

Synthesis, Structure and Characterization of New Metal Complexes of Schiff Bases Derived from Isatin N-Benzylisatin and 4-Aminoantipyrine

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ABSTRACT

The two Schiff bases (z)-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino) indolin-2-one (**L_IH**), and (z)-1-benzyl-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-ylimino)indolin-2-one (**L_{II}**) have been prepared by condensation reaction of isatin and 1-benzyl isatin with 4-aminoantipyrine in dioxane and their structures were characterized by CHN analysis, NMR, IR and mass spectroscopy. A new Hg-metallated bisSchiff base ((E)-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-2-oxoindolin-1-yl((E)-3-(2-methyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazol-3-ylimino)-2-oxoindolin-1-yl)mercury (**Hg(L_I)₂**) was synthesized by condensation reaction of bis(2,3-dioxoindolin-1-yl) mercury(II) (**Hg(isatin)₂**) with 4-aminoantipyrine(4-AAP). Reaction of **L_IH** with Pt(II) and Cu(II) complexes in basic medium led to binding of the metal ions at N-1 atom of isatin ring while reaction of **L_IH** and **L_{II}** with metal salts in neutral medium resulted in the formation of metal complexes where the metal ion is coordinated to carbonyl and azomethine groups of the two ligands. The metal complexes were characterized and their structures were suggested depending on CHNM and thermal analysis, FTIR and electronic spectra, magnetic susceptibility as well as conductivity measurements. The structures of the Ni(II), Pt(II) and Hg(II) complexes were further supported by NMR spectroscopy.

Keywords: Schiff bases, isatin, 4-aminoantipyrine, bis(isatin)mercury(II)

1. INTRODUCTION

The high affinity for the chelation of the isatin Schiff bases towards the transition metal ions were reported to exhibit a wide range of biological activities such as analgesic¹, anticonvulsant^{1,2}, antidepressant³, anti-inflammatory³, antifungal³⁻⁷, antiviral^{3,4,7,8}, antitumor^{3,9-11}, antileukemic^{3,12}, anticancer⁶ and antiglycation activity¹³. Schiff bases derived from 4-aminoantipyrine (4-AAP) have been tested as antibacterial and antiparasitic agents¹⁴ and their complexes with metal ions such as Co(II), Ce(II), Pt(II), UO₂⁺², Cu(II), Mn(II), Fe(II), Ni(II) have been extensively investigated because of their biological, clinical, pharmacological and analytical importance^{5,15,16}. These applications gave us motives to study the coordination behavior of the two Schiff base ligands: (z)-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)indolin-2-one (**L_IH**), and (z)-1-benzyl-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-ylimino)indolin-2-one (**L_{II}**) with some transition metal ions to study their activity as anticancer agents in future work. The synthesis of the two ligands by reacting isatin or N-benzyl isatin with 4-aminoantipyrine in refluxing ethanol[17] was unsuccessful as no product was formed until more than 40 h after the addition of glacial acetic acid. In this work we report the immediate synthesis of **L_IH** and **L_{II}** in dioxane containing catalytic amount of glacial acetic acid. We also report for the first time the formation the N-1 metallated bis-Schiff base ((E)-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-2-oxoindolin-1-yl((E)-3-(2-methyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazol-3-ylimino)-2-oxoindolin-1-yl)mercury (**Hg(L_I)₂**) from the condensation reaction of 4-aminoantipyrine with bis(2,3-dioxoindolin-1-yl) mercury **Hg(isatin)₂**¹⁸. Such mercury adducts are important in understanding the effect of this metal ion on enzymatic and DNA functions.

2. EXPERIMENTAL

Melting points were determined on Gallenkamp M.F.D 600-010f melting point apparatus. Purity of Products was detected by using TLC techniques using a mixture of acetone: chloroform (1:1, 1:2 and 2:1 v/v) and acetone and chloroform only, as eluents. Infrared spectra were recorded using (KBr) and (CsI) discs on SHIMADZU FTIR-8400S, Fourier Transform, Infrared spectrophotometer. Electronic spectra of compounds in different solvents were recorded on SHIMADZU U.V-visible recording spectrophotometer U.V 1650 region (250-1100)nm. Elemental microanalyses were performed on Eurovector EA 3000A. The metal contents were determined by using Shimadzu AA 6200 Flame Atomic Absorption Spectrophotometer. Mass spectra were recorded on Shimadzu Qp 5050A. ¹H and ¹³C NMR were performed by using Bruker Ultra Shield 300 MHz NMR spectrophotometer. Thermal analyses of some metal complexes were carried out by using STA 409 PC Lux from NETZSCH (Germany). Electrical conductivity measurements for complexes in DMF, DMSO and DMA (10⁻³M) at room temperature, were carried out by using Radiometer Copenhagen CDM 83 conductivity meter. Magnetic moments μ_{eff} (B.M) for the prepared complexes in the solid state at room temperature were carried out by using Bruker Magent B.M-6 and Magnetic susceptibility balance Model MSB-MK-1. The chloride contents for complexes were determined by Mohr's method.

All chemicals were of pure grade and were used as supplied except ethanol and DMF which were dried and distilled prior to use. Dichlorobis(benzonitrile)palladium(II) [PdCl₂(PhCN)₂]¹⁹, cis-platinum(II) bis(triphenylphosphine) chloride (cis-PtCl₂(PPh₃)₂)²⁰, bis(2,3-dioxindolin-1-yl)mercury **Hg(isatin)₂**¹⁸ and N-benzylisatin^{21,22} were prepared according to methods reported in the literature.

2.1 Synthesis of Ligands

1. (Z)-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)indolin-2-one(**L_IH**):

- a) To a stirred solution of isatin (0.6906g, 4.7 m.mol) in dioxane (3.6 ml) was added a solution of 4-aminoantipyrine (0.9552 g, 4.7 m.mol) dissolved in (6.3 ml) of the same solvent. Then glacial acetic acid (6 drops) was added and the mixture was heated at temperature range of 75-85°C with continuous stirring. The color of solution changed from orange isatin color to deep red and the product was formed immediately. Heating was continued for 5h to achieve complete 4.7 m.mol precipitation. The product was filtered, washed several times with hot ethanol, followed by ether and vacuum dried, giving brown red microcrystals. yield 67.24%, m.p. 146-148°C. IR (ν cm⁻¹): 3425(NH), 1620(C=N), 1728(isatin C=O), 1650(C=O, 4-AAP). MS(EI) calculated for C₁₉H₁₆N₄O₂, m.wt 332.36, m/z(I%): (332.6) [M]⁺ (28) 240[M-C₆H₆N] (5), 213 [M-C₇H₅NO](19.5), 198[M-C₇H₅NO-CH₃](5.5), 159[M-C₇H₅NO-CH₂-N=C=CH₂](3.5), 146[M-C₇H₅NO-CH₃-C₃H₂N](4), 119[M-C₇H₅NO-CH₃-C₃H₂N-HCN](5.5), 102[M-C₇H₅NO-CH₃-C₃H₂N-CONH₂](1.7), 84[77(Ph)[M-C₇H₅NO-CH₃-C₃H₂N-HCN-HN=C=O](6.4), 56[M-C₆H₆N-C₁₁H₈N₂O](30) and 51[M-C₇H₅NO-CH₃-C₃H₂N-HCN-HN=C=O-C₂H₂](1). Elemental analysis (%) calculated for C₁₉H₁₆N₄O₂: C,68.67; H,4.85; N,16.86% found: C,69.07; H,5.22; N,17.08. ¹HNMR δ (ppm)(DMSO): 10.75(1H, s, N-H protons), 6.084-7.018(4H, d, indole ring), 7.216-7.573(5H, t, Ph), 3.2(3H, s, N-CH₃), 2.6-2.4(3H, m, C-CH₃); ¹³CNMR δ (ppm): 165 (2C, s, 2C=O), 156.1(1C, azomethine C=N), 149-145(2C, C-C=O + C₃-CH₃), 135-110(13C, m, aromatic C+C₄-N). Electronic spectra ((λ_{max}, nm ν_{max}cm⁻¹) ((ε_{max}, L.mol⁻¹.cm⁻¹) DMF: 263, 312, 452 nm (38022, 32052, 22124 cm⁻¹ (11511, 9375, 4000 L.mol⁻¹.cm⁻¹) π→π*; DMA (257, 307, 430 nm, (38888sh, 32573, 23256 cm⁻¹) (5476, 12727, 17185 L.mol⁻¹.cm⁻¹), π→π*.
- b) The same procedure was conducted by adding a solution of 4-aminoantipyrin (0.9552 g, 4.7 m.mol) in super dry ethanol (18.3 ml) to 4.7 ml of an ethanolic solution of isatin (4.7 m.mol) containing 6 drops of glacial acetic acid. Heating was continued for 44h to achieve complete precipitation. Yield 40.3 %.

2. (Z)-1-benzyl-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-ylimino)indolin-2-one(**L_{II}**):

A solution of N-benzylisatin (1.1186 g, 4.7 m.mol) in dioxane (5.5 ml)(99%) was added to solution of 4-aminoantipyrine (0.9552 g, 4.7 m.mol) in the same solvent (4.5 ml). Six drops of glacial acetic acid were added and the mixture was heated under reflux for 6h to achieve complete precipitation. The product was filtered, washed several times with dioxane followed by cold ethanol and ether and dried under vacuum. to give red powder. Yield 49.9, m.p.244-246°C. IR(ν, cm⁻¹, KBR): 1712 (C=O isatin), 1666(C=O 4-AAP). 1643 (azomethine C=N), ¹HNMR δ(ppm)(DMSO): 7.6-7.2(10H, t, 2Ph), 7-1-6.8(4H, d, indole ring), 4.979-4.862(2H, s, benzyl CH₂), 3.3(3H, s, N-CH₃), 2.5(3H, s, C-CH₃); ¹³C NMR δ(ppm): 129.743-129.165(13C, aromatic, 4 beta CH, isatin 4,6-CH, 2 C=N, 2N-C=O, C-N-N, 2C-N), 127.929-127.768(6C, m, aromatic CH of phenyl and C-7 of isatin), 11.39(2C, N-CH₃, C-CH₃). Elemental analysis (%) calculated for C₂₆H₂₂N₄O₂: C,73.92, H,5.25, N,13.27%. Found: C 74.50, H 4.89, N 13.95%. Electronic spectra λ_{max} nm, (ν_{max} cm⁻¹) ((ε_{max} L.mol⁻¹.cm⁻¹) (DMF): 257, 300, 323, 471nm (38910, 33333sh, 30960sh, 21231 cm⁻¹) (5476, 10645, 7741, 5148 L.mol⁻¹.cm⁻¹) π→π* ; DMSO: 300, 330, 470 nm (33333, 30303, 21277 cm⁻¹)(36193, 19354, 18403 L.mol⁻¹.cm⁻¹) π→π*; DMA: 273, 464 nm (36670, 21570 cm⁻¹) (18720, 7031 L.mol⁻¹.cm⁻¹) π→π*.

3. ((E)-3-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-2-oxindolin-1-yl)((E)-3-(2-methyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazol-3-ylimino)-2-oxindolin-1-yl)mercury(II) (**Hg(L_I)₂**):

To a stirred solution of **Hg(isatin)₂** (0.1 g, 2 m.mol) in DMF (2.85 ml) was added a solution of 4-aminoantipyrine (0.1 g, 4 m.mol) in DMF(1 ml) containing 4 drops of glacial acetic acid, and the mixture was heated under reflux with continuous stirring. An orange yellow precipitate was formed after one hour. Reflux was continued for further 2h to allow complete precipitation. Then the product was filtered off, and washed with DMF, ethanol, ether and vacuum dried.

2.2 Synthesis of metal complexes

2.2.1 Complexes of L_IH

Cobalt (II) and nickel(II) complexes (C₁ and C₂): To a stirred solution of **L_IH** (0.05 g, 0.15 mmol) in absolute ethanol (3.6 ml) was added, an alcoholic solution of CoCl₂.6H₂O and NiCl₂.6H₂O (0.0539 and 0.537g respectively, 0.15 mmol) and the mixture was heated under reflux with continuous stirring. Precipitation of complexes took place after

30 min. and 1h respectively. Reflux was continued for 1h and 2h respectively to achieve complete precipitation. Both products were filtered, then washed with hot ethanol, cold ether and vacuum dried.

Copper (II) bipyridyl complex (C₃): To a stirred solution of (**L_IH**) (0.05 g, 0.15 m.mol) in absolute ethanol (3.6 ml) was added an alcoholic solution of CuCl₂.2H₂O (0.0511 g, 0.3 m.mol) followed by (0.0468g, 0.3mmol) of bipyridyl in a minimum amount of ethanol. Then triethylamine (Et₃N) (0.5 ml) was added and the mixture was heated under reflux for (4 h) on a water bath with continuous stirring. A green precipitate was formed after 30 min. The product was filtered, washed with hot ethanol followed by ether and vacuum dried.

Platinum(II) complex (C₄): A solution of (**L_IH**) (0.0184 g, 0.0548 m.mol) in dry methanol containing Et₃N (0.5 ml) was added to a stirred suspension of cis-[PtCl₂(PPh₃)₂] (0.0432 g, 0.0548 m.mol) in methanol and the mixture was heated on a water bath at (45-50)°C for (3.5 h) with continuous stirring. The solvent was evaporated under reduced pressure to leave a red solid residue. The product was re-dissolved in dichloromethane (20ml). Water (75 ml) was used to extract the NEt₃H⁺Cl⁻, produced in the reaction. The organic layer was separated, dried with MgSO₄.H₂O, and filtered. Most of solvent was evaporated. A red solid was formed and recrystallized from light petroleum ether (30-40)°C. The product was filterd, washed with light petroleum ether and dried under vacuum.

2.2.2 Complexes of L_{II}

Co(II), Ni(II), Cu(II) and Pd(II) complexes (C₅₋₇, C₉): To a stirred solution of (**L_{II}**) (0.1 g, 0.23 m.mol) in absolute butanol (6 ml) was added a solution of CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O and PdCl₂(PhCN)₂ (0.0608 g, 0.0608 g, 0.0804 g, 0.097g respectively, 0.23 m.mol) in a minimum amount of n-butanol, and the mixture was heated under reflux for 3h, 30 miutes, 3h, 10 minutes respectively until the formation of precipitates. The products were washed and purified from starting materials using hot butanol followed by ethanol and ether and vacuum dried.

Cu(II) bipyridyl complex (C₈): To a stirred solution of (**L_{II}**) (0.1 g, 0.23 m.mol) in hot ethanol (31 ml) was added, an alcoholic solution (17 ml) of CuCl₂.2H₂O (0.0804 g, 0.46 m.mol) with continuous stirring. The mixture was heated under reflux for (13 min). The colour of solution was changed from red to dark brown. Then a solution of 2,2-bipyridyl (0.0368 g, 0.236 m.mol) in ethanol (1.5 ml) was added and reflux was continued for (3 h) to achieve complete precipitation. A green precipitate was formed. The product was filtered, washed several times with ethanol followed by ether and vacuum dried.

Pt(IV) complex (C₁₀): To stirred solution of **L_{II}** (0.0521 g, 0.123 m.mol) in DMSO (3 ml)(99%) was added a solution of K₂PtCl₆ (0.03 g, 0.06 m.mol) in DMSO (1.5 ml) and the mixture was heated under reflux for (4 h). After cooling to room temperature, a mixture of H₂O:EtOH (2.5:2) was added with continuous stirring. A dark brown precipitate was formed. The product was filtered, washed and purified with the same solvent mixture followed by ether and vacuum dried.

3. RESULTS AND DISCUSSIONS

3.1 Physical properties and elemental analyses

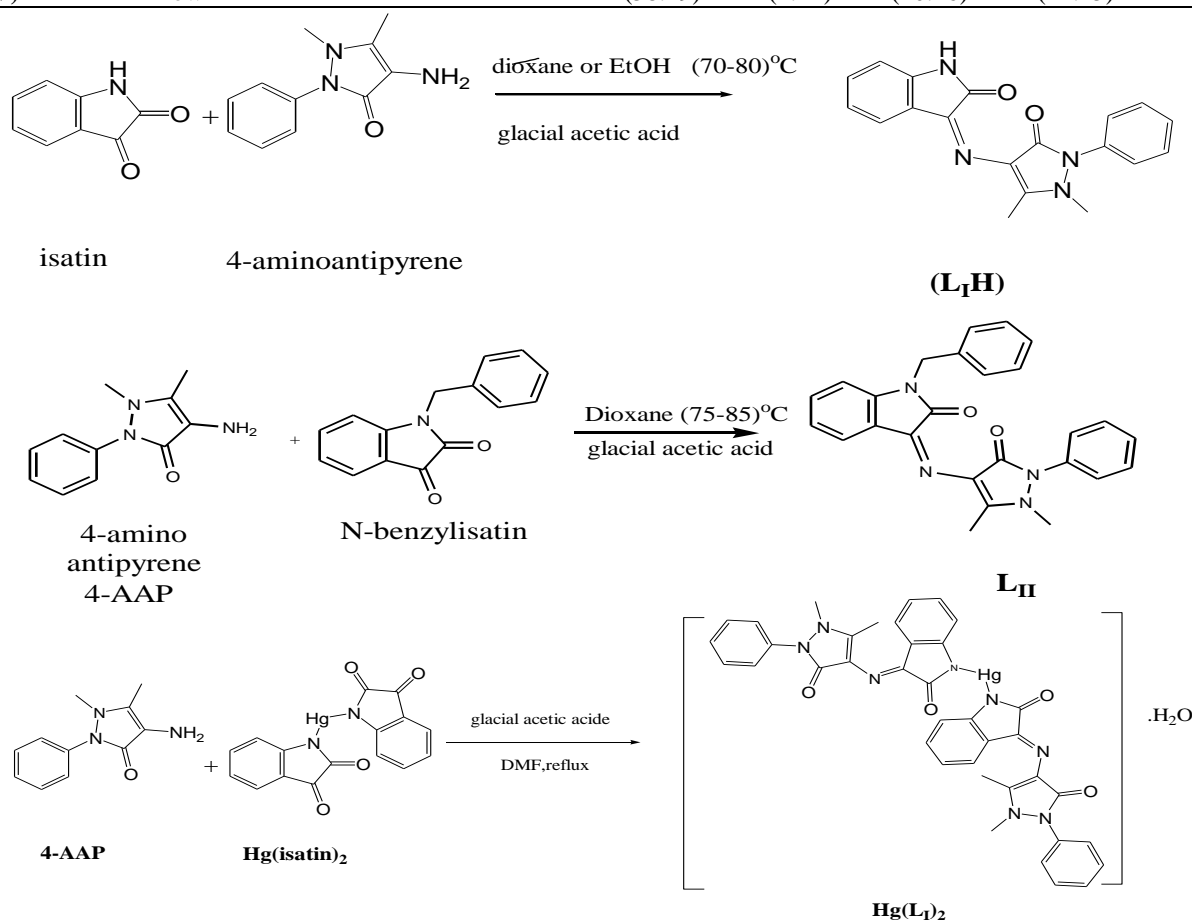
The synthesis routes of the compounds **L_IH**, **L_{II}** and **Hg(L_I)₂** are illustrated in scheme (1). The physical properties and elemental results obtained from C.H.N. analyses and metal contents of the prepared compounds are described in Table-1. The analytical data were almost agreeable with the calculated values. The ligands and their metal complexes were mainly soluble in DMF, DMSO and DMA, sparingly soluble in ethanol, methanol, chloroform, and dichloromethane and insoluble in less polar solvents.

3.2 NMR spectra

The ¹H NMR and ¹³C NMR chemical shifts (ppm) exhibited by the prepared organic compounds shown in figures (1) and (2) gave a good support to the suggested structures and were in agreement with those obtained from other isatin derivatives^{5,23,24}. In addition to the peak related to CH₃ protons which appeared at δ (1-2.7)ppm^{25,26}, the ligand **L_IH** (Figure 1a) exhibited a chemical shift signal assigned to N-H proton of isatin at δ (10.75)ppm²⁵⁻³⁵. The ¹³C NMR spectrum of this ligand (Figure 1b) exhibited a signal of carbon atom of azomethine group located at δ(156.1)ppm³² and of carbon atom of (C=O) group at δ(165)ppm^{30,32}. The ¹H NMR spectrum of **L_{II}** in DMSO (Figure 1c) showed peaks appeared at δ(6.95-7.5) ppm assigned to protons of aromatic rings²⁸. Chemical shifts of (CH₂) protons of benzyl group was observed as a multiplet at δ(4.862-4.979)ppm³⁰. The ¹³C NMR spectrum (Figure 1d) showed the appearance of peaks at (129.734-127.7) ppm assigned to aromatic carbons while that observed at δ(11.39)ppm corresponds to aliphatic carbons¹⁶. The ¹H NMR spectrum of the Pt(II) complex of **L_IH**(C₄) in CDCl₃, shown in (Figure 1e), exhibited one peak observed at δ(2-2.1)ppm attributed to hydroxyl proton of solvent (CH₃OH)[36]. The signals assigned to aliphatic protons appeared at δ(2.24-3.75)ppm^{28,32}, while those of aromatic protons appeared at δ(6.6-8.035)ppm[30,32,36]. The spectrum also showed the disappearance of

Table-1: Physical properties and analytical data for L_IH , L_{II} and their metal complexes

Symbol	Colour	(m.p.) °C	Yield%	% Element Analysis Found (calculated)				
				C	H	N	M	Cl
L_IH	Brown Red	146-148	67.24	69.07 (68.67)	5.22 (4.85)	17.086 (16.86)		
C_1 $Co(II)$	Brown	195	28.57	54.747 (54.47)	3.9 (3.8)	13.472 (13.37)	14.025 (13.155)	8.25 (7.99)
C_2 $Ni(II)$	Brown	>290	53.23	48.257 (48.413)	3.981 (3.61)	12.50 (11.89)	11.55 (12.46)	14.35 (15.07)
C_3 $Cu(II) + bipy$	Greenish Brown	202	14.44	44.97 (44.86)	2.86 (3.35)	10.15 (10.82)	17.33 (16.42)	18.65 (18.3)
C_4 $Pt(II)$	Red	200-202	46.22	60.66 (60.80)	4.81 (4.71)	4.55 (5.10)	17.80 (17.94)	3.15 (3.267)
$Hg(L_I)_2$	Orange Yellow	>290	55.56	51.60 (51.78)	3.75 (3.63)	13.10 (12.71)	22.80 (22.77)	-
L_{II}	Red	244-246	49.9	74.50 (73.90)	4.89 (5.21)	13.95 (13.27)		
C_5 $Co(II)$	Brown Yellow	>290	26.6	64.5 (64.07)	4.61 (4.52)	12.10 (11.41)	6.40 (6.95)	7.55 (7.29)
C_6 $Ni(II)$	Brown	276-278	44.83	63.85 (63.93)	4.63 (4.50)	12.22 (11.47)	5.59 (6.01)	7.93 (7.27)
C_7 $Cu(II)$	Light Brown	>290	13.81	61.50 (60.96)	3.60 (4.29)	11.20 (10.94)	7.80 (8.2)	9.50 (9.24)
C_8 $Cu(II)$	Green	264	23.02	41.20 (41.60)	3.41 (3.47)	8.902 (8.12)	19.037 (18.42)	19.84 (20.56)
C_9 $Pd(II)$	Gray	>290	22.84	36.74 (36.7)	3.011 (3.53)	6.695 (6.59)	16.25 (16.72)	24.50 (25.06)
C_{10} $Pt(IV)$	Dark Brown	145-146	13.56	57.87 (58.29)	4.10 (4.12)	9.74 (10.46)	11.75 (12.15)	9.34 (8.84)

**Scheme-1:** Synthetic route of L_IH , L_{II} and $Hg(L_I)_2$

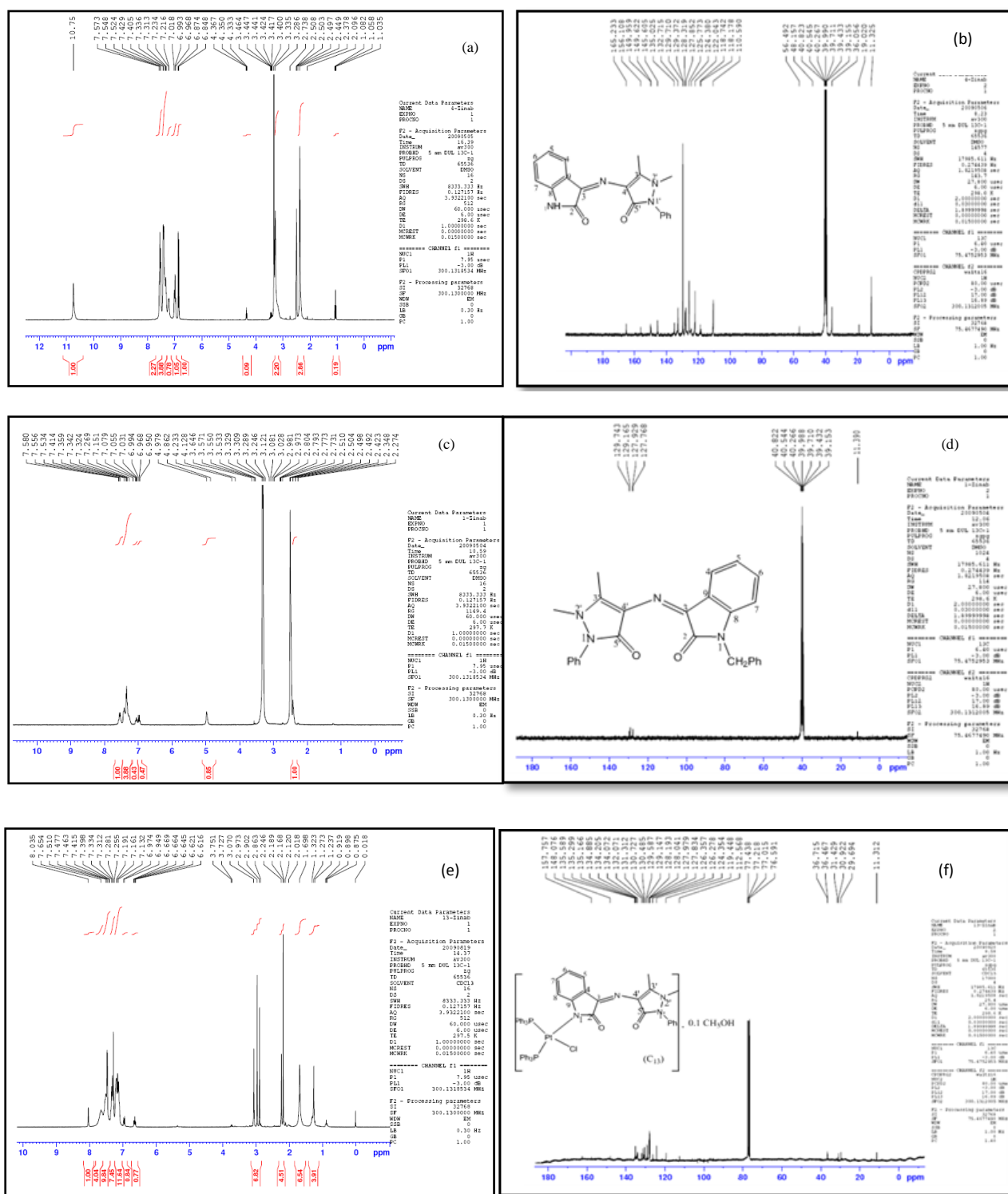


Fig-1: ^1H NMR and ^{13}C NMR spectra of L_IH (a and b) L_{II} (c and d) and $\text{PtL}_I(\text{PPh}_3)_2\text{Cl}$ (e and f) respectively

(N-H) proton signal of isatin ring. This means that platinum(II) ion is bonded directly to the nitrogen atom of isatin ring³⁰. The ^{13}C NMR spectrum of (C_4) (Figure 1f) showed a peak at $\delta(11.3)$ ppm assigned to carbon atom of methyl group at 2' position of antipyrine ring ($\text{N}-\text{CH}_3$)^{30,32,36}, while the peak appeared at $\delta(29-36)$ ppm was attributed to methyl carbon at position 3' ($\text{C}-\text{CH}_3$)³⁶. Signals of aromatic carbons appeared at $\delta(124-135)$ ppm³⁶. The peak observed at $\delta(112)$ ppm is attributed to the two olefinic carbons^{5,36}. Peaks appeared at $\delta(157)$ ppm and $\delta(162)$ ppm were assigned to azomethine and carbonyl carbons respectively^{33,35}. The ^1H NMR spectrum of $\text{Hg}(\text{L}_I)_2$ in DMSO shown in (Figure 2c) exhibited signals related to aliphatic protons appeared at (2.24-3.75) ppm³⁰, while that of aromatic protons appeared at (6.6-8.035) ppm^{4,30,32,36}. The disappearance of (N-H) proton signal of isatin ring indicates that the mercury(II) ion is directly bonded to nitrogen atom of isatin ring³⁰. The ^{13}C NMR spectrum of $\text{Hg}(\text{L}_I)_2$ (Figure 2d) exhibited two peaks at $\delta(11.39)$ and (19.2) ppm attributed to carbon atoms of the two methyl groups^{28,32}. Peaks assigned to the carbonyl and azomethine carbon atoms appeared at (165, 162 and 160) ppm respectively^{21,36}, while the

chemical shift of the olefinic carbon atoms were located at (119)ppm³⁶. Peaks assigned to aromatic carbon atoms were observed at δ (123.115-136.544) ppm^{2,30,32,36}. The ¹H NMR spectrum of the Ni(II) complex of L_{II} (C₆) in DMSO (Figure 2a) exhibited peaks observed at (2.43 and 3.25) ppm attributed to the two methyl protons (CH₃)^{32,36}. The signal assigned to methylene protons appeared as a singlet at δ (4.91)ppm²¹. Aromatic protons showed a multiple peak at δ (6.5-8.8) ppm^{21,30}. The ¹³C NMR spectrum of (C₆) (Figure 2b) exhibited two peaks observed at δ (11.39) and (39.23) ppm attributed to methyl carbon atoms^{28,32}. The benzylic methylene carbon atom signal appeared at δ (43.15)ppm²¹. The chemical shift of olefinic and aromatic carbon atoms were located at δ (109.68) ppm and δ (122.7-136.8) ppm respectively^{30,36}.

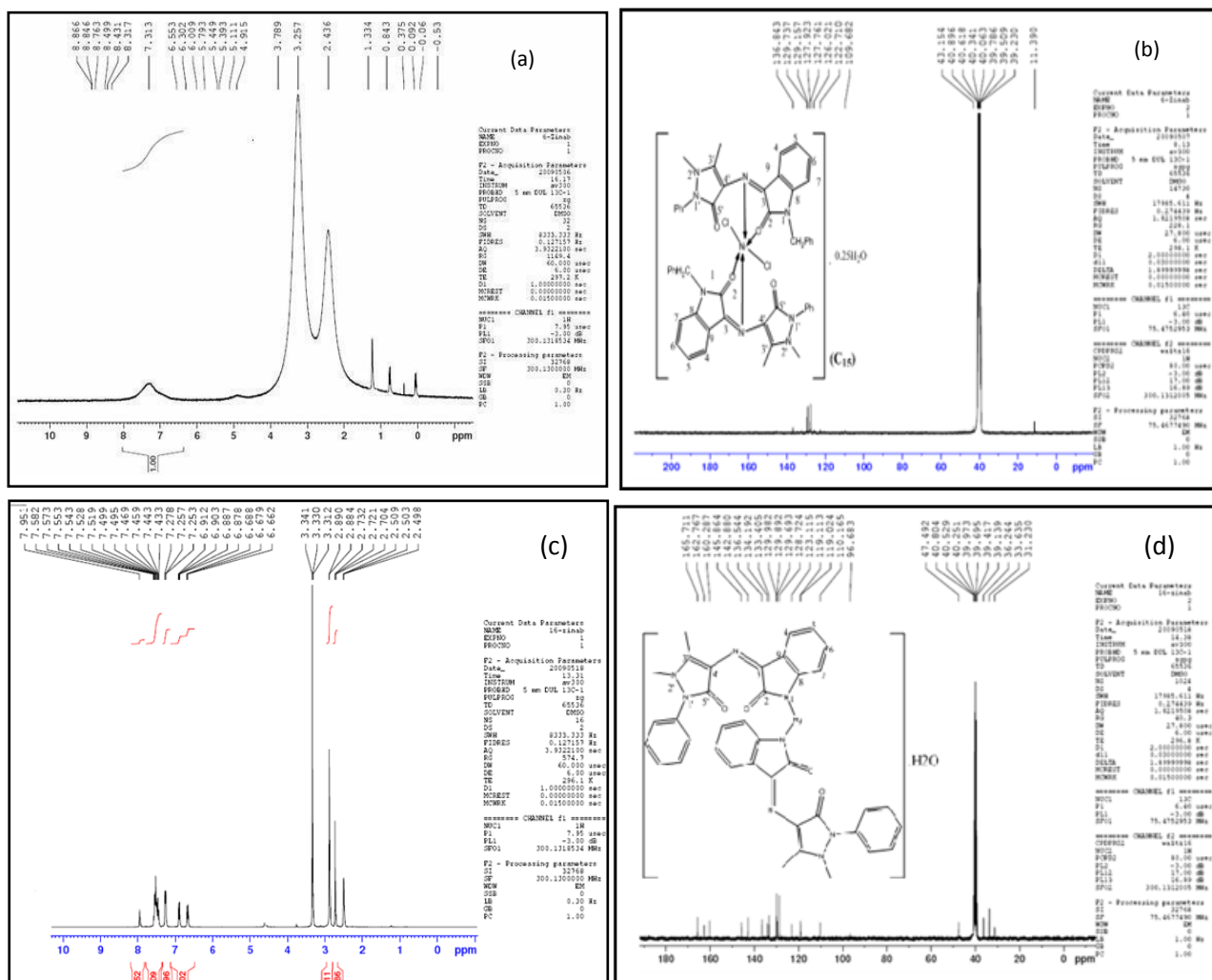


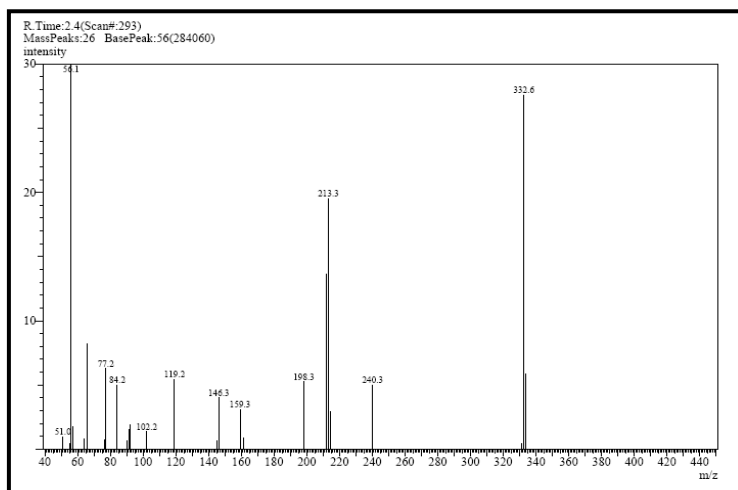
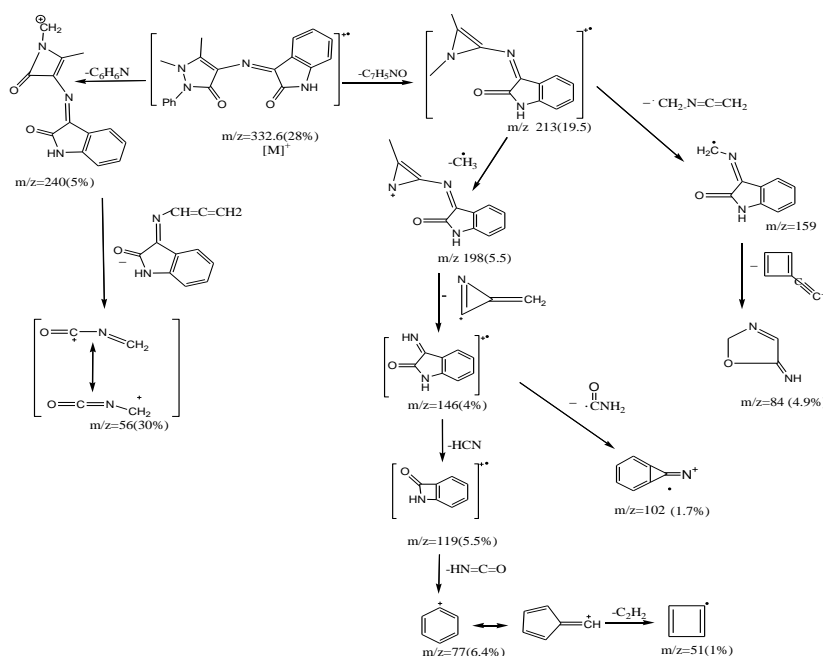
Fig-2: ¹H NMR and ¹³C NMR spectra of [Ni(L_{II})₂Cl₂] (a and b) and Hg(L_I)₂ (c and d) respectively

3.3 Mass spectra

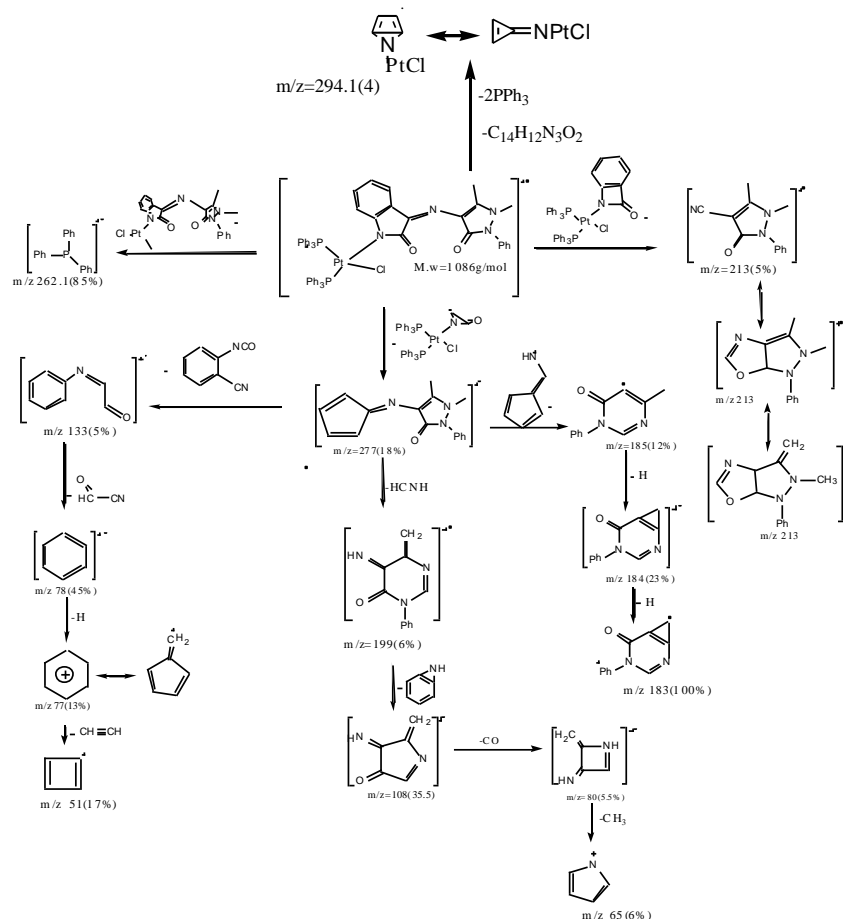
The mass spectrum of L_IH shown in Fig-3 exhibited a peak at (332.6) which was assigned to [M]⁺. Some other characteristic peaks were observed at m/z values that have been reported in the mass spectra of other isatin and antipyrine derivatives^{4,37,38} and were assigned to fragments described in scheme (2). The EI mass spectrum of the Pt(II) complex C₄ at 70 eV showed characteristic peaks observed at (m/z 294, 277, 262, 213, 199, 183, 170, 157, 133, 108, 92, 78, 65 and 51). The peak observed at m/z 262.1 corresponds to the two PPh₃ ion fragments. Suggested fragmentation pathways and structural assignments are described in scheme-3.

3.4 Infrared spectra

The important IR vibrations and tentative assignments of L_IH, L_{II} and their metal complexes are described in table (2). The infrared spectrum of L_IH exhibited the absence of bands attributed to ν_{NH_2} of 4-aminoantipyrine^[36] and $\nu_{\text{C}=\text{O}}$ of isatin at position C-3^{36,39} and the appearance of a single band assigned to C=N stretching mode of Schiff base at 1620cm⁻¹^{5,36}. A sharp band was observed at 3479cm⁻¹ was attributed to ν_{OH} of enolic form of isatin ring at C-2⁴⁰. The bands appeared at 3085 and 3016 are assigned to aromatic C-H while those appeared at 2970, 2893 and

Fig-3: Mass spectrum of L_1H Scheme-2: Suggested Fragmentation pathways of L_1H

2815 cm^{-1} were assigned to aliphatic C-H^{36,39}. Two bands were observed at 1728 and 1650 cm^{-1} were assigned to two C=O stretching vibration of isatin and 4-AAP rings respectively^{4,5,36}. The band related to aromatic C=C vibration appeared at 1455 cm^{-1} ^{32,36}. The antipyrine ring showed two other bands at 1604 and 1296 cm^{-1} attributed to C=C and C-N vibrations respectively³⁶. The spectra of Co(II), Ni(II) complexes and Cu(II) mixed ligand complex with bipyridyl (C_1 , C_2 and C_3 respectively), exhibited shifts of vibrations assigned to $\nu_{C=N}$ of azomethine group and $\nu_{C=O}$ of the two carbonyl groups to lower frequencies. This is attributed to coordination of these groups with metal ions^{4,25,31,41,42}. The spectrum of the mixed ligand Cu(II) complex with bipyridyl (C_3), exhibited the absence of N-H and C=O stretching bands of isatin ring and the appearance of two new bands at 3450 and 1600 cm^{-1} related to OH and C=N stretching vibrations of the enolic form of the isatin ring respectively. This refers to bonding of Cu(II) ion complex of bipyridyl to N_1 and C-2 OH of isatin ring. Bands related to bipyridyl ring vibrations were observed at 3075, 1450 and (1250, 1330) cm^{-1} attributed to aromatic C-H, C=C and C-N respectively³⁶. The complex exhibited also vibrational modes of coordinated water⁴² whereas the spectra of the Ni(II) and Pt(II) complexes showed vibrational modes of water and methanol respectively in their crystal lattice. The spectrum of the Pt(II) complex (C_4) exhibited no significant changes in stretching vibrations of the carbonyls and azomethine groups which rules out bonding with Pt(II) ion. The absence of the sharp band of N-H group of isatin refers to bonding of the nitrogen atom of indole ring with Pt(II) ion by ionic bond⁴³. Additional bands appeared at 3055 and 1530 were attributed to aromatic C-H and C=C vibrations respectively of triphenylphosphine. Bands appeared at lower frequencies were assigned to M-N, M-O, M-P and M-Cl stretching modes^{5,16,42}.

Scheme-3: Fragmentation pathways of C_4

The spectrum of $Hg(isat)_2$ exhibited absence of isatin ring N-H stretching vibration and no significant changes in two carbonyl vibrational mode of isatin. This refers to bonding of nitrogens only with the metal ion¹⁸. The band observed at 3500-3460 is attributed to OH stretching vibrations of lattice water⁴². The spectrum of $Hg(L_I)_2$ exhibited the absence of NH_2 stretching vibration of 4-AAP and the appearance of a new band at 1620 cm^{-1} attributed to azomethine stretching vibration³⁶. Aromatic and aliphatic C-H stretching vibration appeared at 3000, 2950 cm^{-1} respectively^{6,16}. The strong sharp band appeared at 1481 cm^{-1} was attributed to aromatic C=C vibration^{6,36}. The bands observed at lower frequencies attributed to M-N stretching mode⁴². The infrared spectrum of L_{II} exhibited the absence of the bands attributed to stretching vibrations of (C=O) at position (C-3) of N-benzylisatin and NH_2 of 4-AAP stretching vibrations³⁶. Group vibrations of antipyrine ring of $Hg(L_I)_2$ and L_{II} were observed at 1604-1500, 1390-1345 and 1060 cm^{-1} and assigned to aromatic C=C and C-N stretching and CH_3 rocking vibrations respectively^{4,5,36}. The spectra of all complexes exhibited shifts in $\nu_{C=O}$ vibrations of N-benzyl isatin to lower frequencies except the Pt(IV) complex (C_{10}) which refers to coordination of this group with metal ions⁴². The spectra of Cu(II)-bipyridyl, Cu(II) and Pd(II) complexes (C_7 - C_9) respectively exhibited shifts of $\nu_{C=O}$ of antipyrine ring to lower frequencies due to coordination of this group with metal ions⁴². The spectrum of Cu(II) mixed ligand bipyridyl complex (C_7) exhibited additional bands at 3100-3150, 1442 and 1250 cm^{-1} attributed to aromatic C-H, C=C, and C-N vibrations³⁶. Bands related to lattice water molecules were observed in the spectra of Ni(II), Pd(II) complexes (C_6 , C_9) at 3348 and 3471 cm^{-1} respectively, while the Cu(II) complex (C_8) showed vibrational modes of coordinated water at 3400, 902, 771 cm^{-1} . New bands appeared at lower frequencies were assigned to M-N, M-O and M-Cl stretching modes^{5,16,42}.

3.5 Electronic spectra, magnetic moments, and conductivity measurements

The spectrum of L_IH in DMF exhibited two single bands appeared at $(32052\text{ and }22124)\text{ cm}^{-1}$ with a shoulder at $(38022)\text{ cm}^{-1}$ and showed two sharp single bands at $(32573\text{ and }23256)\text{ cm}^{-1}$ with a shoulder at $(38888)\text{ cm}^{-1}$ in DMA. These bands were assigned to $\pi \rightarrow \pi^*$ transitions³⁶. The spectrum of L_{II} in DMF exhibited two single bands with a shoulder appeared at $(38910, 21231)\text{ cm}^{-1}$, in dimethylsulfoxide (DMSO) a multiplet with three bands appeared at $(33333, 30303\text{ and }21277)$ and in dimethylacetamide (DMA) two bands appeared at $(36670, 21570)\text{ cm}^{-1}$ and they were also assigned to $\pi \rightarrow \pi^*$ transition³⁶. The spectra of the Co(II) and Ni(II) complexes (C_1 and C_2) in dimethylformamide (DMF) exhibited changes in positions of ligand band components which were shifted to $(37174, 21881)\text{ cm}^{-1}$ and $(37174, 21834)\text{ cm}^{-1}$ respectively, while the spectrum of the Cu(II) complex (C_3) in DMF exhibited the disappearance of the first ligand band component and the appearance of other two components at 34722 and

Table-2: Characteristic IR stretching vibrations $\nu(\text{cm}^{-1})$ of the Schiff base ligands and their metal complexes

Symbol	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$ isatin	$\nu_{\text{C=O}}$ 4-AAP	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
L_IH	3425	1620	1728	1650	-		
C₁, Co(II)	3430	1575	1697	1640	578	509	375
C₂, Ni(II)	3425	1589	1704	1638	578	509	325
C₃, Cu(II)	-	1580	-	1666	475	410	302 ^a 275 ^b
C₄, Pt(II)	-	1615	1728	1674	-	524	350
Hg(L_I)₂	-	1620	1728	1666	-	501	-
L_{II}		1643	1712	1666	-	-	-
C₅, Co(II)		1620	1700	1665	502	425	360
C₆, Ni(II)		1627	1695	1674	509	455	324
C₇, Cu(II)		1560	1697	1633	510	455	347
C₈, Cu(II)		1566	1650	1625	470	410	362 ^a 285 ^b
C₉, Pd(II)		1575	1700	1635	501	455	339 ^a 277 ^b
C₁₀, Pt(IV)		1612	1735	1681	—	470	370

a: terminal; , b: bridging; ν_{OH} of lattice water = 3475 cm^{-1} (**C₂**), 3325 cm^{-1} **Hg(L_I)₂**; methanol = 3500 cm^{-1} (**C₄**); coordinated water vibrations 3480, 890, 780 (**C₃**)

32250 cm^{-1} respectively. The spectra of the Co(II), Ni(II) and Cu(II) complexes of **L_{II}** (**C₅-C₇**) in DMF exhibited changes in the positions of ligand band components appeared at (37037, 31250 and 22222) cm^{-1} , (37313, 31152 and 21645) cm^{-1} and (38167, 37037 and 28985) cm^{-1} respectively. Additional bands were observed in the visible and near infrared regions of the spectra of transition metal complexes and were attributed to d-d or ligand field transitions^{44,45}. By applying observed band energies and band ratio on Tanabe-Saugano diagrams of the specific ions, the values of Dq/B' , B' and $10Dq$ as well as the energy of unobserved bands were obtained. The values of the nephelauxetic ratio, β , of the Ni(II) and Co(II) complexes indicated some covalent character⁴⁵. The magnetic moments of the Co(II) and Ni(II) complexes came in agreement with high spin octahedral geometry. The magnetic moment of the Ni(II) and Cu(II) complexes of **L_IH** indicated octahedral binuclear complexes⁴⁵. The Cu(II) complexes of both ligands **C₃** and **C₇** gave bands related distorted octahedral geometry^{38,39,45}. The spectrum of triphenyl phosphine Pt(II) complex (**C₄**) in DMA, table (3) exhibited one band observed at 20202 cm^{-1} assigned to $^1A_{1g} \rightarrow ^1A_{2g}$ transition of square planar Pt(II) complexes. The spectra of **Hg(isatin)₂** and **Hg(L_I)₂** in DMSO exhibited high intensity bands in the UV region at (36900, 31447), and (38610 cm^{-1} respectively attributed to $\pi \rightarrow \pi^*$ transition of the conjugated system. The bands observed at 22075, and 28818 cm^{-1} respectively are attributed to ligand to metal charge transfer transitions⁴⁵. The spectrum of the mixed ligand Cu(II) complex (**C₈**) in DMA exhibited bathochromic shift of the two ligand bands to 34246 and 32362 cm^{-1} . The band was observed at 13869 cm^{-1} was attributed to the $^2E_g \rightarrow ^2T_{2g}$ transition of distorted octahedral Cu(II) complexes and it equals to $10Dq$ value⁴⁵. Magnetic moment of the complex ($\mu_{\text{eff}} = 1.9$ B.M) comes in agreement with binuclear tetragonal Cu(II) complexes. The Pd(II) complex (**C₉**) was diamagnetic and its spectrum in DMA exhibited the appearance of one single ligand band at 37174 cm^{-1} assigned to $\pi \rightarrow \pi^*$ transition and two additional bands at 16835 cm^{-1} attributed to $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{1g} \rightarrow ^1B_{1g}$ transitions of square planar palladium(II) complexes⁴⁵. The spectrum of the diamagnetic Pt(IV) complex **C₁₀** in DMSO exhibited two bands assigned to spin-forbidden transitions of Pt(IV) octahedral complexes⁴⁵. Molar conductivity of metal complexes in their specified solvents showed electrolytic nature of **C₁**, **C₃**, and **C₇** and **C₁₀** with ionic ratio of 1:1⁴⁶ while the other complexes were non electrolytes⁴⁶. According to these data and results of elemental analyses and I.R. spectra the structures of **L_IH** and **L_{II}** complexes were suggested as is illustrated in scheme (4).

3.6 Thermal analysis of metal complexes

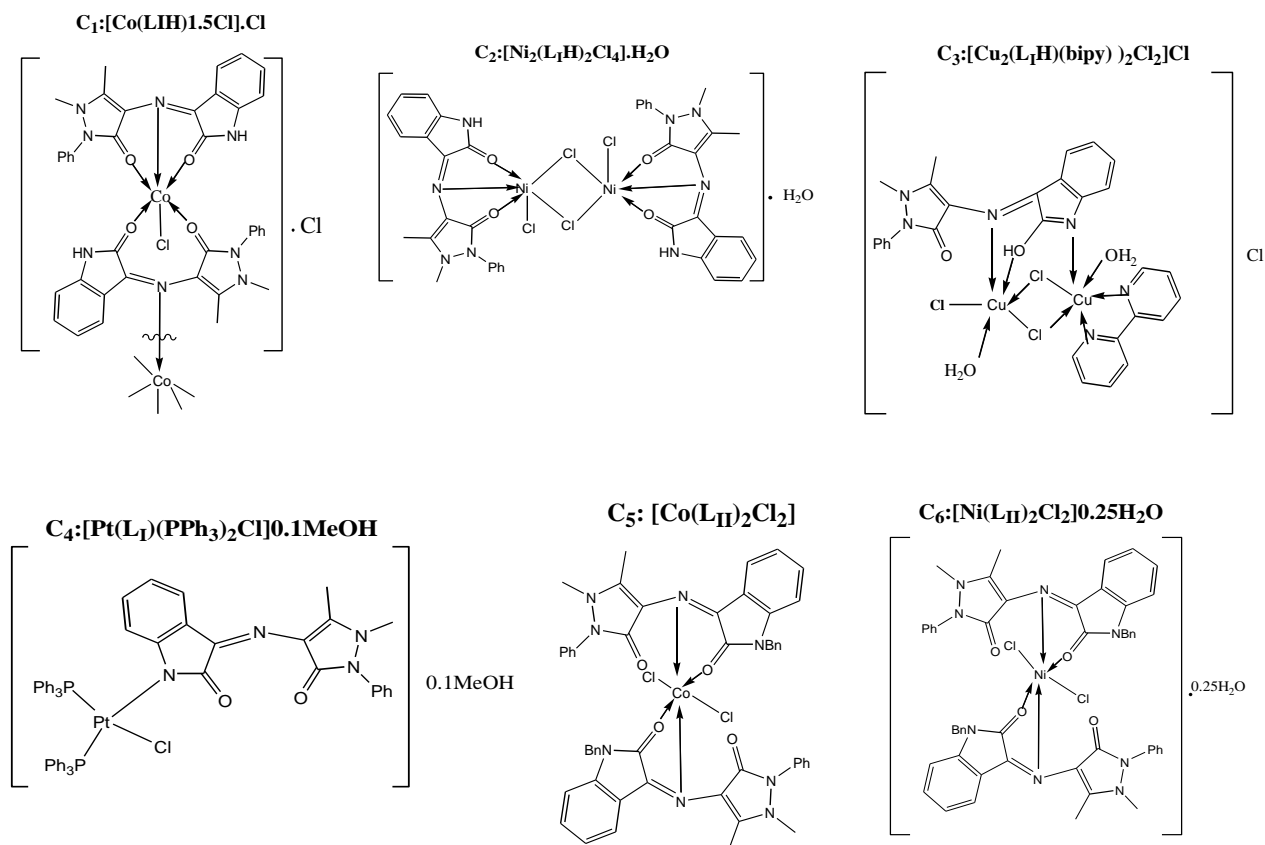
Thermal decomposition of metal complexes (**C₂**, **C₆**, **C₈** and **C₉**) by (T.G, DTG and DTA) techniques was carried out under nitrogen atmosphere at heating range of (50-1000°C). Thermographs of the selected complexes are shown in figure (4). The first three complexes were stable up to 270°C. Generally, water molecules of the crystal lattice were lost at temperature range of (50-150)°C as was observed from the curvature in the T.G. curves. Transition, at higher temperature, from solid to gas phase causes endothermic reactions demonstrated by depression or decline in DTA curves⁴⁷. At temperature range of (250-350)°C the DTA curve of **C₆** [Ni(L_{II})Cl₂].0.25H₂O, showed the occurrence of endothermic reaction at (278°C) which may be attributed to melting point of the metal complex⁴⁷. At temperatures higher than 350°C the progress of weight loss was combined with continuous rising of DTA curve. This refers to further decomposition of metal complexes leading to fragments that undergo exothermic reactions⁴⁷. At the final stage of thermal decomposition the weight loss of the Ni(II) complex of **L_IH**(**C₂**) suggests the formation of Ni(OH)Cl while that of the copper complex refers to the formation of metal oxides (CuO+Cu₂O)⁴⁷. The Ni(II) and Pd(II) complexes of

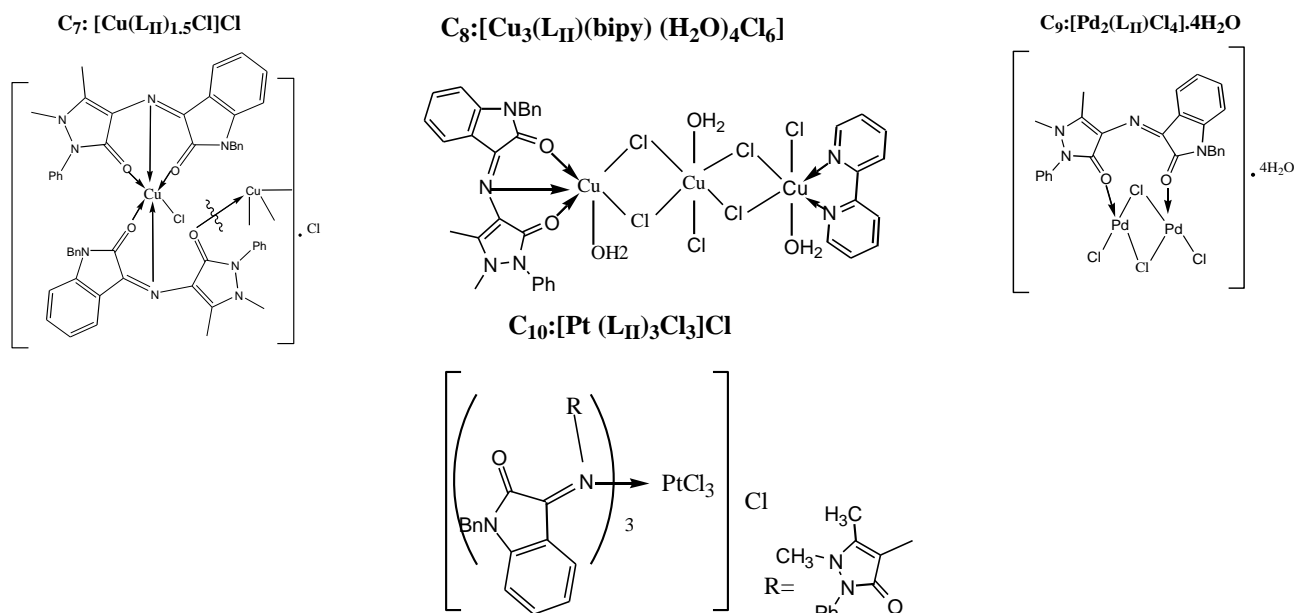
L_{II} (C_6 and C_9), were incompletely decomposed within the heating range which refers to the formation of more stable products.

Table-3: Electronic spectra spectral parameters and molar conductance of L_IH and L_{II} complexes in a:DMF, b:DMSO and c:DMA solutions

Comp. no.	Band positions	Assignment	Dq/\bar{B}	\bar{B} (cm^{-1})	β	$10Dq$ (cm^{-1})	μ_{eff} B.M.	Molar conductivity $S.mol^{-1}.cm^2$
C_1 Co(II)	ν_1 4507 * ν_2 10224 ν_3 15500)	$^4T_{1g} \rightarrow ^4T_{2g}$ $^4T_{1g} \rightarrow ^4A_{2g}$ $^4T_{1g_F} \rightarrow ^4T_{1g_P}$	0.647	760.6	0.783	4921	4.9	61 ^a
C_2 Ni(II)	ν_1 10172 ν_2 15267 ν_3 28678*	$^3A_{2g} \rightarrow ^3T_{2g_g}$ $^3A_{2g} \rightarrow ^3T_{1g}$ $^3A_{2g} \rightarrow ^3T_{1g_P}$	1.19	911	0.884	10840	2.8	30.5 ^a
C_3 Cu(II)	15576 21097	$^2B_{1g} \rightarrow ^2B_{2g}$ $^2B_{1g} \rightarrow ^2E_g$					1.8	78.8 ^a
C_4 Pt(II)	20202	$^1A_{1g} \rightarrow ^1A_{2g}$					Diamag	4.62 ^c
Hg(L_I) ₂	38610 28818	$\pi \rightarrow \pi^*$ LMCT					Diamag	3.632 ^b
C_5 Co(II)	ν_1 4995 * ν_2 10256 ν_3 17007	$^4T_{1g} \rightarrow ^4T_{2g}$ $^4T_{1g} \rightarrow ^4A_{2g}$ $^4T_{1g_F} \rightarrow ^4T_{1g_P}$	0.757	675	0.695	5109	4.5	30 ^a
C_6 Ni(II)	ν_1 10152 ν_2 17392 ν_3 27345 *	$^3A_{2g} \rightarrow ^3T_{2g}$ $^3A_{2g} \rightarrow ^3T_{1g_f}$ $^3A_{2g} \rightarrow ^3T_{1g_P}$	1.1	571	0.554	10563	2.8	29.5 ^a
C_7 Cu(II)	13333	$^2E_g \rightarrow ^2T_{2g}$				13333	1.9	103.2 ^a
C_8 Cu(II)	13869	$^2E_g \rightarrow ^2T_{2g}$				13869	1.8	14 ^c
C_9 Pd(II)	ν_1 13750 ν_2 16835	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$					Diamag	4.5 ^c
C_{10} Pt(IV)	ν_1 14127 ν_2 21978	$^1A_{1g} \rightarrow ^3T_{1g_P}$ $^1A_{1g} \rightarrow ^3T_{2g_P}$					Diamag	45 ^b

*calculated





Scheme-4: Suggested structures of the prepared metal complexes

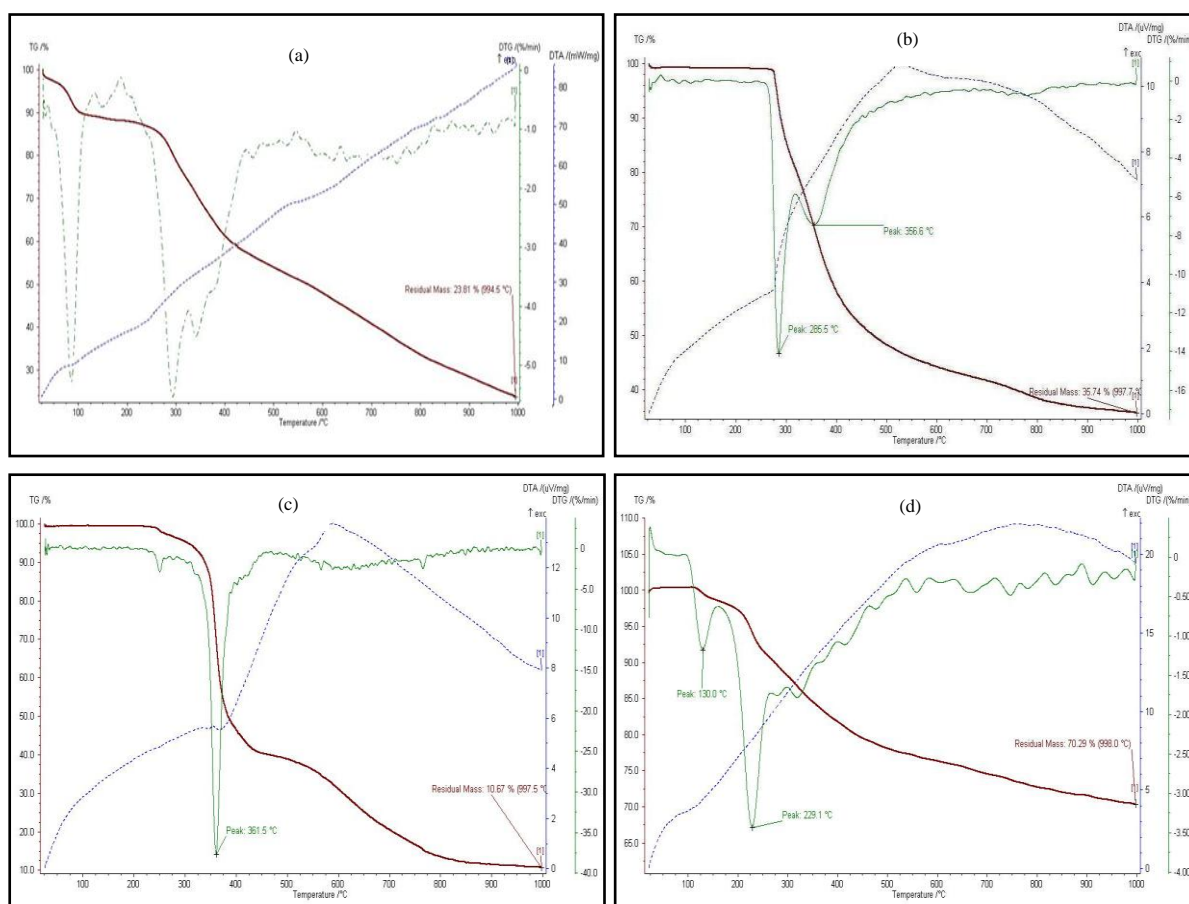


Fig-4: TG, DTG and DTA Thermograms of **a** -[Ni₂(L_I)₂Cl₄]H₂O (**C₂**) **b**-[Ni₂(L_{II})₂Cl₂]0.25H₂O (**C₆**) **c**-Cu₃L_{II}(bipy)Cl₆(H₂O)₄ (**C₈**) and **d**-[Pd₂L_{II}Cl₄(H₂O)₄]0.1H₂O(**C₉**) complexes under nitrogen atmosphere

4. CONCLUSIONS

The two Schiff base ligands in this work have been readily prepared and their structures were characterized from condensation reaction of isatin and N-benzylisatin with 4-AAP in dioxane. The coordination behaviors with some metal ions have been studied. The suggested structures have been confirmed by elemental analyses, thermal analyses,

NMR and mass spectra as well as magnetic moments and conductivity measurements. Condensation reaction of **Hg(isatin)₂** with 4-AAP gave the diSchiff base complex **Hg(L₁)₂**. Reaction of PtCl₂(PPh₃)₂ and Cu(II)-bipyridyl complexes with L₁H in basic medium led to bond formation between N-1 of isatin ring moiety and the two metal ions with the latter being coordinated to OH and N-1 of enol form of isatin ring as was confirmed by the IR spectra of the complexes. The chelating potency of the studied ligands to form bi-, tri- and polynuclear metal complexes as well as the N-metallated derivatives form synthetic models for biologically important molecules in enzymology and medicinal chemistry as will be studied in future work.

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