

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 = $[CuL_I Cl(H_2O)]Cl \cdot 0.5BuOH$, C_4 = $[Pd(L_I)_2Cl]Cl$, C_5 = $[Pt(L_I)_2Cl_2]Cl_2 \cdot 1.8EtOH \cdot H_2O$, C_{6a} = $[CoL_{II}Cl]Cl \cdot 0.4H_2O \cdot 0.3DMSO$, C_{6b} = $[CoL_{II}Cl]Cl \cdot 0.3H_2O \cdot 0.1BuOH$, C_7 = $[NiL_{II}Cl_2]$, C_8 = $[CuL_{II}]Cl_2 \cdot H_2O$, C_9 = $[Pd(L_{II})_2]Cl_2$, C_{10} = $[Pt(L_{II})_{2.5}Cl]Cl_3$, 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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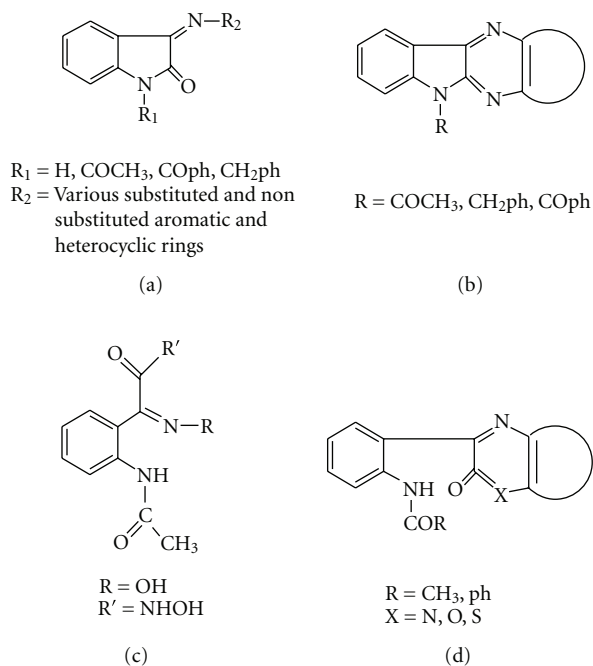
1. Introduction

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,

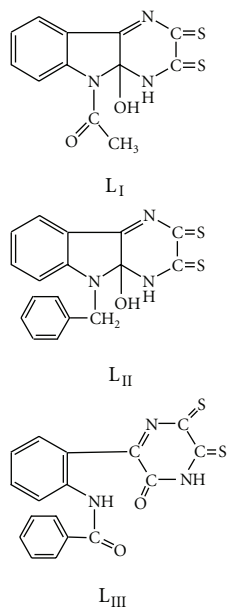
and thermal properties [15–17] as well as being used as semiconductors antibacterial and antifungal agents [18–20].

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 ($\lambda(200–1100)$ 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-acetylisatin, 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-fluoren-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-Acetylisatin: 1-(9a-Hydroxy-2,3-dithiooxo-1,2,3,9a-tetrahydro-1,4,9-triaza-fluoren-9-yl)-ethanone (L_I). A powdered mixture of N-acetylisatin (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,CH₃); 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, CH₂ 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-dithio-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 cm³) 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),

m/z(%): 296.6(13), 267.5(7), 232.6(20), 195.6(15), 149.5(6), 104.4(27), 83.4(6). Anal. for $C_{17}H_{11}N_3O_2S_2$ Calcd.: C, 57.79; H, 3.11; N, 11.89%; Found: C, 57.39; H, 3.54; N, 11.30%.

4. Preparation of Metal Complexes

(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 $[(C_{12}H_9N_3O_2S_2CuCl(H_2O))Cl \cdot 0.5(C_4H_{10}O)]$ 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;

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)%.” “ C_9 ”: colour(dark brown). Yield (43.38%). Anal. for $[(C_{34}H_{26}N_6O_2S_4Pd)Cl_2]$ 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)%.” “ C_{10} ”: colour(dark brown). Yield (32.42%). Anal. for $[(C_{17}H_{13}N_3OS_2)_{2.5}PtCl)Cl_3]$ 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 $[(C_{17}H_{11}N_3O_2S_2Co)Cl_2 \cdot H_2O]$ 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)%.” “ C_{12} ”: colour(brown). Yield (34.37%). Anal. for $[(C_{34}H_{22}N_6O_4S_4Ni)Cl_2]$ 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)%.” “ C_{13} ”: colour(brown). Yield (34.03%). Anal. for $[(C_{34}H_{22}N_6O_4S_4Pd)Cl_2]$ 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 $CoCl_2 \cdot 6H_2O$ (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 $(C_{24}H_{18}N_6O_4S_4Co_2Cl_3)Cl$ Calcd.: C, 34.21; H, 2.13; N, 9.97; S, 15.20%; Found: C, 34.15; 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 $[(C_{17}H_{13}N_3OS_2CoCl)Cl \cdot 0.3(H_2O) \cdot 0.1(C_4H_{10}O)]$ 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 $[(C_{17}H_{11}N_3O_2S_2Co)Cl_2 \cdot 0.2H_2O]$ 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)%.”

5. Microbiological Test Methods

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

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 Saugano 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 | 273 |
| C _{6b} Co(II) | 3250 | 1720 | 1612 | 1560 | 1450 | 1180 | 864 | 3450 | 493 | 450 | 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 | — |
| C ₉ Pd(II) | 3147 | 1720 | 1612 | 1550 | 1465 | 1180 | 856 | — | 500 | 400 | — |
| C ₁₀ Pt(IV) | 3294 | 1720 | 1612 | 1548 | 1472 | 1170 | 850 | — | 500 | 400 | 330 |
| Pt(IV) | 3147 | | | | | | | | 370 | | |

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 |

Latic 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 | $^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1(\text{F})$ $^4A_2 \rightarrow ^4T_1(\text{P})$ L → 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 | $^4A_2 \rightarrow ^4T_2$ $^4A_1 \rightarrow ^4T_1(\text{F})$ $^4A_2 \rightarrow ^4T_1(\text{P})$ L → 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.) | $^3A_2g \rightarrow ^3T_2g$ $^3A_2g \rightarrow ^3T_1g(\text{F})$ $^3A_2g \rightarrow ^3T_1g(\text{P})$ | 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 → 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 | $^1A_1g \rightarrow ^3T_1g(\text{H})$ $^1A_1g \rightarrow ^3T_2g$ | | | | Diamagnetic | Octahedral | 154.13 |
| C _{6a} Co(II) | ν_1 6535 (cal.) ν_2 10526 ν_3 16666 ν_4 21551 | $^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1$ $^4A_2 \rightarrow ^4T_1(\text{P})$ L → 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 | $^4A_2 \rightarrow ^4T_2$ $^4A_2 \rightarrow ^4T_1(\text{F})$ $^4A_2 \rightarrow ^4T_1(\text{P})$ L → 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 | $^3T_1(\text{F}) \rightarrow ^3T_2(\text{F})$ $^3T_1(\text{F}) \rightarrow ^3A_2(\text{F})$ $^3T_1(\text{F}) \rightarrow ^3T_1(\text{P})$ L → 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 | ¹ A _{1g} → ¹ A _{2g} ¹ A _{1g} → ¹ B _{1g} (C.T) | | | | Diamagnetic | Square planar | 125.4 |
| C ₁₀ Pt(IV) | ν_1 14388 ν_2 20576 | ¹ A _{1g} → ³ T _{1g} ¹ A _{1g} → ³ T _{2g} (C.T) | | | | Diamagnetic | Octahedral | 196.6 |
| C _{11a} Co(II) | ν_1 6410 (cal.) ν_2 10000 ν_3 15641 (avr.) | ⁴ A ₂ → ⁴ T ₂ ⁴ A ₂ → ⁴ T ₁ (F) ⁴ A ₂ → ⁴ T 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.) | ⁴ A ₂ → ⁴ T ₂ ⁴ A ₂ → ⁴ T ₁ (F) ⁴ A ₂ → ⁴ T 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.) | ³ T ₁ (F) → ³ T ₂ (F) ³ T ₁ (F) → ³ A ₂ (F) ³ T ₁ (F) → ³ T ₁ (P) | 0.74 (0.653) | 673.1 | 4980 | 2.746 | Tetrahedral | 159.4 |
| C ₁₃ Pd(II) | ν_1 12820 ν_2 16666 | ¹ A _{1g} → ¹ A _{2g} ¹ A _{1g} → ¹ B _{1g} | | | | Diamagnetic | Square planar | 148.2 |

¹A_{1g} → ³T_{1g} and ¹A_{1g} → 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.

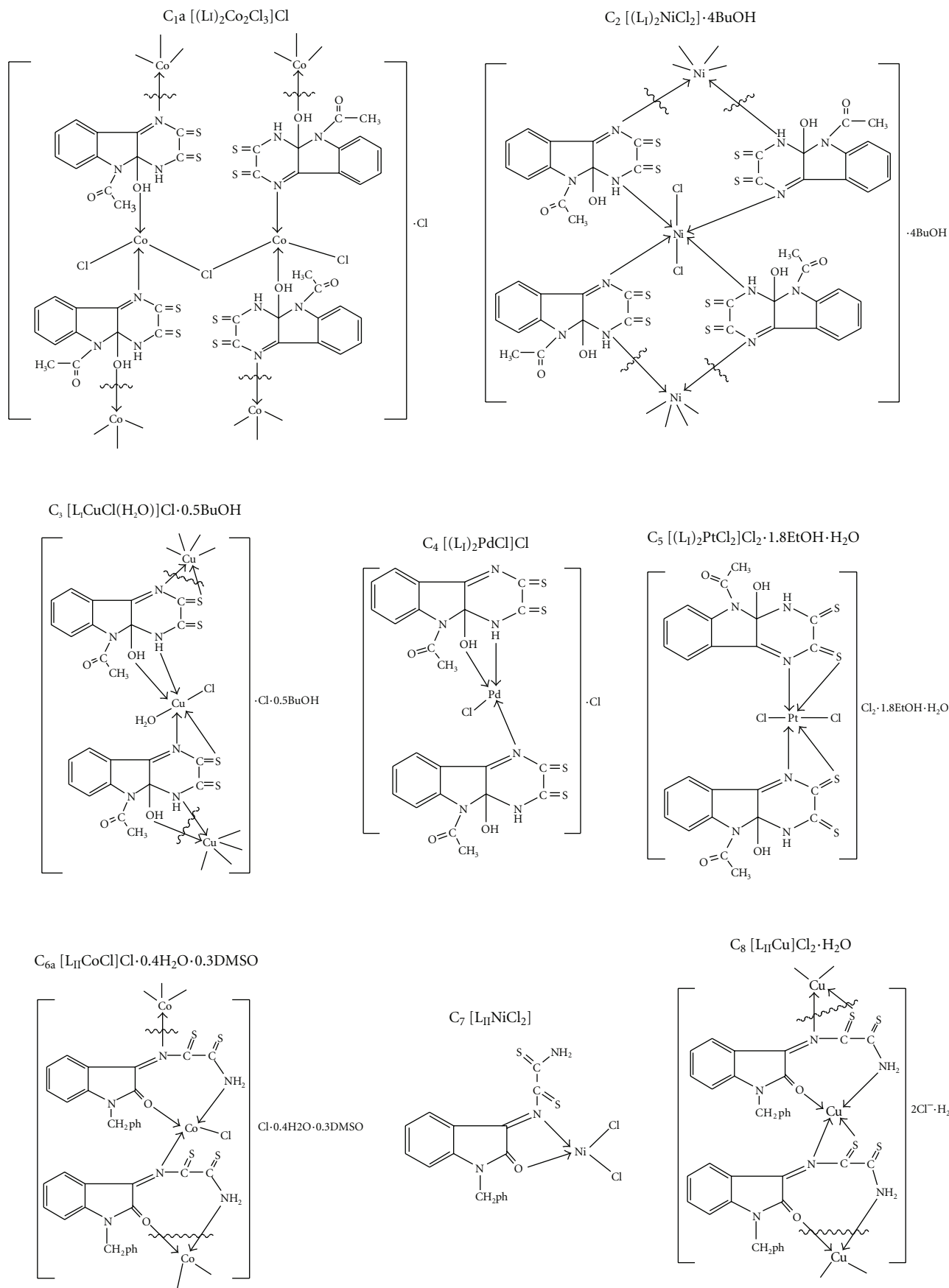
TABLE 3: Thermal decomposition of C₁, C₃, C₄, and C₇.

| (a) | | |
|----------------------------------------------------------------------------------|---------------------------------------|----------------------------|
| C ₁ | | |
| $[(L_1)_2Co_2Cl_3]Cl$ 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) |

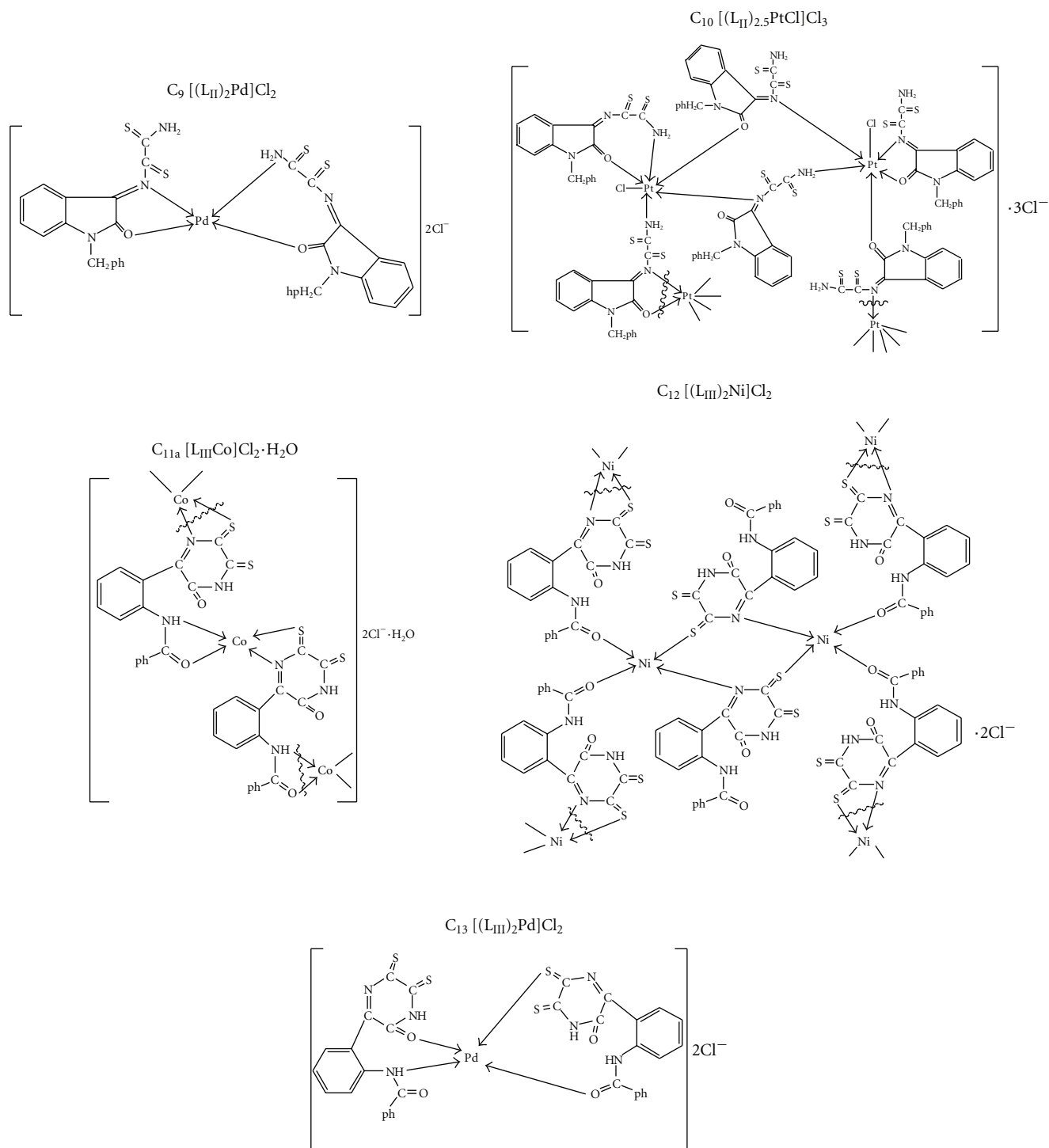
| (b) | | |
|-----------------------------------------------------|--------------------------------------|----------------------------|
| C ₃ | | |
| $[L_1CuCl(H_2O)]Cl \cdot 0.5BuOH$ M · wt = 480.5 | Temperture range of decomposition °C | %Weight loss found (calc.) |
| -BuOH | | |
| -Cl | | |
| -H ₂ 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 | | |
| $[(L_1)_2PdCl]Cl$ 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 | | |
| $[L_{II}NiCl_2]$ 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 | | <i>Proteus vulgris</i> inhibition | | <i>Candida albicans</i> inhibition | | <i>Aspergillus niger</i> growth | |
|--------------------------|-----------------------------------------|----------|-----------------------------------|----------|------------------------------------|----------|---------------------------------|----------|
| | diameter (mm) | 1000 ppm | diameter (mm) | 1000 ppm | diameter (mm) | 1000 ppm | 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.

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