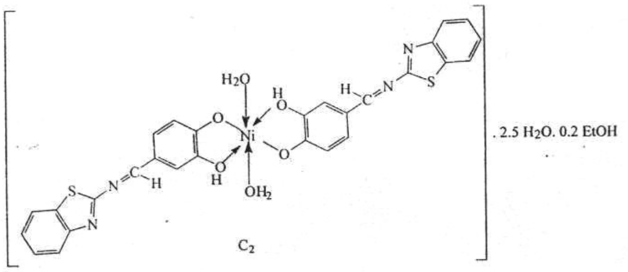
Symbol	**Maximum absorrption υmax(cm^{-1})**	**Band assignment**	**Dq/B´**	**B´ (cm^{-1})**	**β**	**10Dq (cm^{-1})**	**υ_2/υ_1**	**Conductivity Scm^{2}mo^{-1}**	**µeff BM**	**Suggested geometry**
C_7 (Co(II))	$\upsilon_1$6333(cal) $\upsilon_2$13600 $\upsilon_3$16965	$^4T_1g \rightarrow {}^4T_2g$ (F) $^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	0.91	771	0.79	7017	2.15	15.7	5.33	Octahedral
C_8 (Cu(II))	$\upsilon_1$12048 $\upsilon_2$15646 $\upsilon_3$18868 $\upsilon_4$22727	$^2B_1g \rightarrow {}^2A_1g$ $^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$ CT	-	-	-	-	-	42.8	2.72	Octahedral
C_9 (Pd(II))	$\upsilon_1$23256	$^1A_1g \rightarrow {}^1B_1g$	-	-	-	23256	-	14.1	Diamagnetie	Square planar
C_{10} (Pt(IV)	$\upsilon_1$18868 $\upsilon_2$22222 $\upsilon_3$27701	$^1A_1g \rightarrow {}^3T_1g$ $^1A_1g \rightarrow {}^3T_2g$ $^1A_1g \rightarrow {}^1T_1g$	-	-	-	-	-	40.5	Diamagnetie	Octahedral
C_{11} (Ru(III))	$\upsilon_1$13333 $\upsilon_2$18700 $\upsilon_3$25000	$^2T_1g \rightarrow {}^4T_1g$ $^2T_2g \rightarrow {}^2A_2g, {}^2T_1g$ L→MCT	-	-	-	-	-	27.1	1.41	Octahedral
C_{12} Co(II)	$\upsilon_1$6154(cal) $\upsilon_2$13333 $\upsilon_3$17969	$^4T_1g \rightarrow {}^4T_2g$ (F) $^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	0.82	856	0.88	7016	2.17	3.4	5.54	Octahedral

Table (3): (Continued)

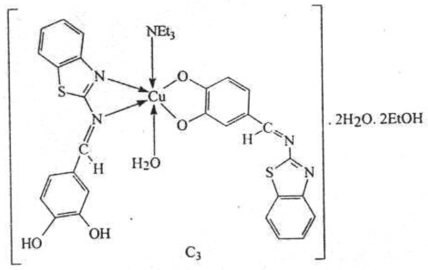
Symbol	**Maximum absorrption υmax(cm^{-1})**	**Band assignment**	**Dq/B′**	**B′ (cm^{-1})**	**β**	**10Dq (cm^{-1})**	**υ_2/υ_1**	**Conductivity Scm^{2}mo^{-1}**	**μeff BM**	**Suggested geometry**
C_{13} Co(II)	$\upsilon_1$6459(cal) $\upsilon_2$13812 $\upsilon_3$18750 $\upsilon_3$26385	$^4T_1g\rightarrow{}^4T_2g$ (F) $^4T_1g\rightarrow{}^4A_2g$ (F) $^4T_1g\rightarrow{}^4T_1g$ (P) M→L CT	0.76	897	0.93	6818	1.9	18.5	4.44	Octahedral
C_{14} Pt(IV)	$\upsilon_1$21739 $\upsilon_2$25510	$^1A_1g\rightarrow{}^3T_1g$ $^1A_1g\rightarrow{}^1T_1g$						39	Diamagnetie	Octahedral
C_{15} Cu(II)	$\upsilon_1$15873 $\upsilon_2$19531 $\upsilon_3$23866	$^2B_1g\rightarrow{}^2B_2g$ $^2B_1g\rightarrow{}^2Eg$ CT, $\pi\rightarrow\pi$ *						35.3	2.24	Octahedral
C_{16} Ru(III)	$\upsilon_1$12346 $\upsilon_2$20833 $\upsilon_3$25316	$^2T_2g\rightarrow{}^4T_2g$ $^2T_1g\rightarrow{}^2A_2g$, ^2T_1g, L→M CT						16.9	1.38	Octahedral



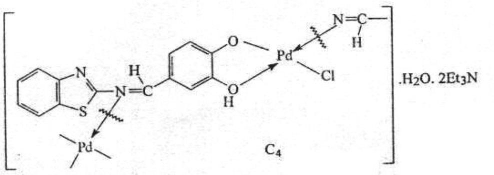
C₁



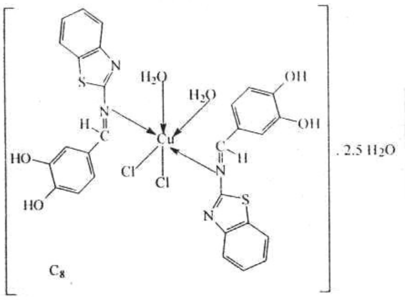
C₂



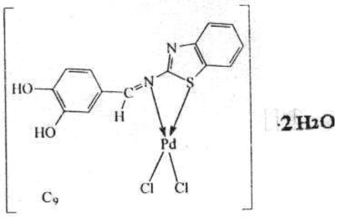
C₃



C₄

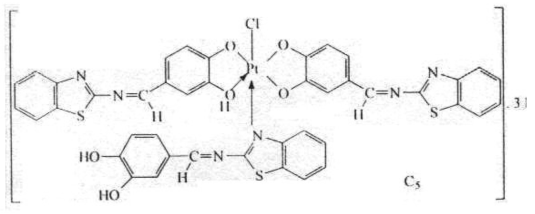


C₈

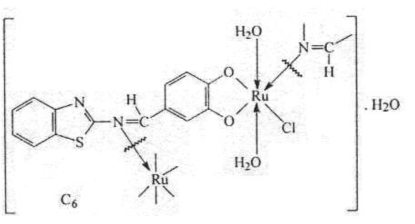


C₉

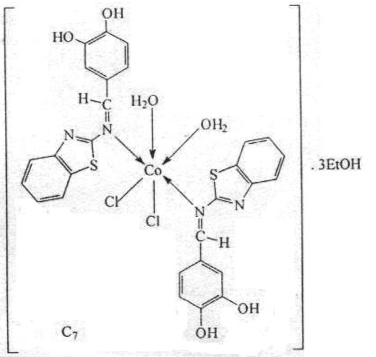
Scheme (1): Suggested stereochemical structures and names of H_2L_I and mixed ligands metal complexes



C₅

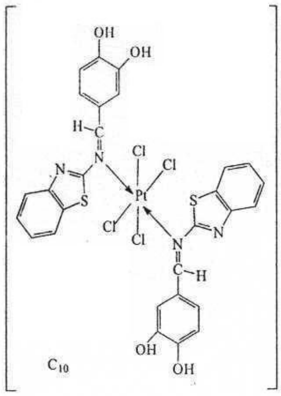


C₆

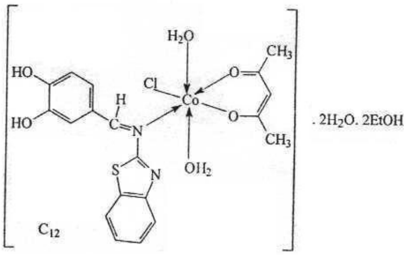


C₇

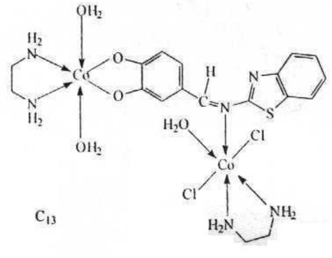
C_1	[Chlorodiaqua{N-2-(benzothiozolyl) -4-oxo-3-hydroxobenzylidene-iminato}cobalt(II)]Water(3)
C_2	[Diaquabis{N(4-oxo-3-hydroxo benzylidene-imino) benzothiazole} nickel(II)]Ethanol(0.2) Water(2.5).
C_3	[Aqua{N-(3,4-dioxobenzylidene)-benzothiazole}{N-2-(benzothia-zolyl)-3,4-dihydroxybenzylidene iminato}copper(II)].Ethanol(2) Water(2).
C_4	[Chloro{N-2(benzothiazolyl-4-oxo-3-hydroxobenzylideneiminato} palladium(II)].Triethylamine(2) Water(1)
C_5	[Chlorobis{N-(4-oxo-3-hydroxo benzylidene)benzothiazole}{N`-2-(benzothiazolyl)-3,4-dihydroxy bezylidene-imino}platinum(IV)]. Water(3)
C_6	[Chlorodiaqua{N-2-(benzothiazo-lyl)-3,4-dioxobenzylideneiminato} ruthenium(III)]. Water(1)
C_7	[Dichlorodiaquabis{N-2-(benzothiazolyl)-3,4-dihydroxybenzylidene iminato}cobalt(II)]. Ethanol(3)
C_8	[Dichlorodiaquabis{N-2-(benzo-thiazolyl)-3,4-dihydroxy benzylidene-iminato}copper(II)] Water(2.5).
C_9	[Dichloro{N-2-(benzo-thiazolo-S)-3,4-dihydroxy benzylideneiminato} palladium(II)]Water(2)



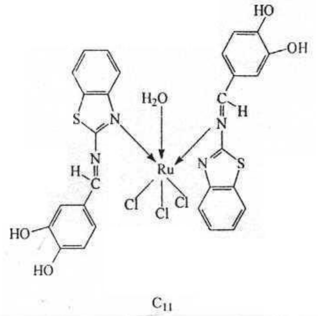
C_{10}



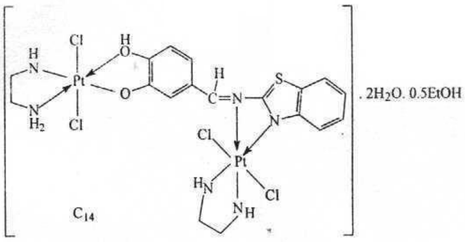
C_{12}



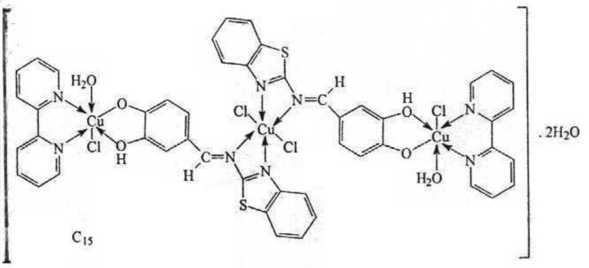
C_{13}



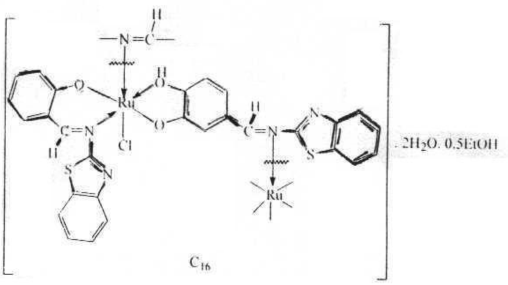
C_{11}



C_{14}



C_{15}



C_{16}

C_{10}	**[Tetrachlorobis{N-2-(benzothiazo-lyl)-3,4-dihydroxybenzylidene-iminato}platinum(IV)] Ethanol(1.5)**
C_{11}	**Trichloroaqua{N-2-(benzoyhiazo- lyl)-3,4-dihydroxybenzylidene-iminato}{3,4-dihydroxy-benzyli- dene} ruthenium(III)**
C_{12}	**[Acetylacetonatochlorodiaqua{N-2-(benzo-thiazolyl)-3,4-dihydroxy-benzylidene - iminato}cobalt(II)]Ethanol(2)Water(2).**
C_{13}	**Dichloro-μ-{N-2-(benzothiazolyl)-3,4-dioxo-benzylideneiminato}{diaquaethylene diaminocobalt(II)}aquaethylene-diaminocobalt (II)**
C_{14}	**[Dichloroethyleneamidoamino-μ-{N-2-(benzothiazolo-N`)-4-oxo-3-hydroxobezyli-deneiminato}platinum(IV)} dichloro-ethylenediamidoplatinum(IV)]. Ethanol (0.5) Water(2).**
C_{15}	**[Dichlorobis{chloro-4-oxo-3-hydroxo-benzylideneiminato(N-2-benzothiazolo-N`)aquabipyridylcopper(II)}copper(II)]. Water(2)**
C_{16}	**[Chloro{N-2-(benzothiazolyl)-4-oxo-3-hydroxobezylideneiminato}{N-2-(benzo-thia zolyl)-O-salicylideneiminato} ruthenium (III)]Ethanol(0.5)Water(2).**

Scheme (1): (Continued)

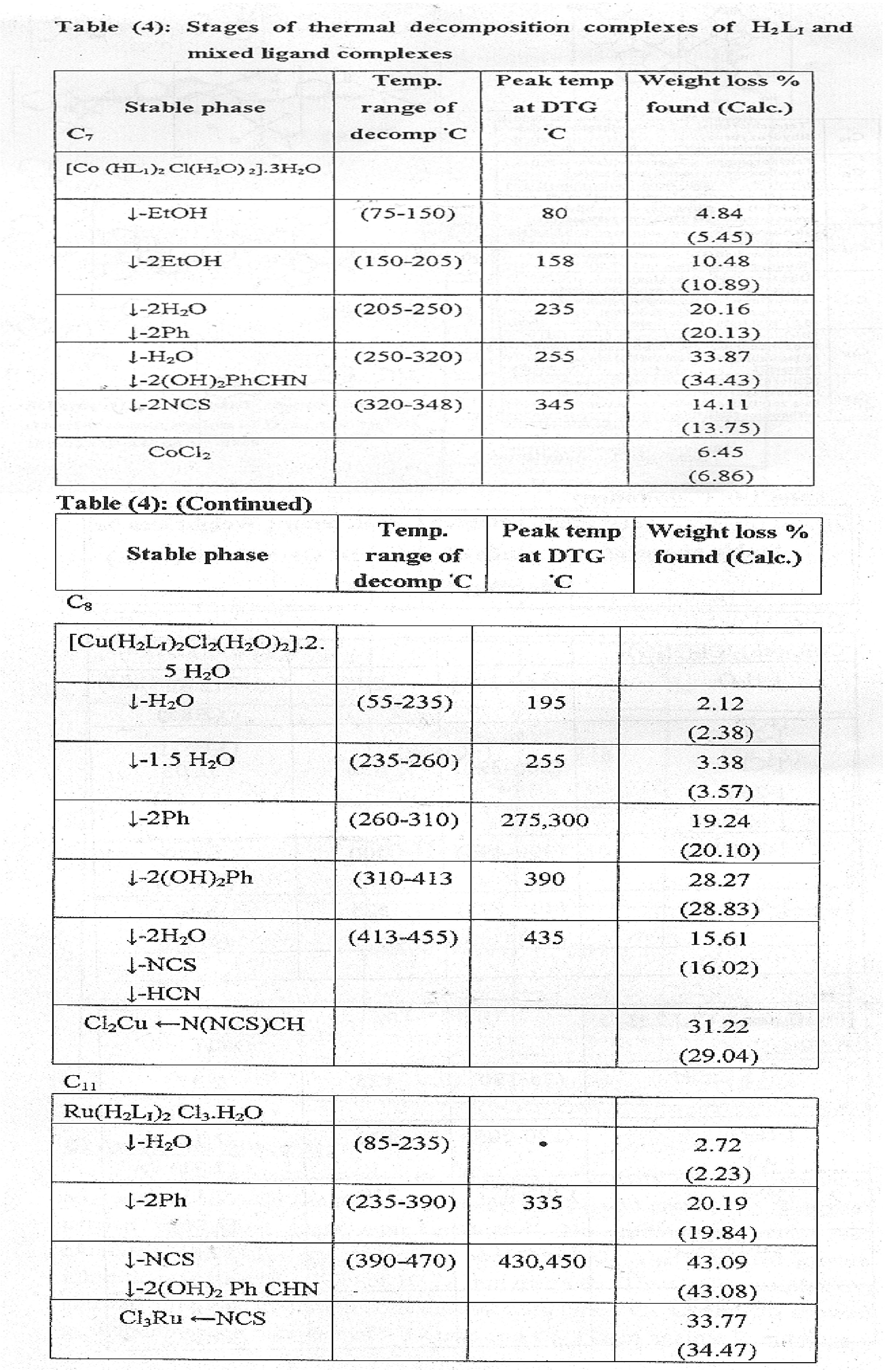


Table (4): Stages of thermal decomposition complexes of H_2L_I and mixed ligand complexes

Stable phase C_7	Temp. range of decomp ˚C	Peak temp at DTG ˚C	Weight loss % found (Calc.)
$[Co\ (HL_1)_2\ Cl(H_2O)_2].3H_2O$			
↓-EtOH	(75-150)	80	4.84 (5.45)
↓-2EtOH	(150-205)	158	10.48 (10.89)
↓-$2H_2O$ ↓-2Ph	(205-250)	235	20.16 (20.13)
↓-H_2O ↓-$2(OH)_2PhCHN$	(250-320)	255	33.87 (34.43)
↓-2NCS	(320-348)	345	14.11 (13.75)
$CoCl_2$			6.45 (6.86)

Table (4): (Continued)

Stable phase	Temp. range of decomp ˚C	Peak temp at DTG ˚C	Weight loss % found (Calc.)
C_8			
$[Cu(H_2L_I)_2Cl_2(H_2O)_2].2.5\ H_2O$			
↓-H_2O	(55-235)	195	2.12 (2.38)
↓-$1.5\ H_2O$	(235-260)	255	3.38 (3.57)
↓-2Ph	(260-310)	275,300	19.24 (20.10)
↓-$2(OH)_2Ph$	(310-413	390	28.27 (28.83)
↓-$2H_2O$ ↓-NCS ↓-HCN	(413-455)	435	15.61 (16.02)
$Cl_2Cu \leftarrow N(NCS)CH$			31.22 (29.04)
C_{11}			
$Ru(H_2L_I)_2\ Cl_3.H_2O$			
↓-H_2O	(85-235)	•	2.72 (2.23)
↓-2Ph	(235-390)	335	20.19 (19.84)
↓-NCS ↓-$2(OH)_2\ Ph\ CHN$	(390-470)	430,450	43.09 (43.08)
$Cl_3Ru \leftarrow NCS$			33.77 (34.47)

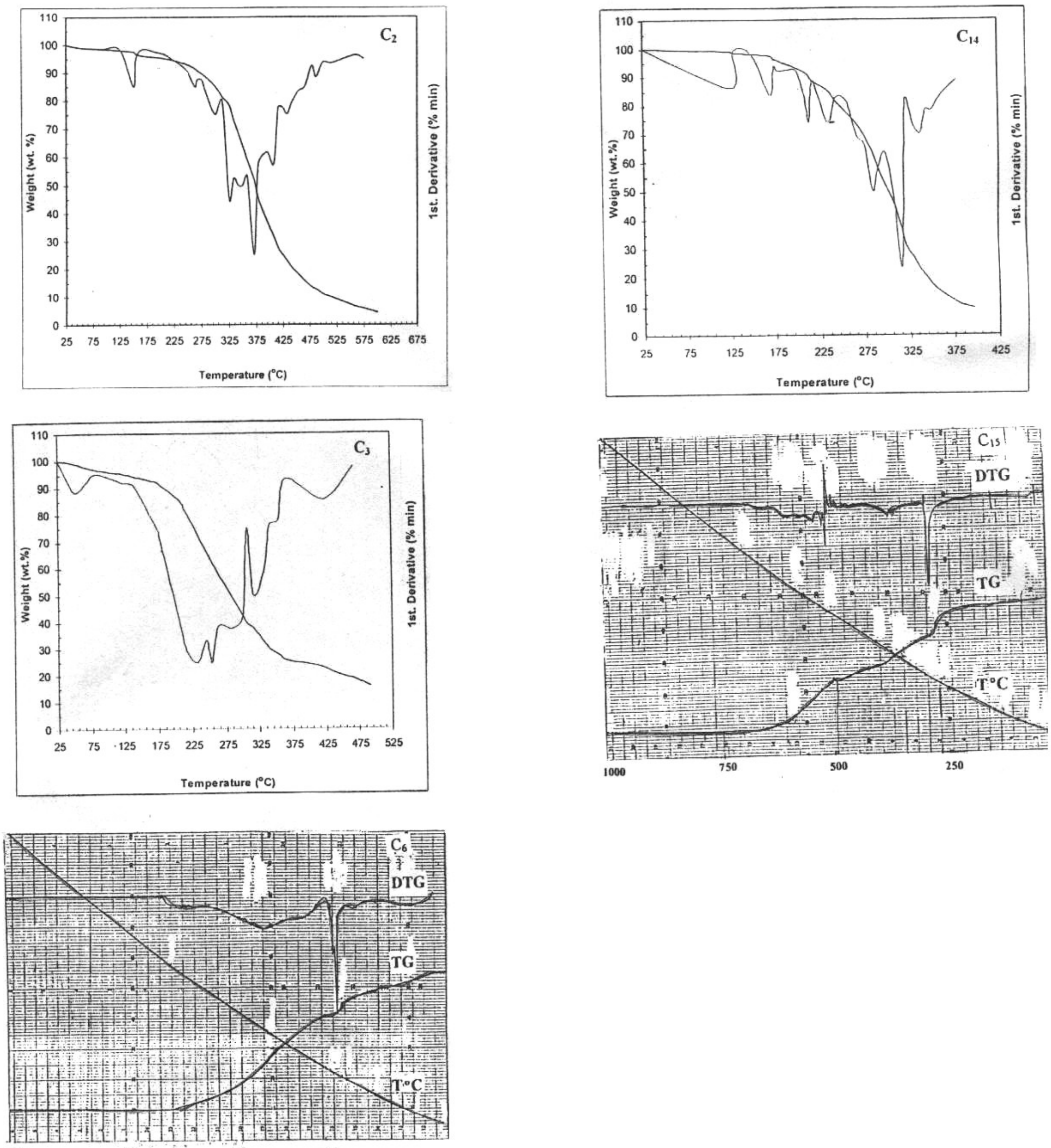


Figure (1) : Thermograms of some metal complexes of H_2L_1 and mixed ligand complexes by TG and DTG.

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