Research Article

Synthesis and Structural Properties of Copper(II), Nickel(II) and Cobalt(II) Complexes with 2,4-Furyliminobenzylacetophenone

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The new Schiff base ligand (FIAS) 2,4-furyliminobenzylacetophenone has been synthesized with 4-aminoacetophenone and furane-2-carboxaldehyde by condensation in ethanol. Metal complexes of the ligand were prepared with chloride salts of copper(II), nickel(II) and cobalt(II) in ethanol. The ligand and its metal complexes have been characterized by microanalysis, magnetic susceptibility, FTIR, ¹H and ¹³C NMR, mass spectrum, and UV-visible spectroscopy techniques. From these findings, it is suggested that metal ion coordinate by imines nitrogen and carboxylic oxygen atoms of FIAS to form octahedral geometry. All the newly compounds were tested antimicrobial activity against bacterial and fungal species.

1. Introduction

The chemistry of transition metal complexes with multidentate [1–6] ligands have been attracted particular attention because these metal ions can exhibit several oxidation states. The different oxidation states of these complexes showed a strong role in bioinorganic chemistry and redox enzyme system. This may provide the basis of models for active sites of biological systems or act as catalysts. Although numerous transition metal complexes [7–10] of Schiff bases have structurally characterized relatively few free Schiff bases have been similarly characterized. A combination of distinctly different metal ions bind with one ligand can lead to materials with interesting new properties [11–15] for example, specific sensors, molecular wire, magnetic and optical devices. The flexibility of Schiff base ligands can be improved by hydrogenation of their C=N bonds; they should thus coordinate metal ions move easily. For these reasons, reduced Schiff base have recently gained considerable attention. Schiff bases of 4-aminoantipyrine and its complexes are known for their variety of applications [16–22] in the areas of catalysis, clinical applications and

pharmacologically. Antipyrine and its derivatives [23–30] show antibacterial and antitumor activities. Our research was ongoing to establish the fact that nonbiologically active compounds become biologically active, and less biologically active become more upon coordination/chelation with metal ions. In this paper, we synthesized the Schiff base and their metal complexes were characterized by their IR, NMR, molar conductance, and magnetic moments electronic elemental analysis mass spectrum and UV-Visible spectroscopy. Schiff base ligands and their metal complexes were screened for their antimicrobial activity against *Staphylococcus aureus* (ATCC 25923), *Staphylococcus aureus* (ATCC 3160) bacterial species and *Candida albicans* (227), and *Staphylococcus cerevisiae* (361) fungal species. The Schiff base showed varied antibacterial and antifungal activity against one or more strains, respectively, and their activity was enhanced on coordination or chelation.

2. Experimental

2.1. Material and Methods. Solvents and metals salts were used analytical grade. IR spectra used were analytical grade.

SCHEME 1: Route for the synthesis of the 2-furanecarboxaldehydeacetophenone.

SCHEME 2: Route for the synthesis of the Metal complexes.

IR spectra were recorded on Shimadzu-160 Spectrometer using KBr discs in the range $4000\text{--}400\text{ cm}^{-1}$. NMR spectra were recorded on a Bruker DPX-400 Spectrometer using DMSO- d_6 solvent and TMS as the internal reference at room temperature. UV-visible spectra were obtained in DMSO/DMF. CHN analyses were performed using a Carlo-Erba 1106 Elemental Analyzer; conductance and magnetic measurements were carried out on solid compounds using the respective instruments. Antimicrobial activities were done at ACBR, Delhi University, India.

2.2. Synthesis of Ligand. In a round bottom flask, furan-2-carboxaldehyde (0.01 mmol, 0.35 mL) in methanol (15 mL) and 4-aminoacetophenone (0.1 mmol, 0.203 g) in methanol (15 mL) were stirred by a magnetic stirrer for about 30 minutes. The mixture was refluxed for 2 h on the heating mental at 50°C . After completion of the reaction monitored through TLC, it was cooled at room temperature to afford a yellow solid product which was filtered, washed with cold methanol then with ether and dried (Scheme 1).

Yield. 52%; M.P. 240°C , Mol. wt. 281, color: yellow; analytical data for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$ found (calc.): C, 62.32 (61.99); H, 5.33 (4.91); N, 14.94 (13.97). IR (KBr/ cm^{-1}) $1637\text{ }\nu_{\text{CH=N}}$, $1690\text{ }\nu_{\text{C=O}}$, $1530\text{ }\nu_{\text{C-O}}$, $1298\text{ }\nu_{\text{N-N}}$. ESI-MS, m/z Data found (calc.): 321 (320), ^1H NMR (DMSO- d_6) δ ppm: 1.601 (s, 3H, $\text{H}_3\text{C-C}$), 1.714 (s, 3H, $\text{H}_3\text{C-N}$), 7.158–7.953 (m, 9H, Ar), 3.18 (s, 3H, $\text{H}_3\text{C-O}$), 8.92 (s, 1H, CH=N). ^{13}C NMR (DMSO- d_6) δ ppm: 10.07 (1C, $\text{CH}_3\text{-C}$), 18.97 (1C, $\text{CH}_3\text{-N}$), 56.33 (1C, $\text{CH}_3\text{-O}$), 117.53–121.07 (12C, CH-Ar.), 143.23 (1C, C-N), 153.88 (1C, C=O), 164.95 (1C, CH=N).

2.3. Synthesis of Metal Complexes. For the synthesis of metal complexes, a solution of 2-furanecarboxaldehyde-4-iminoacetophenone ligand (0.1 mmol, 0.317 g) in methanol (50 mL) was added to a magnetically stirred solution of $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ (0.1 mmol) in methanol (30 mL) at a required equimolar ratio of M:L (1:2). The mixture was refluxed for 3 h and then cooled to room temperature. On cooling,

a colored solid product was formed. The solid was filtered, washed with methanol, then ether and dried. Crystallization from methanol gave the desired metal complexes (Scheme 2).

2.3.1. $[\text{Ni}(\text{L}_2)\text{Cl}_2]$ Complex

Yield. 38%; M.P.: 320° ; Mol. wt. 869; color: dark green; analytical data for $[\text{NiC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2]$ found (calc.): C, 44.18 (44.01), H, 3.45 (3.22), N, 9.66 (9.35). IR (KBr/ cm^{-1}): $1598\text{ }\nu_{\text{CH=N}}$, $1650\text{ }\nu_{\text{C=O}}$, $512\text{ }\nu_{\text{M-N}}$, $453\text{ }\nu_{\text{M-O}}$, $390\text{ }\nu_{\text{M-Cl}}$. ^1H NMR (DMSO- d_6) δ ppm: 1.601 (s, 3H, $\text{H}_3\text{C-C}$), 1.714 (s, 3H, $\text{H}_3\text{C-N}$), 7.158–7.953 (m, 9H, Ar), 3.18 (s, 3H, $\text{H}_3\text{C-O}$), 8.12 (s, 1H, CH=N). ^{13}C NMR (DMSO- d_6) δ ppm: 10.07 (1C, $\text{CH}_3\text{-C}$), 18.97 (1C, $\text{CH}_3\text{-N}$), 56.33 (1C, $\text{CH}_3\text{-O}$), 117.53–121.07 (12C, CH-Ar.), 143.23 (1C, C-N), 153.12 (1C, C=O), 164.25 (1C, CH=N). UV-vis (DMSO): λ_{max} (cm^{-1}), 16,670, 27,780. B.M. (μ_{eff}): 2.5. Molar conductance ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$): 16.45.

2.3.2. $[\text{Cu}(\text{L}_2)\text{Cl}]\text{Cl}$ Complex

Yield. 32%; M.P.: 345°C , Mol. wt. 802; color: light green; analytical data for $[\text{CuC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}]\text{Cl}_2$ found (calc.): C, 47.88 (46.85); H, 3.74 (3.01); N, 10.47 (10.17). IR (KBr/ cm^{-1}): $1602\text{ }\nu_{\text{CH=N}}$, $1678\text{ }\nu_{\text{C=O}}$, $1530\text{ }\nu_{\text{C-O}}$, $1296\text{ }\nu_{\text{N-N}}$, $544\text{ }\nu_{\text{M-N}}$, $447\text{ }\nu_{\text{M-O}}$, $398\text{ }\nu_{\text{M-Cl}}$. ^1H NMR (DMSO- d_6) δ ppm: 1.601 (s, 3H, $\text{H}_3\text{C-C}$), 1.714 (s, 3H, $\text{H}_3\text{C-N}$), 7.158–7.953 (m, 9H, Ar), 3.18 (s, 3H, $\text{H}_3\text{C-O}$), 8.13 (s, 1H, CH=N). ^{13}C NMR (DMSO- d_6) δ ppm: 10.07 (1C, $\text{CH}_3\text{-C}$), 18.97 (1C, $\text{CH}_3\text{-N}$), 56.33 (1C, $\text{CH}_3\text{-O}$), 117.53–121.07 (12C, CH-Ar.), 143.23 (1C, C-N), 153.10 (1C, C=O), 164.05 (1C, CH=N). UV-vis (DMSO): λ_{max} (cm^{-1}), 14,920, 16,390, 27,250. B.M. (μ_{eff}): 3.5. Molar conductance ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$): 16.45.

2.3.3. $[\text{Co}(\text{L}_2)\text{Cl}]\text{Cl}$ Complex

Yield. 30%; M.P.: 320° ; Mol. wt. 870; color: dark green; analytical data for $[\text{CoC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}]\text{Cl}_2$ found (calc.): C, 44.13 (43.45), H, 3.44 (3.01), N, 9.65 (9.25). IR (KBr/ cm^{-1}):

TABLE 1: Antibacterial screening data of metal complexes of 2-furanecarboxaldehyde-4-iminoacetophenone Schiff base.

Compound	Average % inhibition after 48 h. (conc. in ppm)			
	<i>Staphylococcus aureus</i> (ATCC 25923)		<i>Staphylococcus aureus</i> (ATCC 3160)	
	500	1000	500	1000
FIAS	30	42	31	35
[Co(L ₂)]Cl ₂	44	51	42	53
[Ni(L ₂)]Cl ₂	44	50	42	44
[Cu(L ₂)]Cl ₂	43	51	43	55
Bavistin	84	100	80	99

TABLE 2: Fungicidal screening data of metal complexes of 2-furanecarboxaldehyde-4-iminoacetophenone Schiff base.

Compound	Average % inhibition after 48 h. (conc. in ppm)			
	<i>Cabdidia albicans</i> (ATCC 227)		<i>Staphylococcus cereviscae</i> (ATCC 361)	
	500	1000	500	1000
FIAS	5	8	5	10
[Co(L ₂)]Cl ₂	8	14	7	15
[Ni(L ₂)]Cl ₂	9	11	8	16
[Cu(L ₂)]Cl ₂	9	17	9	12
Streptomycin	16	18	16	18

1602 $\nu_{\text{CH=N}}$, 1648 $\nu_{\text{C=O}}$, 567 $\nu_{\text{M-N}}$, 450 $\nu_{\text{M-O}}$, 390 $\nu_{\text{M-Cl}}$. ^1H NMR (DMSO- d_6) δ ppm: 1.465 ($\text{H}_3\text{C-C}$), 1.714 ($\text{H}_3\text{C-N}$), 7.158–7.953 (CH-Ar), 3.18 ($\text{H}_3\text{C-O}$), 8.12 (CH=N). ^{13}C NMR (DMSO- d_6) δ ppm: 10.07 ($\text{CH}_3\text{-C}$), 18.97 ($\text{CH}_3\text{-N}$), 56.33 ($\text{CH}_3\text{-O}$), 117.53–121.07 (CH-Ar), 143.23 (C-N), 153.12 (C=O), 164.25 (CH=N). UV-vis (DMSO): λ_{max} (cm^{-1}), 15000, 16390 and 27250. B.M. (μ_{eff}): 1.55. Molar conductance ($\Omega_{\text{M}}^{-1} \text{cm}^2 \text{mol}^{-1}$): 11.1.

3. Biological Activity

3.1. Antibacterial Activity. The newly synthesized metal complexes were screened in vitro for their antibacterial activity against *Staphylococcus aureus* (ATCC 25923), and *Staphylococcus aureus* (ATCC 3160) bacterial species using the agar well diffusion method. 12–24 h bacterial solution containing $\sim 10^4$ – 10^6 colony forming units (CFU)/mL were used. The test sample's (1 mg/mL in DMF) concentration (100 μL) was introduced in the petric disc. New petric dishes were incubated immediately at 37°C for 24 h activities was determine by measuring the diameter of zones showing complete inhibition (mm). Growth inhibition was compared with the standard drug (Table 1).

3.2. Antifungal Activity. Antifungal activities of all compounds were studies against two fungal cultures *Cabdidia albicans* (227) and *Staphylococcus cereviscae* (361) fungal species. Sabouraud dextrose agar was seeded with 10^5 mL^{-1} fungal spare suspension and transferred to petric plates. Dishes soaked in 20 mL (10 $\mu\text{g/mL}$ in DMF) of the entire agar surface. The plates were incubated at 32°C for 24 h.

the results were recorded as zones of inhibition (mm) and compared with the standard drug Streptomycin (Table 2).

3.3. Minimum Inhibitory Concentration. Compounds showing antibacterial activity over 8% were selected for minimum inhibitory concentration studies. The MIC was determined using the disc diffusion technique by prepared uses containing 500 and 1000 $\mu\text{g/mL}$ of the compounds (Figure 1).

4. Result and Discussion

The structure of newly synthesized ligand was established with the help of their IR, NMR (^1H & ^{13}C), mass spectrum and microanalytical data. All the metal complexes and Schiff base ligand were stable in air and moisture and they were synthesized by the stoichiometric reaction of the corresponding metal (II) chloride with ligand in a molar ratio M:L of 1:2. All of the metal complexes were insoluble in the common organic solvents and only soluble in DMF/DMSO. Molar conductance value of the soluble complexes in DMF (10^{-3} M solution at 25°C) indicated that chloride ion were in the outer sphere and show the non-electrolytic in nature but in the Ni(II) complex, chloride ions coordinated in the inner sphere and it was nonelectrolytic in nature. We agree with the proposed structure of the ligand on the basis of elemental analysis data in which the ligand contain two donor sites—one is azomethine (HC=N) nitrogen and other carbonyl (C=O) oxygen atom. IR spectra of the ligand observed at 1615 cm^{-1} are assigned to the $\nu(\text{C=N})$ mode and a band at 810 cm^{-1} due to $\nu(\text{C-N})$ pyrrolyl ring. The peak of azomethine group was found in the lower wave frequency in the IR spectra of the complexes which was evidence of the nitrogen

FIGURE 1: Plot of antibacterial (a) and antifungal (b) activity of ligand and their metal complexes in 1000 ppm conc.

bonding of the azomethine group to the central metal ions. The $\nu(\text{C}=\text{O})$ carbonyl band in the ligand appeared at 1645 cm^{-1} . This frequency was shifted to the lower frequency in the spectra of the complexes which was indicated the coordination of the carbonyl oxygen atom to the central metal ions. This is further confirmed by the appearance of the new band at $515\text{--}525$ and $425\text{--}430\text{ cm}^{-1}$ due to the $\nu(\text{M}\text{--}\text{N})$ and $\nu(\text{M}\text{--}\text{O})$ [35, 36]. The NMR spectrum of the ligand was done in $\text{DMSO-}d_6$. The ^1H NMR spectral data are reported along with the possible assignments in the experimental section. All the protons due to aromatic groups were found to be in their expected region. The conclusions of these studies lend further support to the mode of bonding discussed in their IR spectra. ^{13}C NMR spectrum of the ligand, signals between 111.9 and 181.5 due to aromatic ring carbons. The peak of carbonyl carbon at 169.7 ppm was shifted to the lower frequencies. The mass spectrum of the ligand shows a peak at 321.22 . This suggests that the ligand exists in a dimeric form probably through H-bonding. The presence of fragments values 121 , 23 , 67 and 320 show that the fragmentation has taken place at --C=N-- . The mass spectrum clearly suggests existence of ligand in the hydrazones form. The UV-visible spectrum of copper(II) complex in DMSO solution displays a broad band at 10718 cm^{-1} and a well-defined shoulder around 22831 cm^{-1} attributable to $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ transitions which strongly favour octahedral geometry around the Cu(II) ion [34]. This is further supported by the magnetic susceptibility value (1.83 BM). The cobalt complex shows a d-d band at 16216 cm^{-1} as signed to $^2\text{A}_{1g} \rightarrow ^2\text{B}_{1g}$ transition which confirmed square-planar geometry. This is further confirmed by its magnetic susceptibility value (3.85 BM). The electronic spectra of the nickel(II) complex exhibited [31–33] absorption bands at $\sim 16,670$ and $\sim 27,780\text{ cm}^{-1}$, attributable to $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$ and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$, transitions, respectively, in an octahedral geometry. The calculated values of the ligand field parameters lie in

the range reported for an octahedral structure [35, 36]. Also, the values of the magnetic moment ($3.2\text{--}3.7\text{ B.M.}$) may be taken as additional evidence for their octahedral structure. The magnetic moment values are of great significance in a structural context in the case of Co(II) complexes. Magnetic moments of tetrahedral, octahedral and square planar complexes differ significantly and therefore structural type can be easily identified using magnetic data. In octahedral complexes, the ground state ($^4\text{T}_{1g}$) is orbitally degenerate and this causes large orbital contribution to the magnetic moment. The μ_{eff} value measured for the Co(II) complex is 5.32 B.M. , indicating octahedral geometry [37] of the Co(II) ion in the complex. The reflectance spectrum of the complex showed a band at 656 nm and a shoulder at 477 nm , besides the ligand absorptions. The former band would be due to a $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$ electronic transition, indicating an octahedral configuration around Co(II) ions. On the basis of the above observations, it is tentatively suggested that all of the complexes show an octahedral geometry in which ligands act as bidentates. These possibly accommodate themselves around the metal atom in such a way that a stable chelate ring is formed giving, in turn, stability to the formed metal complexes.

5. Conclusions

In this paper we have described that the all the synthesized transition metal complexes of Schiff base by condensation method. In the present investigations, all the complexes found to be mononuclear were obtained for Cu(II), Ni(II) and Co(II), cations in presence of ligand. The results of antimicrobial activities show that the metal-complexes exhibit antimicrobial properties and it is important to note that they show enhanced inhibitory activity compared to parent ligand. All the investigated compounds showed less to good activity against *S. aureus*.

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