

Research Article

Synthesis and Characterization of New Schiff Bases Derived from N (1)-Substituted Isatin with Dithiooxamide and Their Co(II), Ni(II), Cu(II), Pd(II), and Pt(IV) Complexes

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Three new Schiff bases of N-substituted isatin L_I , L_{II} , and L_{III} = Schiff base of N-acetyl isatin, N-benzyl isatin, and N-benzoyl isatin, respectively, and their metal complexes $C_{1a,b}$ = $[Co_2(L_I)_2Cl_3]Cl$, C_2 = $[Ni(L_I)_2Cl_2] \cdot 0.4BuOH$, C_3 = $[Cu(L_I)Cl(H_2O)]Cl \cdot 0.5BuOH$, C_4 = $[Pd(L_I)_2Cl]Cl$, C_5 = $[Pt(L_I)_2Cl_2]Cl_2 \cdot 1.8EtOH \cdot H_2O$, C_{6a} = $[Co(L_{II})Cl]Cl \cdot 0.4H_2O \cdot 0.3DMSO$, C_{6b} = $[Co(L_{II})Cl]Cl \cdot 0.3H_2O \cdot 0.1BuOH$, C_7 = $[Ni(L_{II})Cl_2]$, C_8 = $[Cu(L_{II})Cl_2] \cdot H_2O$, C_9 = $[Pd(L_{II})_2]Cl_2$, C_{10} = $[Pt(L_{II})_2.5Cl]Cl_3$, C_{11a} = $[Co(L_{III})]C_{12} \cdot H_2O$, C_{11b} = $[Co(L_{III})]Cl_2 \cdot 0.2H_2O$, and C_{12} = $[Ni(L_{III})_2]Cl_2$, C_{13} = $[Ni(L_{III})_2]Cl_2$ were reported. The complexes were characterized by elemental analyses, metal and chloride content, spectroscopic methods, magnetic moments, conductivity measurements, and thermal studies. Some of these compounds were tested as antibacterial and antifungal agents against *Staphylococcus aureus*, *Proteus vulgaris*, *Candida albicans*, and *Aspergillus niger*.

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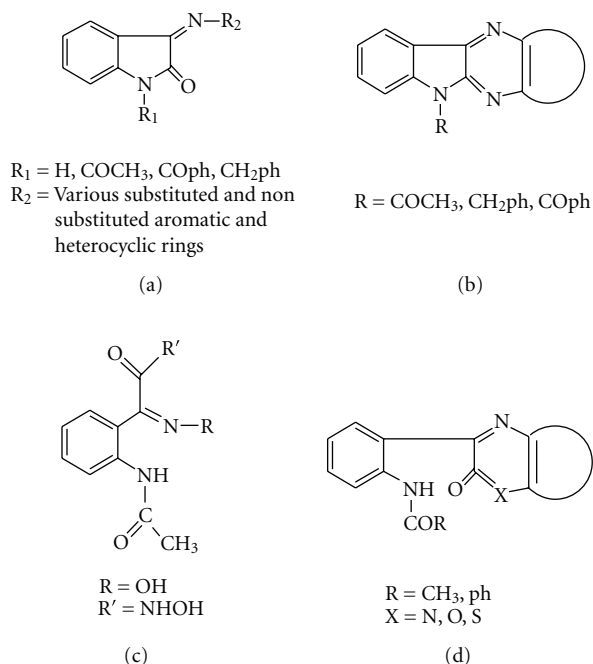
1. Introduction

Isatin (indole-2,3-dione) and its derivatives have shown a wide scale of biological activities such as antibacterial [1–3], antifungal [1, 3–5], anticonvulsant [2, 6], anti-HIV [7], anticancer [1, 2], antiviral [1], and enzyme inhibitors [2]. The Schiff bases (a) and (b) (Scheme 1) derived from isatin and its derivatives with different amines have been studied [1, 2, 6, 8–13]. The reaction of N-acetyl, N-benzoyl, and N-tosyl isatin and their Schiff base derivatives (c) and (d) (Scheme 1) with ethanol, methanol, isopropyl alcohol, allyl alcohol, $TsNH_2$, pyrrolidine, and water yield products resulting from nucleophilic attack at the C-2 carbonyl that leads to heterocyclic ring cleavage [8, 14]. The present work aims to study the synthesis and antibacterial activity of three new ligands derived from condensation of N-acetyl, N-benzyl, and N-benzoyl isatin with the chelating agent dithiooxamide (ethanedithioamide or rubeanic acid) *dto* and their metal complexes. The Schiff bases of dithiooxamide and their complexes have received most of the attention because of the semiconductive, magnetic, spectroscopic,

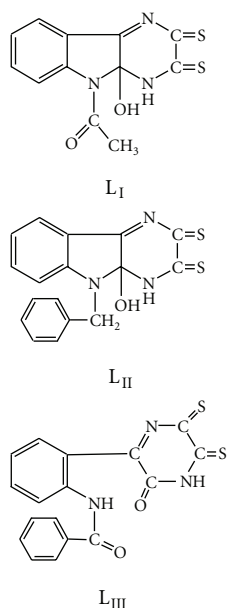
and thermal properties [15–17] as well as being used as semiconductors antibacterial and antifungal agents [18–20].

2. Experimental/Materials and Methods

All chemicals used were of analytical reagent grade (AR) except *dto* and ethanol which were purified prior to use [21]. FTIR spectra were recorded on SHIMADZU FTIR-8400S, Fourier Transform, Infrared spectrophotometer. The electronic spectra ($\lambda(200\text{--}1100\text{ nm})$) in different solvents were recorded on Shimadzu (UV-Vis)-160 spectrophotometer. Elemental microanalyses were performed on Euro vector EA 3000 A. The metal contents of the complexes were determined by atomic absorption technique using Varian-AA775, Atomic Absorption Spectrophotometer. Mass spectra were recorded on Shimadzu QP 5050A. 1H NMR was performed by using Bruker Ultra Shield 300 MHz NMR spectrophotometer. Thermal analyses (TG and DTG) were carried out by using Shimadzu Thermal Analyzer Type 50 H. Electrical conductivity measurements for complexes



SCHEME 1: Schiff bases of isatin derivatives.

SCHEME 2: The structures of the prepared ligands L_I , L_{II} , and L_{III} .

(10^{-3} M) in DMF and DMSO at room temperature were carried out by using Hunts Capacitors Trade Mark British made. Magnetic moments (μ_{eff} , B.M) for the prepared complexes in the solid state at room temperature were measured by using Bruker Magnet B.M-6. The chloride content for complexes was determined by Mohr's method. N-acetyl isatin, N-benzylisatin, N-benzoylisatin, and $\text{PdCl}_2(\text{phCN})_2$ were prepared by methods reported in literature [6, 22–25].

3. Synthesis of Ligands

All attempts to prepare 1-(9a-Hydroxy-2,3-dithiooxo-1,2,3,9a-tetrahydro-1,4,9-triaza-fluorene-9-yl)-ethanone (L_I) (Scheme 2) and 9-Benzyl-9a-hydroxy-9,9a-dihydro-1H-1,4,4-triaza-fluorene-2,3-dithione (L_{II}) (Scheme 2) in solutions were unsuccessful; therefore solid reaction was carried out to prepare the two ligands.

3.1. Schiff Base of N-Acetyl isatin: 1-(9a-Hydroxy-2,3-dithiooxo-1,2,3,9a-tetrahydro-1,4,9-triaza-fluorene-9-yl)-ethanone (L_I). A powdered mixture of N-acetyl isatin (0.3092 g, 1.6 mmol) and *dto* (0.0983 g, 0.8 mmol) in a sealed Carius tube was heated in a stirred oil bath at 160–170°C for 2 hours. The melt colour was changed from orange to dark brown. After cooling to room temperature, the solid product was ground and dissolved in butanol, followed by precipitation with ether. A black precipitate was formed. The product was filtered off and washed several times with ether to remove the unreacted materials giving brown crystals. Yield (0.116 g, 48.76%), m.p (220°C decomp.). ^1H NMR data δ (ppm), (CDCl_3): 2.508 (3H,s, CH_3); 3.34 (2H,s,OH and NH thioamide); 7.074–7.853 (4H, m, aromatic protons). MS(EI), m/z(%): 207(21), 161(10), 146(23), 133(9), 92(10), 78(59), 63(84), 44(100). Anal. for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2\text{S}_2$ Calcd. C, 49.48; H, 3.09; N, 14.43%; Found: C, 50.54; H, 3.22; N, 13.23%.

3.2. Schiff Base of N-Benzylisatin: 9-Benzyl-9a-hydroxy-9,9a-dihydro-1H-1,4,4-triaza-fluorene-2,3-dithione (L_{II}). A powdered mixture of N-benzylisatin (0.829 g, 3.5 mmol) and *dto* (0.85 g, 7 mmol) was heated in a sealed Carius tube in an oil bath at 140°C for 10 hours. Colour of melt was changed from orange to dark brown. After cooling to room temperature, a solid mass was formed. The product was ground and purified several times in refluxing ethanol, filtered off, washed with hot ethanol followed by acetone and dried, giving dark brown crystals. Yield (0.2679 g, 22.3%), m.p (>250°C). ^1H NMR data δ (ppm), (DMSO): 3.45(2H, s, OH and NH thioamide); 5.1(2H, w, CH_2 benzyl); 6.9–7.2(9H, m, aromatic protons). MS(EI), m/z(%): 156(11), 149(15), 127(13), 105(11), 78(100), 63(100). Anal. for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{OS}_2$ Calcd.: C, 60.17; H, 3.83; N, 12.38%; Found: C, 61.10; H, 3.43; N, 12.98%.

3.3. Schiff Base of N-Benzoylisatin: N-[2-(3-oxo-5,6-dithiooxo-3,4,5,6-tetrahydro-pyrazin-2-yl)-phenyl] benzamide (L_{III}). Equimolar amounts of benzoylisatin (0.2 g, 0.79 mmol) and *dto* (0.0957 g, 0.79 mmol) in butanol (2 cm^3) containing 4 drops of piperidine were heated under reflux with stirring for 5 hours during which the colour of solution was changed from orange to brown. The solution mixture was left to stand overnight and then cooled down to 0°C. Cold ether was added until a dark brown precipitate was formed. The product was filtered off, washed several times with acetone followed by ether. Yield (0.0857 g, 30.51%), m.p. (250°C decomp.), ^1H NMR data (ppm), (DMSO): 4.902–5.101(1H, b, NH thioamide); 7.144–7.860(9H, m, aromatic protons); 10.124(1H, b, NH benzoyl moiety). MS(EI),

H, 3.05; N, 8.54%; S, 13.02%; Found: C, 42.15; H, 2.74; N, 8.16; S, 12.94%. M, 12.91(Calcd), 13.12(Found)%; Cl, 14.44(Calcd), 14.55(Found)%. “C₉”: colour(dark brown). Yield (43.38%). Anal. for [(C₃₄H₂₆N₆O₂S₄Pd)(Cl₂)] Calcd.: C, 47.71; H, 3.04; N, 9.82%; S, 14.97%; Found: C, 47.75; H, 3.11; N, 9.69; S, 15.52%. M, 12.39(Calcd), 13.00(Found)%; Cl, 8.30(Calcd), 8.47(Found)%. “C₁₀”: colour(dark brown). Yield (32.42%). Anal. for [((C₁₇H₁₃N₃OS₂)_{2.5}PtCl)Cl₃] Calcd.: C, 43.05; H, 2.74; N, 8.86%; S, 13.50%; Found: C, 43.84; H, 2.55; N, 9.17; S, 14.09%. M, 16.46(Calcd), 15.87(Found)%. “C_{11a}”: colour(brown). Yield (33.43%). Anal. for [(C₁₇H₁₁N₃O₂S₂Co)Cl₂·H₂O] Calcd.: C, 40.72; H, 2.59; N, 8.38 %; Found: C, 40.05; H, 2.34; N, 7.82%; M, 11.75(Calcd), 12.25(Found)%. Cl, 14.17(Calcd), 14.85(Found)%. “C₁₂”: colour(brown). Yield (34.37%). Anal. for [(C₃₄H₂₂N₆O₄S₄Ni)(Cl₂)] Calcd.: C, 48.82; H, 2.63; N, 10.05%; Found: C, 49.62; H, 2.46; N, 9.41; % M, 7.02(Calcd), 7.50(Found)%. Cl, 8.49(Calcd), 8.56(Found)%. “C₁₃”: colour(brown). Yield (34.03%). Anal. for [(C₃₄H₂₂N₆O₄S₄Pd)(Cl₂)] Calcd.: C, 46.20; H, 2.46; N, 9.51; S, 14.49%; Found: C, 46.47; H, 2.66; N, 9.79; S, 14.78%. M, 12.00(Calcd), 11.50(Found)%. Cl, 8.04(Calcd), 8.63(Found)%.

(B) To a solution mixture of N-acetyl, N-benzyl, or N-benzoylisatin (0.02 mmol) 0.0037, 0.0047, and 0.005 g, respectively, with *dto* (0.01 mmol) (0.0012 g), (0.04 mmol) (0.0048 g), and (0.02 mmol) (0.0024 g), respectively, in butanol was added a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.02 mmol) in butanol. The mixture was heated under reflux. Precipitation took place immediately. Heating was continued for 4 hours to achieve complete precipitation. The product was filtered, washed with hot butanol, followed by ethanol, acetone, ether, and vacuum dried. “C_{1b}”: colour (dark brown). Yield (25.15%). Anal. for $(\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}_4\text{S}_4\text{Co}_2\text{Cl}_3)\text{Cl}$ Calcd.: C, 34.21; H, 2.13; N, 9.97; S, 15.20%; Found: C, 34.15; H, 1.95; N, 10.31; S, 15.07%. M, 13.99(Calcd), 13.30(Found)%; Cl, 16.86(Calcd), 16.19(Found)%. “C_{6b}”: colour (dark brown). Yield (71.42%). Anal. for $[(\text{C}_{17}\text{H}_{13}\text{N}_3\text{OS}_2\text{CoCl})\text{Cl} \cdot 0.3(\text{H}_2\text{O}) \cdot 0.1(\text{C}_4\text{H}_{10}\text{O})]$ Calcd.: C, 43.34; H, 3.03; N, 8.71; S, 13.28%; Found: C, 43.89; H, 3.35; N, 8.54; S, 13.48%. M, 12.22(Calcd), 12.25(Found)%; Cl, 14.73(Calcd), 14.44(Found)%. “C_{11b}”: colour (brown). Yield (41.72%). Anal. for $[(\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2\text{Co})\text{Cl}_2 \cdot 0.2\text{H}_2\text{O}]$ Calcd.: C, 41.93; H, 2.34; N, 8.63%; Found: C, 42.56; H, 2.53; N, 8.73; % M, 12.10(Calcd), 12.11(Found)%. Cl, 14.59(Calcd), 14.71(Found)%.

The two following methods were used to perform the antimicrobial tests.

(A) A solution mixture of the ligands L_I and L_{II} (0.01 mmol) (0.0029, 0.0033 g), respectively, with the metal salts $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$ (0.01 mmol) and (0.02 mmol) (0.0058, 0.0067 g) of L_I and L_{II} , respectively, with the metal salts $PdCl_2(phCN)_2$ and K_2PtCl_6 (0.01 mmol), in DMF (C_1), butanol (C_2 and C_3), or DMSO (C_4 – C_{10}) was heated under reflux for four hours. Precipitation of L_I complexes took place within 30 minutes while those of L_{II} was precipitated at the end of reflux time. The products were filtered, washed with hot ethanol and acetone, followed by ether and vacuum dried. Complexes of L_{III} were prepared in the same manner using a mixture of L_{III} (0.01 mmol, 0.0035 g) with the metal salts $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ (0.01 mmol), and (0.02 mmol, 0.007 g) of L_{III} with $PdCl_2(phCN)_2$ (0.01 mmol). “ C_{1a} ”: colour(dark brown) Yield (26.24%). Anal. for $(C_{24}H_{18}N_6O_4S_4Co_2Cl_3)Cl$ Calcd.: C, 34.21; H, 2.13; N, 9.97; S, 15.20%; Found: C, 34.32; H, 2.50; N, 9.42; S, 15.13%. M, 13.99(Calcd), 14.0(Found)%; Cl, 16.86(Calcd), 16.20(Found)%. “ C_2 ”: colour(dark brown). Yield (23.51%). Anal. for $[(C_{24}H_{18}N_6O_4S_4NiCl_2)0.4(C_4H_{10}O)]$ Calcd.: C, 47.63; H, 5.75; N, 8.33%; Found: C, 48.32; H, 5.45; N, 8.83%. M, 5.82(Calcd), 5.72(Found)%. “ C_3 ”: colour(dark brown). Yield (23.35%). Anal. for $[(C_{12}H_9N_3O_2S_2CuCl(H_2O))Cl.0.5(C_4H_{10}O)]$ Calcd.: C, 34.96; H, 3.32; N, 8.74%; Found: C, 34.01; H, 3.72; N, 9.73%. M, 13.21(Calcd), 13.85(Found)%. Cl, 14.77(Calcd), 14.70(Found)%. “ C_4 ”: colour(dark brown). Yield (35.18%). Anal. for $[(C_{24}H_{18}N_6O_4S_4PdCl)Cl]$ Calcd.: C, 37.94; H, 2.37; N, 11.06; S, 16.86%; Found: C, 38.40; H, 2.38; N, 11.15; S, 16.78%. M, 13.96(Calcd), 13.71(Found)%. Cl, 9.35(Calcd), 10.5(Found)%. “ C_5 ”: colour(brown). yield (19.08%). Anal. for $[(C_{24}H_{18}N_6O_4S_4PtCl_2)Cl_2 \cdot 1.8(C_2H_6O) \cdot H_2O]$ Calcd.: C, 32.47; H, 3.02; N, 8.23%; Found: C, 32.85; H, 3.27; N, 9.16%. M, 19.12(Calcd), 19.10(Found)%. “ C_{6a} ”: colour(dark brown). Yield (36.06%). Anal. for $[(C_{17}H_{13}N_3OS_2CoCl)Cl \cdot 0.4(H_2O) \cdot 0.3(C_2H_6SO)]$ Calcd.: C, 42.28; H, 3.12; N, 8.40; S, 12.81%; Found: C, 41.85; H, 2.72; N, 8.15; S, 12.00%. M, 11.79(Calcd), 12.11(Found)%; Cl, 14.21(Calcd), 14.58(Found)%. “ C_7 ”: colour(dark brown). Yield (45.30%). Anal. for $[C_{17}H_{13}N_3OS_2NiCl_2]$ Calcd.: C, 43.52; H, 2.77; N, 8.96%; Found: C, 44.20; H, 3.05; N, 9.24%. M, 12.52(Calcd), 12.23(Found)%; Cl, 15.14(Calcd), 15.47(Found)%. “ C_8 ”: colour(dark brown). Yield (45.39%). Anal. for $[(C_{17}H_{13}N_3OS_2Cu)Cl_2 \cdot H_2O]$ Calcd.: C, 41.50;

5.1. Agar Diffusion Method. In this method the colonies of the selected bacteria, namely, *Staphylococcus aureus* (G^+), *Proteus vulgaris* (G^-), and the fungus *Candida albicans* were spread on the surface of solidified nutrient agar. Suitably separated 7 mm diameter holes were made in each agar plate. Each hole was injected with 0.1 mL of 150, 350, 650, and 1000 ppm of the studied compound in DMSO. The agar plates were incubated at 37°C for 24 hours. Diameters of growth inhibition zones were measured in mm depending on diameter and clarity.

5.2. Agar Dilution Method. In this method the antifungal activity of 250 ppm of some selected compounds in DMSO was screened against *Aspergillus niger*. 2.5 cm³ of 2000 ppm of tested solution was added to 20 cm³ of hot agar solution. The homogenized mixture was then poured into petridish and left to solidify. The *Aspergillus* colony (9 mm diameter) was fixed on the solidified agar, and the medium was incubated at 37°C for 8 days.

6. Results and Discussion

The IR spectra showed that the three ligands exhibited vibrational modes of $\nu_{C=N}$ of azomethine group [4, 6, 26–28], (ν_{C-N} , δ_{NH}), (ν_{C-N} , ν_{C-S}), ν_{C-S} , and $\nu_{C=S}$ of *dto* moiety [29, 30] (Table 1). Spectra of L_I and L_{II} showed vibrational bands related to stretching modes of OH groups [31, 32]. The position of the bands assigned to ν_{NH} vibrations of the cyclic rings was dependent on their environment. ν_{NH} of L_{II} and L_{III} were observed at lower frequencies compared with that of L_I (Table 1) [27, 32]. The latter exhibited bands assigned to $\nu_{C=O}$ and ν_{NH} of amide and lactam rings [6, 27, 31, 32]. The spectra of L_I complexes with Co(II), Cu(II), and Pd(II) ions exhibited shift in ν_{OH} and $\nu_{C=N}$ (azomethine) vibrations. The latter two complexes together with Ni(II) complex showed additional shifts in ν_{NH} to lower frequencies while no significant changes were observed on vibrational modes of C=O group which rules out coordination with carbonyl oxygen. Shifts of thioamide bands (III and IV) were observed in the spectra of Cu(II) and Pt(IV) complexes and were attributed to coordination of metal ion with sulfur atom [33]. Metal complexes of L_{II} showed bands assigned to $\nu_{C=O}$ and ν_{NH_2} vibrations (Table 1). This may be attributed to cleavage of thioamide ring on complexation leading reappearance of $\nu_{C=O}$ and ν_{NH_2} of both C-2 and NH₂ of isatin and *dto* moieties, respectively. Shifts in ν_{NH_2} (compared with ν_{NH_2} of the free *dto* (3296, 3203 cm⁻¹)) [34] to lower frequencies were observed in all spectra of complexes except that of Ni(II) which was shifted to higher frequency. Bands related to $\nu_{C=O}$ vibrations in spectra of both Ni(II) and Cu(II) complexes were shifted to higher frequencies while spectra of the other complexes showed shifts to lower frequencies. Additional shifts were observed in the bands assigned to $\nu_{C=N}$ (azomethine) in all complexes except that of Cu(II). The latter complex exhibited shift of $\nu_{C=S}$ band to lower frequency which refers to coordination of sulfur to Cu(II) ion [33]. The spectra of L_{III} metal complexes exhibited shifts in vibrational modes of $\nu_{C=O}$ and band

IV of thioamide group as a result of coordination with metal ions [33, 35]. Additional shift in position of bands assigned to $\nu_{C=N}$ was observed in the spectra of Co(II) and Ni(II) complexes. Shifts in the position of ν_{NH} amide and $\nu_{C=O}$ of lactam ring were observed in the spectra of the Pd(II) complex as a result of coordination. Bands related to vibrational modes of lattice solvent, coordinated water were observed at 3500–3400 cm⁻¹ [36–38]. Bands appeared at lower frequencies were referred to M–O, M–N, M–S, and M–Cl stretching modes [36–38]. Further data are collected in (Table 1).

The electronic spectra of L_I , L_{II} , and L_{III} exhibited high-intensity multiple bands in DMF and DMSO at 36231–20000 cm⁻¹. These bands were assigned to $\pi \rightarrow \pi^*$ transition of conjugated system. L_{III} exhibited additional low-intensity band which was assigned to $n \rightarrow \pi^*$ transition. Changes in positions and profile (C_8 – C_{10}) of bands were observed in the spectra of metal complexes. Bands related to the (CT) transition were observed as a shoulder on the ligand band in the spectra of C_1 , C_3 , C_6 , C_7 , C_9 , and C_{10} complexes (Table 2). The bands observed in the spectra of Co(II) complexes in the visible region were assigned to $^4A_2 \rightarrow ^4T_2(\nu_1)$, $^4A_2 \rightarrow ^4T_1(F)(\nu_2)$, and $^4A_2 \rightarrow ^4T_1(P)(\nu_3)$. The magnetic moment values of Co(II) complexes were in the range of (3.959–4.6 BM) (Table 2). This indicates tetrahedral geometry around Co(II) ions [36–39] (Scheme 3). The Ni(II) complex C_2 gave a greenish yellow colour in DMF indicating the exchange of weak ligand atoms with solvent molecules [40–43]. The spectrum of this complex showed bands characteristic of octahedral Ni(II) complex [36–38, 40–43] (Table 2), while the other Ni(II) complexes (C_7 and C_{12}) showed tetrahedral geometries (Scheme 3).

The electronic spectra and magnetic moments (μ_{eff} B.M) (Table 2) of these complexes were consistent with these assignment [36–38, 40–43]. Spectral data (B' , Dq/B' , $10Dq$ and β) (Table 2), for the Co(II) and Ni(II) complexes were calculated by applying band energies on Tanabe Sugano diagrams. The energy of ν_1 for Co(II) complexes (C_1 , C_6 , C_{11}) and Ni(II) complexes (C_7 , C_{12}) and ν_3 for Ni(II) complex C_2 were also calculated from the diagrams. The spectrum of the Cu(II) complex C_3 exhibited three bands (Table 2) attributed to the spin allowed transitions $^2B_{1g} \rightarrow ^2A_{1g}(\nu_1)$, $^2B_{1g} \rightarrow ^2B_{2g}(\nu_2)$ and $^2B_{1g} \rightarrow ^2E_g(\nu_3)$ of Jahn Teller tetragonally distorted octahedral Cu(II) complexes [34]. The magnetic moment of the complex (2.36 B.M) indicated paramagnetic character with a high spin orbital coupling [40–43]. The spectrum of Cu(II) complex C_8 exhibited two bands (Table 2) which were assigned to $^2B_{1g} \rightarrow ^2A_{1g}(\nu_1)$, and $^2B_{1g} \rightarrow ^2B_{2g}(\nu_2)$. These bands were attributed to square planar Cu(II) complexes [44] (Scheme 3). Magnetic moment ($\mu_{eff} = 1.84$ B.M) of the complex supported such conclusion [36–38, 44]. The spectra of the diamagnetic Pd(II) complexes (C_4 , C_9 , and C_{13}) showed two bands assigned to $^1A_{1g} \rightarrow ^1A_{2g}(\nu_1)$ and $^1A_{1g} \rightarrow ^1B_{1g}(\nu_2)$ and the additional band $^1A_{1g} \rightarrow ^1E_g(\nu_3)$ for C_4 . These bands are attributed to square planar Pd(II) complexes [34–38, 40–43]. The spectra of the diamagnetic Pt(IV) complexes exhibited two bands which were assigned to forbidden transitions

TABLE 1: FTIR vibrations for the ligands and their metal complexes.

(a)

Symbol	ν_{OH}	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	Thioamide				$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
					Band I $\nu_{\text{C-N}} + \delta_{\text{NH}}$	Band II $\nu_{\text{C-N}} + \nu_{\text{C-S}}$	Band III $\nu_{\text{C-S}}$	Band IV $\nu_{\text{C=S}}$			
L _I	3400	3298	1710	1650	1540	1465	1170	881	—	—	—
C _{1a} Co(II)	3344	3295	1718	1631	1545	1460	1162	877	559	389	277*
C _{1b} Co(II)	3350	3295	1718	1631	1545	1460	1165	877	559	389	277*
C ₂ Ni(II)	3402	3227	1706	1631	1540	1396	1165	880	—	335	320
C ₃ Cu(II)	3347	3260	1716	1627	1520	1450	1150	780	408	350	339
C ₄ Pd(II)	3395	3250	1720	1630	1573	1458	1170	889	586	350	331
C ₅ Pt(IV)	3400	3295	1715	1666	1510	1483	1134	850	—	340	300

Lattice butanol, C₂, C₃ = 3500, 3750 cm⁻¹, Lattice ethanol, C₅ = 3495 cm⁻¹ Coord·H₂O, C₃ = 3456, 750, 675; Lattice H₂O, C₅ = 3425 cm⁻¹ $\nu_{\text{M-S}}$, C₃ and C₅ = 345 and 370 cm⁻¹ respectively, *bridging.

(b)

Symbol	ν_{NH_2}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	Thioamide				H ₂ O Lattice	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
				Band I $\nu_{\text{C-N}} + \delta_{\text{NH}}$	Band II $\nu_{\text{C-N}} + \nu_{\text{C-S}}$	Band III $\nu_{\text{C-S}}$	Band IV $\nu_{\text{C=S}}$				
L _{II}	—	—	1604	1554	1461	1170	848	—	—	—	—
C _{6a} Co(II)	3255	1724	1612	1555	1446	1165	868	3417	547	466 401	273
C _{6b} Co(II)	3250	1720	1612	1560	1450	1180	864	3450	493	450 385	230
C ₇ Ni(II)	3450	1750	1620	1550	1448	1150	870	—	520	400	316
C ₈ Cu(II)	3224	1751	1589	1548	1448	1188	817	3450	560	478 385	—
C ₉ Pd(II)	3147	1720	1612	1550	1465	1180	856	—	500	400 380	—
C ₁₀ Pt(IV)	3294	1720	1612	1548	1472	1170	850	—	500	400 370	330

ν_{OH} , L_{II} = 3400 cm⁻¹; ν_{NH} , L_{II} = 3145 cm⁻¹; Lattice butanol, C_{6b} = 3550 cm⁻¹ $\nu_{\text{M-S}}$, C₈ = 320 cm⁻¹.

(c)

Symbol	$\nu_{\text{N-H}}$ amide	$\nu_{\text{C=O}}$ amide	$\nu_{\text{N-H}}$ lactam	$\nu_{\text{C=O}}$ lactam	$\nu_{\text{C=N}}$	Thioamide group				$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$
						Band I $\nu_{\text{C-N}} + \delta_{\text{NH}}$	Band II $\nu_{\text{C-N}} + \nu_{\text{C-S}}$	Band III $\nu_{\text{C-S}}$	Band IV $\nu_{\text{C=S}}$			
L _{III}	3394	1635	3247	1674	1600	1535	1465	1103	880	—	—	—
C _{11a} Co(II)	3410	1625	3247	1674	1587	1535	1450	1095	830	590	480	320
C _{11b} Co(II)	3410	1620	3247	1674	1580	1535	1450	1100	840	600	480	300
C ₁₂ Ni(II)	3456	1625	3250	1670	1589	1535	1450	1100	860	580	450	308
C ₁₃ Pd(II)	3386	1620	3250	1666	1600	1535	1473	1095	850	617	401	310

Lattic H₂O, C_{11a}, C_{11b} = 3500 cm⁻¹

TABLE 2: Electronic spectra, spectral parameters and magnetic moment with suggested structures of L_I , L_{II} , and L_{III} complexes.

Symbol	Band positions (cm ⁻¹)	Assignment	Dq/ \bar{B} (β)	\bar{B} (cm ⁻¹)	10Dq (cm ⁻¹)	μ_{eff} (B.M)	Suggested structure	Molar conductivity S·mol ⁻¹ ·cm ² in DMF and DMSO*
C _{1a} Co(II)	ν_1 6388 (cal.) ν_2 10752 ν_3 16930 (avr.) ν_4 21008	$^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1(F)$ $^4A_2 \rightarrow ^4T_1(P)$ L \rightarrow M (C.T)	1.3 (0.484)	470.2	6112	4.5	Tetrahedral	32.12*
C _{1b} Co(II)	ν_1 6388 (cal.) ν_2 10752 ν_3 16930 (avr.) ν_4 21881	$^4A_2 \rightarrow ^4T_2$ $^4A_1 \rightarrow ^4T_1(F)$ $^4A_2 \rightarrow ^4T_1(P)$ L \rightarrow M (C.T)	1.3 (0.484)	470.2	6112	4.61	Tetrahedral	29.7*
C ₂ Ni(II)	ν_1 12345 ν_2 16806 ν_3 27035 (cal.)	$^3A_2g \rightarrow ^3T_2g$ $^3A_2g \rightarrow ^3T_1g(F)$ $^3A_2g \rightarrow ^3T_1g(P)$	2.8 (0.440)	454.2	12717	3.31	Octahedral	46.45
C ₃ Cu(II)	ν_1 12150 ν_2 16666 ν_3 18761 ν_4 19646	$^2B_1g \rightarrow ^2A_1g$ $^2B_1g \rightarrow ^2B_2g$ $^2B_1g \rightarrow ^2Eg$ L \rightarrow M (C.T)				2.36	Octahedral	68.19
C ₄ Pd(II)	ν_1 12048 ν_2 16949 ν_3 20618	$^1A_1g \rightarrow ^1A_2g$ $^1A_1g \rightarrow ^1B_1g$ $^1A_1g \rightarrow ^1Eg$				Diamagnetic	Square planar	60.37
C ₅ Pt(IV)	ν_1 17825 ν_2 22371	$^1A_1g \rightarrow ^3T_1g(H)$ $^1A_1g \rightarrow ^3T_2g$				Diamagnetic	Octahedral	154.13
C _{6a} Co(II)	ν_1 6535 (cal.) ν_2 10526 ν_3 16666 ν_4 21551	$^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1$ $^4A_2 \rightarrow ^4T_1(P)$ L \rightarrow M (C.T)	1.25 (0.501)	487.3	6091	4.21	Tetrahedral	34.3*
C _{6b} Co(II)	ν_1 6389 (cal.) ν_2 10504 ν_3 16612 ν_4 20876	$^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1(F)$ $^4A_2 \rightarrow ^4T_1(P)$ L \rightarrow M (C.T)	1.25 (0.503)	488.5	6107	4.30	Tetrahedral	30.52*
C ₇ Ni(II)	ν_1 5473 (cal.) ν_2 11074 ν_3 15873 ν_4 18867	$^3T_1(F) \rightarrow ^3T_2(F)$ $^3T_1(F) \rightarrow ^3A_2(F)$ $^3T_1(F) \rightarrow ^3T_1(P)$ L \rightarrow M (C.T)	0.82 (0.70)	721.5	5768	2.73	Tetrahedral	7.9*
C ₈ Cu(II)	ν_1 13440 ν_2 19230	$^2B_1g \rightarrow ^2A_1g$ $^2B_1g \rightarrow ^2B_2g$				1.84	Square planar	155.8

TABLE 2: Continued.

Symbol	Band positions (cm ⁻¹)	Assignment	Dq/ \bar{B} (β)	\bar{B} (cm ⁻¹)	10Dq (cm ⁻¹)	μ_{eff} (B.M)	Suggested structure	Molar conductivity S·mol ⁻¹ ·cm ² in DMF and DMSO*
C ₉ Pd(II)	ν_1 16949 ν_2 21367	$^1A_1g \rightarrow ^1A_2g$ $^1A_1g \rightarrow ^1B_1g$ (C.T)				Diamagnetic	Square planar	125.4
C ₁₀ Pt(IV)	ν_1 14388 ν_2 20576	$^1A_1g \rightarrow ^3T_1g$ $^1A_1g \rightarrow ^3T_2g$ (C.T)				Diamagnetic	Octahedral	196.6
C _{11a} Co(II)	ν_1 6410 (cal.) ν_2 10000 ν_3 15641 (avr.)	$^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1$ (F) $^4A_2 \rightarrow ^4T_1$ (P)	1.5 (0.449)	436.8	6552	3.959	Tetrahedral	143.5
C _{11b} Co(II)	ν_1 6410 (cal.) ν_2 10000 ν_3 15641 (avr.)	$^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1$ (F) $^4A_2 \rightarrow ^4T_1$ (P)	1.5 (0.449)	436.8	6552	3.997	Tetrahedral	150.6
C ₁₂ Ni(II)	ν_1 4994 (cal.) ν_2 10482 ν_3 15483 (avr.)	$^3T_1(F) \rightarrow ^3T_2(F)$ $^3T_1(F) \rightarrow ^3A_2(F)$ $^3T_1(F) \rightarrow ^3T_1(P)$	0.74 (0.653)	673.1	4980	2.746	Tetrahedral	159.4
C ₁₃ Pd(II)	ν_1 12820 ν_2 16666	$^1A_1g \rightarrow ^1A_2g$ $^1A_1g \rightarrow ^1B_1g$				Diamagnetic	Square planar	148.2

$^1A_1g \rightarrow ^3T_1g$ and $^1A_1g \rightarrow ^3T_2g$ showing octahedral geometry around Pt(IV) ion [40–43] (Scheme 3). The molar conductivities (Table 2) showed that electrolytic nature of the Pt(IV) complex (C₁₀) was 1 : 3, Pt(IV), Cu(II), Pd(II), Co(II) and Ni(II) complexes (C₅, C₈, C₉, C₁₁, C₁₂, and C₁₃) 1 : 2, and Co(II), Cu(II), and Pd(II) complexes (C₁, C₃, C₄, and C₆) 1 : 1, while the Ni(II) complexes (C₂ and C₇) were nonelectrolyte [45]. From these observations, together with the results obtained from other analytical data, the stereochemical structures of the complexes were suggested (Scheme 3).

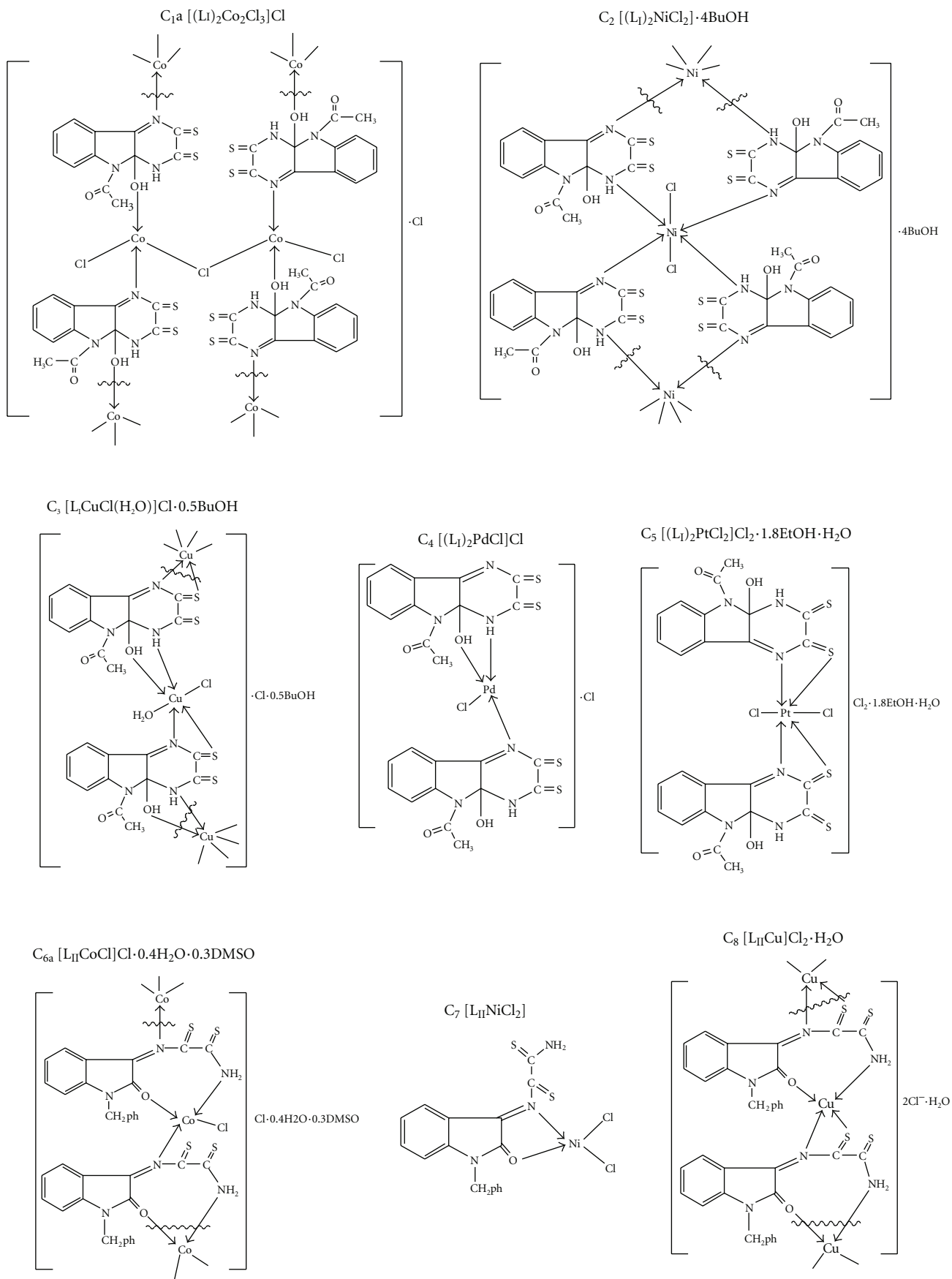
Thermogravimetric analyses (TG and DTG) have been studied at heating range of 50–800°C for the complexes (C₁, C₃, C₄, and C₇) under nitrogen atmosphere. The following results (Table 3) were explained according to analytical suggestions mentioned in literature [46–48]. (i) Lattice water, free ions, and organic fragments that are not directly coordinated to the metal ions were found to leave the complex at earlier stages compared with coordinated fragments, (ii) The heating range (50–800°C) produced incomplete decomposition of metal complexes, and the final products were dependent on the type of metal ion and on (M-L) affinity [36–38, 46, 49] which reflects the stability of complexes.

7. Biological Screening

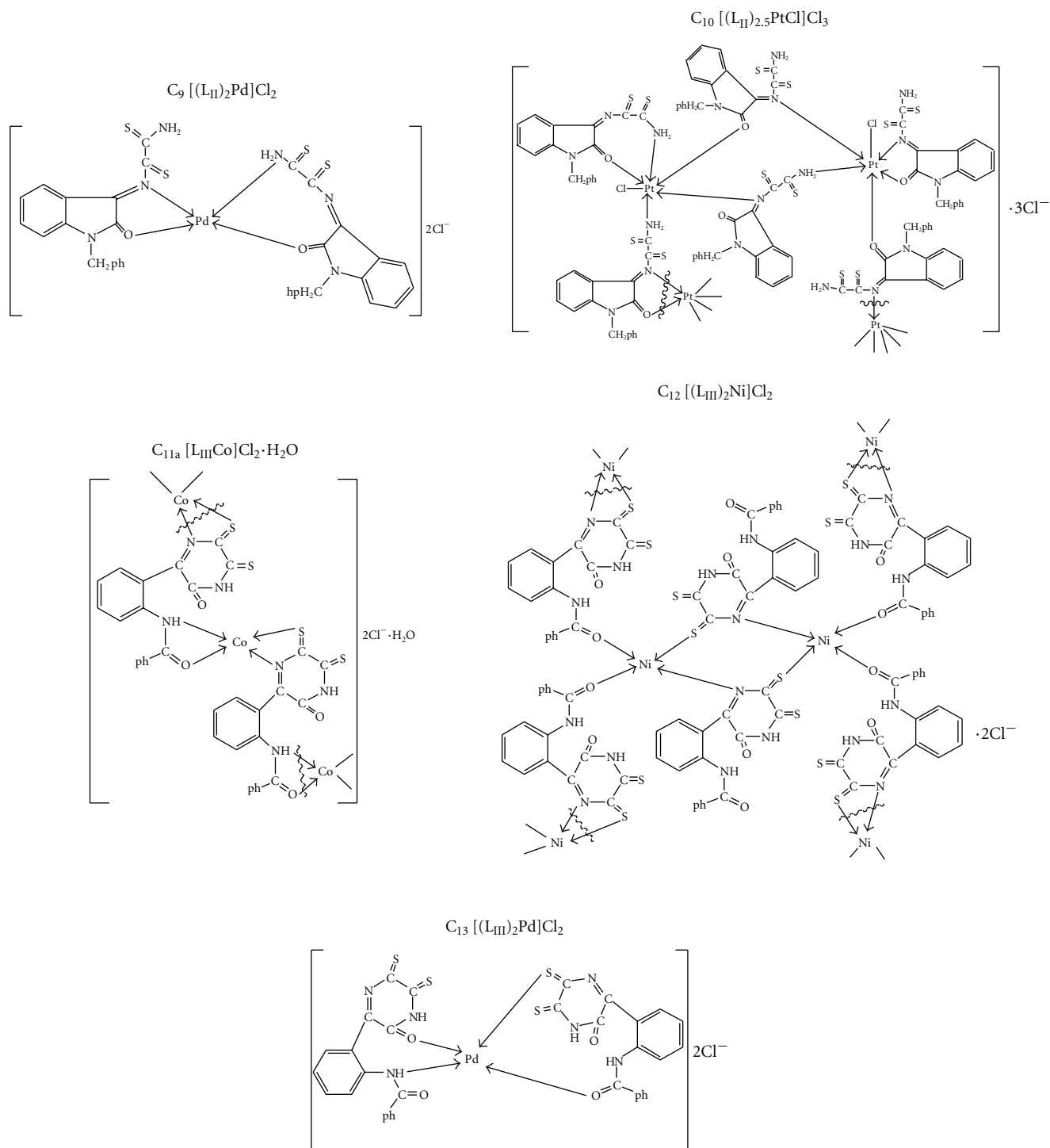
The antibacterial activity for precursors, L_I and L_{III}, and some of their complexes was evaluated against *Staphylococcus aureus* (G⁺) and *Proteus vulgaris* (G⁻) using the agar diffusion method. Diameter (mm) of growth inhibition zones was measured after incubation for 24 hours at 37°C. The results showed that no antibacterial action was recorded by the studied compounds using concentration of 150, 350, and 650 ppm. Using 1000 ppm (Table 4), L_I and its complexes were more active against *Staphylococcus aureus*, while L_{III} and its complexes (except C₁₃) were more active against *Proteus vulgaris* than the other studied compounds. The antifungal activity was evaluated against *Candida albicans* by the agar diffusion method and *Aspergillus niger* colony (9 mm diameter) by the agar dilution method using concentration of 250 ppm in DMSO. The results showed that L_I and L_{III} were inactive against *Candida albicans*; Co(II) (C₁₁), Ni(II) (C₁₂), and Pd(II) (C₁₃) complexes were more active than the parent ligand (L_{III}) while those of L_I were inactive except Cu(II) complex (C₃). L_I, L_{III}, and C₄ which were inactive against *Candida albicans* showed moderate activity against *Aspergillus niger* which refer to the effective selectivity of specific inhibitor on the microorganisms.

TABLE 3: Thermal decomposition of C₁, C₃, C₄, and C₇.

(a)		
C ₁		
$[(\text{Li})_2\text{Co}_2\text{Cl}_3]\text{Cl}$ M · wt = 841.8	Temperature range of decomposition °C	%Weight loss found (calc.)
-2Cl		
-2ph	251–369	41.128 (41.45)
-C ₅ H ₆ N ₂ O ₂		
-OH	370–421	2.798 (2.01)
-2Cl	465 – 547	7.932 (8.43)
-(C ₇ H ₃ N ₄ OS ₄) ₂ Co		48.25 (48.08)
(b)		
C ₃		
$[\text{LiCuCl}(\text{H}_2\text{O})]\text{Cl} \cdot 0.5\text{BuOH}$ M · wt = 480.5	Temperture range of decomposition °C	%Weight loss found (calc.)
-BuOH		
-Cl		
-H ₂ O	356–476	36.592 (36.94)
-CS		
-C ₂ H ₃ O		
-C ₂ NS	477–630	18.008 (17.68)
-NH		
-(phCHNO)CuCl		45.41 (45.36)
(c)		
C ₄		
$[(\text{Li})_2\text{PdCl}]\text{Cl}$ M · wt = 759	Temperture range of decomposition °C	%Weight loss found (calc.)
-2Cl	145–219	14.925(15.01)
-C ₂ H ₃ O		
-phC ₃ H ₄ NO ₂	219–351	21.189 (21.34)
-ph	482–568	10.538 (10.01)
-CN	679–735	3.188 (3.42)
-(C ₆ H ₃ N ₄ OS ₄)Pd		50.096 (50.197)
(d)		
C ₇		
$[\text{LiNiCl}_2]$ M · wt = 468.7	Temperture range of decomposition °C	%Weight loss found (calc.)
-CO	50–127	9.183 (9.38)
-NH ₂		
-phCH ₂	239–377	19.672 (19.415)
-2Cl	432–565	34.42 (34.35)
-phN		
-(C ₃ NS ₂)Ni		36.858 (36.84)



SCHEME 3: Continued.



SCHEME 3: Suggested structures of studied compounds.

8. Conclusions

- (1) Condensation reaction of N-acetyl, N-benzyl, and N-benzoyl isatins with *dto* gave Schiff base ligands L_I – L_{III} , as was confirmed by 1H , ^{13}C NMR, and IR spectra.
- (2) The formation of the Schiff base ligand L_{III} took place with ring cleavage at C-2 of the heterocyclic ring of the benzoylisatin. Whereas the formation of L_I and L_{II} took place without ring cleavage.
- (3) The presence of various donor atoms and the stereochemistry of the studied ligands enhanced different

TABLE 4: Antibacterial and Antifungal activities of studied compounds.

Compounds	<i>Staphylococcus aureus</i> inhibition diameter (mm) 1000 ppm	<i>Proteus vulgris</i> inhibition diameter (mm) 1000 ppm	<i>Candida albicans</i> inhibition diameter (mm) 1000 ppm	<i>Aspergillus niger</i> growth diameter (mm) 1000 ppm
DMSO	Zero	Zero	Zero	25
Isatin	3	8	6	
N-acetylisatin	4	Zero	5	
N-benzylisatin	5	5	6	
N-benzoylisatin	5	5	Zero	
L _I	8	5	Zero	9
C ₂ (Ni(II))	4	8	Zero	
C ₃ (Cu(II))	9	5	5	
C ₄ (Pd(II))	18	5	Zero	9
L _{III}	6	8	Zero	9
C ₁₁ (Co(II))	3	10	14	9
C ₁₂ (Ni(II))	Zero	12	11	
C ₁₃ (Pd(II))	3	Zero	11	

complexing behaviours and geometries using the studied metal ions.

- (4) The results of the physical properties and spectral analyses of cobalt complexes prepared by template reaction demonstrated the recommendation of for synthesis of metal complexes of the studied ligands, due to less time consuming and in general more yield of products.
- (5) The study of biological activity of the studied ligands and some of their metal complexes against bacteria and fungi showed selectivity nature of microorganism towards these compounds and indicated the possibility of using some of them as antibacterial and antifungal agents.

References

- [1] G. Cerhiaro and A. M. D. Ferreira, "Oxindoles and copper complexes with oxindole-derivatives as potential pharmacological agents," *Journal of the Brazilian Chemical Society*, vol. 17, no. 8, pp. 1473–1485, 2006.
- [2] S. N. Pandeya, S. Smitha, M. Jyoti, and S. K. Sridhar, "Biological activities of isatin and its derivatives," *Acta Pharmaceutica*, vol. 55, pp. 27–46, 2005.
- [3] V. K. Sharma, S. Srivastava, and A. Srivastava, "Novel coordination complexes of the trivalent ruthenium, rhodium and iridium with hydrazones derived from isatin hydrazide and various aldehydes with spectral and biological characterization," *Polish Journal of Chemistry*, vol. 80, pp. 387–396, 2006.
- [4] V. K. Sharma, A. Srivastava, and S. Srivastava, "Synthetic, structural and antifungal studies of coordination compounds of Ru(III), Rh(III) and Ir(III) with tetradentate Schiff bases," *Journal of the Serbian Chemical Society*, vol. 71, no. 8-9, pp. 917–928, 2006.
- [5] R. M. Abdel Rahman, Z. El Gendy, and M. B. Mahmoud, "Synthesis of some new 3-substituted 1,2,4-triazino-indole derivatives and related compounds of potential antifungal activity," *Indian Journal of Chemistry B*, vol. 29, pp. 352–358, 1990.
- [6] S. N. Pandeya, A. S. Raja, and J. P. Stables, "Synthesis of isatin semicarbazones as novel anticonvulsants-role of hydrogen bonding," *Journal of Pharmacy and Pharmaceutical Sciences*, vol. 5, no. 3, pp. 266–271, 2002.
- [7] T. R. Bal, B. Anand, P. Yogeeswari, and D. Sriram, "Synthesis and evaluation of anti-HIV activity of isatin β -thiosemicarbazone derivatives," *Bioorganic and Medicinal Chemistry Letters*, vol. 15, no. 20, pp. 4451–4455, 2005.
- [8] J. F. M. da Silva, S. J. Garden, and A. C. Pinto, "The chemistry of isatins: a review from 1975 to 1999," *Journal of the Brazilian Chemical Society*, vol. 12, no. 3, pp. 273–324, 2001.
- [9] E. H. El Ashry, E. Ramadan, H. M. Abdel Hamid, and M. Hagar, "Microwave irradiation for accelerating each step for the synthesis of 1,2,4-triazino[5,6-b]indole-3-thiols and their derivatives from isatin and 5-chloroisatin," *Synlett*, no. 4, pp. 723–725, 2004.
- [10] G. Pelosi, C. Pelizzi, M. B. Ferrari, M. C. Rodríguez-Argüelles, C. Vieito, and J. Sanmartín, "Isatin 3-semicarbazone and 1-methylisatin 3-semicarbazone," *Acta Crystallographica Section C*, vol. 61, no. 10, pp. 589–592, 2005.
- [11] D. Sriram, T. R. Bal, and P. Yogeeswari, "Aminopyrimidinimo isatin analogues: design of novel non-nucleoside HIV-1 reverse transcriptase inhibitors with broad spectrum chemotherapeutic properties," *Journal of Pharmacy and Pharmaceutical Sciences*, vol. 8, no. 3, pp. 565–577, 2005.
- [12] K. C. Joshi, P. Chand, and A. Dandia, "Studies in spiroheterocycles—part II—reactions of fluorine containing indole-2,3-diones with 1,2-phenylenediamines & 2,3-diaminopyridine in different media," *Indian Journal of Chemistry B*, vol. 23, pp. 743–745, 1984.
- [13] B. S. Joshi, M. A. Likhate, and N. Viswanathan, "Reaction of N-acylisatins with diamines," *Indian Journal of Chemistry B*, vol. 23, pp. 114–116, 1984.
- [14] P. De Mayo and J. J. Ryan, "The constitution of isamic acid," *Canadian Journal of Chemistry*, vol. 45, no. 15, pp. 2177–2190, 1967.
- [15] P. J. Werkman, A. Schasfoort, R. H. Wieringa, and A. J. Schouten, "Langmuir-blodgett films of a polymerisable N,N'-disubstituted dithiooxamide coordination compound," *Thin Solid Films*, vol. 325, pp. 243–250, 1998.
- [16] J. Muñoz, M. Gallego, and M. Valcárcel, "Speciation of copper by using a new fullerene derivative as a mixed-mode sorbent,"

- Journal of Analytical Atomic Spectrometry*, vol. 21, pp. 1396–1402, 2006.
- [17] H. Al-Maydama, A. El-Shekeil, M. A. Khalid, and A. Al-Karbouly, "Thermal degradation behaviour of some polydithiooxamide metal complexes," *Eclética Química*, vol. 31, no. 1, pp. 45–52, 2006.
 - [18] S. Ando, D. Kumaki, J. Nishida, et al., "Synthesis, physical properties and field-effect transistors of novel thiazolothiazole-phenylene co-oligomers," *Journal of Materials Chemistry*, vol. 17, pp. 553–558, 2007.
 - [19] S. K. Agarwal, "Synthesis & characterization of some mixed ligand complexes of Pd(II), Rh(III) and Pt(IV) with carboxylic hydrazones as primary and dithiooxamide as co-ligand," *Asian Journal of Chemistry*, vol. 19, no. 4, pp. 2581–2585, 2007.
 - [20] O. V. Mikhailov, "Complexing processes in M(II)-dithiomalonamide-diacetyl triple systems (M= Ni, Cu) in ethanol solution and in a metal(II)hexacyanoferrate(II) gelatin-immobilized matrix materials," *Transition Metal Chemistry*, vol. 30, pp. 18–21, 2005.
 - [21] D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, UK, 2nd edition, 1980.
 - [22] T. L. Jacobs, S. Winstein, G. B. Linden, et al., *Organic Syntheses Collective*, vol. 3, John Wiley & Sons, New York, NY, USA, 1955.
 - [23] C. Marti, "Novel approach to spiro-pyrrolidine-oxindoles and its applications to the synthesis of (\pm)-horsfiline and (–)-spirotryprostatin B," Ph.D. thesis, Swiss Federal Institute of Technology, Zürich, Switzerland, 2003.
 - [24] A. I. Vogel, *Practical Organic Chemistry Qualitative Organic Analysis*, Longman, London, UK, 3rd edition, 1972.
 - [25] E. G. Rochow, *Inorganic Synthesis*, vol. 218, McGraw-Hill, New York, NY, USA, 4 edition, 1960.
 - [26] G. Vatsa, O. P. Pandey, and S. K. Sengupta, "Synthesis, spectroscopic and toxicity studies of titanocene chelates of isatin-3-thiosemicarbazones," *Bioinorganic Chemistry and Applications*, vol. 3, no. 3-4, pp. 151–160, 2005.
 - [27] R. A. Kusanur, M. Ghate, and M. V. Kulkarni, "Copper(II), cobalt(II), nickel(II) and zinc(II) complexes of Schiff base derived from benzyl-2,4-dinitrophenylhydrazine with aniline," *Journal of Chemical Sciences*, vol. 116, no. 5, pp. 265–270, 2004.
 - [28] A. S. S. H. Elgazwy, H. T. Zaky, M. I. Mohamed, and N. G. Kandile, "2(3H)-furanones as synthons for polyamides of 1,3-diazines and 1,3,5-triazines," *Arkivoc*, pp. 162–172, 2006.
 - [29] H. Hofmans, H. O. Desseyn, and M. A. Herman, "The infrared spectra of complexes with planar dithiooxamides-III. the Ni(II) polymeric complexes," *Spectrochimica Acta A*, vol. 38, no. 11, pp. 1213–1220, 1982.
 - [30] H. O. Desseyn and M. A. Herman, "The characterization infra-red bands of primary and secondary thio-amides," *Spectrochimica Acta A*, vol. 23, pp. 2457–2463, 1967.
 - [31] R. M. Silverstein and F. X. Webster, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, New York, NY, USA, 6th edition, 1997.
 - [32] J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, Englewood Cliffs, NJ, USA, 1965.
 - [33] E. Labisbal, A. Sousa, A. Castineiras, J. A. Garcia-Vazquez, J. Romero, and D. X. West, "Spectral and structural studies of metal complexes of isatin-3-hexamethyleneimino thiosemicarbazone prepared electrochemically," *Polyhedron*, vol. 19, pp. 1255–1262, 2000.
 - [34] N. M. A. Al-Abidy, "Synthesis, characterization and study of the biological activity of new Mannich-Schiff bases and some metal complexes derived from isatin, 3-amino-1,2,4-triazol and dithiooxamide," Ph.D. thesis, University of Baghdad, Baghdad, Iraq, 2006.
 - [35] R. V. Singh, N. Fahmi, and M. K. Biyala, "Coordination behavior and biopotency of N and S/O donor ligands with their palladium(II) and platinum(II) complexes," *Journal of the Iranian Chemical Society*, vol. 2, no. 1, pp. 40–46, 2005.
 - [36] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, NY, USA, 5th edition, 1997.
 - [37] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, The Netherlands, 1968.
 - [38] N. M. A. Al-Abidy, "Synthesis and study of some transition metal complexes with N and S-containing Schiff bases derived from 4-phenyl-5-(P-amino phenyl)-3-mercapto-1,2,4-triazol," M.S. thesis, Baghdad University, Baghdad, Iraq, 1997.
 - [39] J. R. Allan, A. D. Paton, K. Turvey, D. L. Gerrard, and S. Hoey, "Thermal, structural and electrical studies of the chloro complexes of cobalt, nickel, copper and zinc with 2-methylquinoxaline," *Thermochimica Acta*, vol. 145, pp. 291–300, 1989.
 - [40] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, John Wiley & Sons, Singapore, 4th edition, 1980.
 - [41] B. N. Figgis, *Introduction to Ligand Fields*, Inter-Science, John Wiley & Sons, New York, NY, USA, 1966.
 - [42] K. Burger, *Coordination Chemistry, Experimental Methods*, Butter Worth, London, UK, 1967.
 - [43] D. Sutton, *Electronic Spectra of Transition Metal Complexes*, McGraw-Hill, New York, NY, USA, 1st edition, 1968.
 - [44] M. J. Al-Jeboori, A. J. Abdul-Ghani, and A. J. Al-Karawi, "Synthesis and structural studies of new Mannich base ligands and their metal complexes," *Transition Metal Chemistry*, vol. 33, no. 7, pp. 925–930, 2008.
 - [45] W. J. Geary, "The use of conductivity measurements in organic solvents for the characterization of coordination compounds," *Coordination Chemistry Reviews*, vol. 7, pp. 81–122, 1971.
 - [46] C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier, London, UK, 2nd edition, 1963.
 - [47] T. L. Zhang, J. C. Song, J. Guo, G. X. Ma, and K. B. Yu, "Syntheses, crystal structures and thermal stability of Co(II) and Zn(II) complexes with ethyl carbazate," *Zeitschrift für Naturforschung B*, vol. 60, pp. 505–510, 2005.
 - [48] P. A. Antunes, S. T. Breviglieri, G. O. Chierice, and E. T. G. Cavalheiro, "Solution and solid state thermal stability of morpholine dithiocarbamates," *Journal of the Brazilian Chemical Society*, vol. 12, no. 4, pp. 473–480, 2001.
 - [49] A. J. Abdul-Ghani and R. A. Majeed, "Preparation and characterization of new metal complexes of Schiff bases containing a thiazole ring," *Iraqi Journal of Science*, vol. 46, no. 1, pp. 59–74, 2005.