

Synthesis and Spectroscopic Studies of Transition Metal Complexes of Mononuclear Schiff Base Derived from 4-Methoxybenzaldehyde and Glycine

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A new bidentate nitrogen/oxygen containing Schiff base ligand (L) where L = 4-methoxybenzaldehyde-glycine and their transition metal complexes have been synthesized and well characterized by elemental analysis, infrared spectroscopy, electrons spray ionization mass spectrum, molar conductivity measurement, magnetic moments at the room temperature, electronic spectrum, ^1H NMR, ^{13}C NMR spectrum and physico-chemical studies. On the basis above results confirmed that the synthesized ligand acts as bidentate. The conductivity measurement data in DMSO/DMF solution indicated that all the cholor complexes are essentially non-electrolyte in nature. Thus, a hexa coordinated environment was generated around the metal ions have been proposed by the ligand and all the complexes have been screened for biological activity on several pathogenic fungi and bacteria and were found to possess appreciable fungicidal and bactericidal properties.

Key Words: 4-Methoxybenzaldehyde-glycine, Metal complexes, Spectral studies.

INTRODUCTION

Metal complexes of Schiff base ligands, play an essential role in agriculture, pharmaceutical and industrial chemistry¹⁻⁶. The growing importance of Schiff bases and their metal complexes in modern coordination chemistry are attributable to recent observations about their antibacterial, antifungal and oxygen carrier properties⁷⁻¹⁰. Complexes of thallium(I) with benzothiazolines show antibacterial activity against pathogenic bacteria. Various transition metal complexes in +2 and +4 oxidation state derived with aniline show different behaviour with different types of bacteria^{11,12}. In view of the above applications, the present work relates to the synthesis, spectroscopic studies of the transition metal complexes of mononuclear Schiff base derived from 4-methoxybenzaldehyde and glycine.

EXPERIMENTAL

Synthesis of ligand: In a round bottom flask (100 mL), a methanolic solution (10.0 mL) of 4-methoxybenzaldehyde (2.5 mmol, 1.20 mL), in an aqueous methanolic solution (10.0 mL) of glycine (1.7 mmol, 0.75 g) and potassium hydroxide (3.5 mmol, 0.56 g) in MeOH (20.0 mL) were taken and stirred at 30 °C for 0.5 h and then the reaction mixture was refluxed at 50 °C for 12 h. The resulting solution was cooled at 30 °C temperature and after the completion of this reaction, the reaction mixture was monitored by thin layer chromatography.

The reaction mixture was taken in chloroform and washed with water and then with brine solution. The organic layers were collected and evaporate the solvent under reduced pressure to afford a yellow crystalline solid product (Fig. 1).

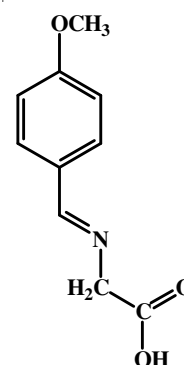


Fig. 1. Structure of ligand

Yield: 52 %; m.p. 220 °C, m.w. 177, colour: yellow; analytical data for $\text{C}_{10}\text{H}_{11}\text{NO}_3$ found (calc.): C, 67.70 (66.99); H, 6.21 (5.91); N, 7.90 (7.87). IR (KBr, ν_{max} , cm^{-1}): 1637 (CH=N), 1690 (C=O), 1530 (C-O), 1298 (N-N). ESI-MS, m/z data found (calc.): 177 (176), ^1H NMR (DMSO- d_6) δ ppm: 1.601 (s, 5H, $\text{H}_3\text{C}_3\text{-N}$), 7.158-7.953 (m, 4H, Ar), 3.18 (s, 3H, $\text{H}_3\text{C-O}$), 8.92 (s, 1H, CH=N), 7.83 (s, 2H, NH).

Synthesis of metal complexes: All the metal complexes were synthesized by the general method. In a round bottom flask (100 mL), a mixture of ligand (0.01 mol, 1.77 g) in an aqueous ethanolic solution (15.0 mL) and a solution of corresponding metal salts (0.01 mol) in a methanolic solution (10.0 mL) were taken then the reaction mixture was refluxed on heating mental at 60 °C for 6-18 h. The resulting solution was cooled at 4 °C. After this, the reaction mixture was taken in chloroform and washed with water (3 × 20 mL) (thrice) and then with brine solution (3 × 20 mL) (thrice). The organic layers were collected and then evaporate the solvent under reduced pressure to afford a green crystalline solid.

[Cu(L)₂Cl₂]: Yield: 38 %; m.p. 260 °C; m.w. 487; colour: dark green; analytical data for [C₂₀H₂₂N₂O₆Cl₂Cu] found (calc.): C, 49.26 (49.12), H, 4.51 (4.35), N, 5.74 (5.17). IR (KBr, ν_{\max} , cm⁻¹): 1598 (CH=N), 1650 (C=O), 512 (M-N), 453 (M-O), 390 (M-Cl). ESI-MS, m/z data found (calc.): 487 (486), ¹H NMR (DMSO-*d*₆) δ ppm: 1.601 (s, 5H, H₃C₃-N), 7.158-7.953 (m, 4H, Ar), 3.18 (s, 3H, H₃C-O), 8.90 (s, 1H, CH=N), 7.83 (s, 2H, NH). UV-VIS (DMSO): λ_{\max} (cm⁻¹), 16670, 27,780 BM (μ_{eff}): 2.5. Molar conductance (Ω^{-1} cm² mol⁻¹): 16.45.

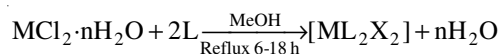
[Ni(L)₂Cl₂]: Yield: 32 %; m.p.: 235 °C, m.w. 482; colour: light green; analytical data for [C₂₀H₂₂N₂O₆Cl₂Ni] found (calc.): C, 49.69 (49.32); H, 4.56 (4.21); N, 5.80 (5.47). IR (KBr, ν_{\max} , cm⁻¹): 1602 (CH=N), 1678 (C=O), 1530 (C-O), 1296 (N-N), 544 (M-N), 447 (M-O), 398 (M-Cl). ESI-MS, m/z data found (calc.): 770 (769), ¹H NMR (DMSO-*d*₆) δ ppm: 1.601 (s, 5H, H₃C₃-N), 7.158-7.953 (m, 4H, Ar), 3.18 (s, 3H, H₃C-O), 8.89 (s, 1H, CH=N), 7.83 (s, 2H, NH). UV-VIS (DMSO): λ_{\max} (cm⁻¹), 14920, 16390, 27250. BM (μ_{eff}): 3.5. Molar conductance (Ω^{-1} cm² mol⁻¹): 16.45.

[Co(L)₂Cl₂]: Yield: 28 %; m.p. 240 °C; m.w. 482; colour: pink; analytical data for [C₂₀H₂₂N₂O₆Cl₂Co] found (calc.): C, 49.69 (49.32); H, 4.56 (4.21); N, 5.80 (5.47). IR (KBr, ν_{\max} , cm⁻¹): 1604 (CH=N), 1670 (C=O), 1530 (C-O), 1295 (N-N), 519 (M-N), 442 (M-O), 392 (M-Cl). ESI-MS, m/z data found (calc.): 771 (770), ¹H NMR (DMSO-*d*₆) δ ppm: 1.601 (s, 5H, H₃C₃-N), 7.158-7.953 (m, 4H, Ar), 3.18 (s, 3H, H₃C-O), 8.90 (s, 1H, CH=N), 7.83 (s, 2H, NH). UV-VIS (DMSO): λ_{\max} (cm⁻¹), 20920, 28570. BM (μ_{eff}): 4.5. Molar conductance (Ω^{-1} cm² mol⁻¹): 16.45.

[Mn(L)₂Cl₂]: Yield: 23 %; m.p. 235 °C; m.w. 478; colour: yellow; analytical data for [C₂₀H₂₂N₂O₆Cl₂Mn] found (calc.): C, 50.11 (50.05); H, 4.60 (5.15); N, 5.85 (5.42). IR (KBr, ν_{\max} , cm⁻¹): 1601 (CH=N), 1652 (C=O), 1530 (C-O), 1288 (N-N), 518 (M-N), 452 (M-O), 397 (M-Cl). ESI-MS, m/z data found (calc.): 727 (728), ¹H NMR (DMSO-*d*₆) δ ppm: 1.601 (s, 5H, H₃C₃-N), 7.158-7.953 (m, 4H, Ar), 3.18 (s, 3H, H₃C-O), 8.88 (s, 1H, CH=N), 7.83 (s, 2H, NH). UV-VIS (DMSO): λ_{\max} (cm⁻¹), 20491, 18903, 14064. BM (μ_{eff}): 1.5. Molar conductance (Ω^{-1} cm² mol⁻¹): 16.45.

RESULTS AND DISCUSSION

The analytical data indicate that all the complexes have the composition [ML₂X₂], where L = 4-methoxybenzaldehyde-glycine, X = Cl⁻, M = Co(II), Ni(II), Cu(II) and Mn(II). The complexes are stable in air and soluble in DMSO solution at room temperature. The formation of the complexes may be represented by the following general equation:



The newly synthesized ligand and their metal complexes was characterized on the bases of their IR, NMR (¹H & ¹³C), mass spectrum, UV-visible and other physico-chemical techniques. The IR spectra of the free ligand shows a band at 3465, 3380, 1690 and 1625 cm⁻¹ due to $\nu(\text{OH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ vibrational modes. The shifted bands at 1600-1606 and 1645-1654 cm⁻¹ region due to the azomethine and carbonyl linkage confirm the formation of the metal complexes¹³. The non-ligand bands at 578-521, 436-422 and 398-385 cm⁻¹ are tentatively assigned to $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{Cl})$, respectively^{14,15}. The Cu(II), Ni(II), Co(II) and Mn(II) complexes are non-electrolytic in nature by their molar conductivity (Λ_m) in DMSO¹⁶ in the range 16.2-20.2 Ω^{-1} cm² mol⁻¹. Mass spectra provide a vital clue for elucidating the structure of compounds. The spectrum shows the molecular ion peak at m/z = 177 (C₁₀H₁₁NO₃, calculated atomic mass 176 amu due to ¹³C and ¹⁵N isotopes). The different competitive fragmentation pathways of ligand give the peaks at different mass numbers at 125. The intensity of these peaks reflects the stability and abundance of the ions. The g_{II} value for metal complexes is less than 2.3 suggesting a small amount of ionic character of the metal-ligand bond. The value $g_{\text{II}} > g_{\perp} > 2.0023$, suggests that the unpaired electron lie predominantly in the dx²-y² orbital characteristic of octahedral geometry in Cu(II) complexes. ¹H NMR spectra of the ligand, the signals of the -NH protons were observed as singlets at δ 11.42-11.83. These signals also appeared in the ¹H NMR spectra of the metal complexes indicating non coordinating the metal ions. The signals of the -CH=N proton which appears as singlets at δ 8.85-8.97 in the ligand show a shift to downfield in δ 0.03-0.08 after complexation. The shift indicates the coordination of the imine nitrogen to the metal ions. The signals of the aromatic protons of the ligand appeared at δ 7.21-7.91 and the resonance lines found correspond to the calculated multiplicity. The electronic spectra of the copper(II) complex display a broad band at 14920 cm⁻¹ due to ²B_{1g} → ²E_g and two bands at 16390 and 27250 cm⁻¹ assigned to *d-d* transitions and a charge transfer band respectively, of an octahedral environment¹⁷. The copper(II) complexes exhibit magnetic moments of 1.55-1.78 BM, respectively, at room temperature. These values are quite close to the spin-allowed values expected for an S = 1/2 system and may be indicative of a distorted octahedral geometry around copper(II) ions. The nickel(II) complex exhibited three bands at 9960-10165, 15850-16155 and 29940-29985 cm⁻¹ assignable, respectively to the transitions ³A_{2g} (F) → ³T_{2g} (F) (ν_1), ³A_{2g} (F) → ³T_{1g} (F) (ν_2) and ³A_{2g} (F) → ³T_{2g} (P) (ν_3), which are characteristic of nickel(II) in octahedral geometry¹⁸. The electronic spectra of the cobalt(II) complex showed three bands at 8780-8810, 17475-17775 and 30235-30270 cm⁻¹, which may be assigned to ⁴T_{1g} → ⁴T_{2g} (F), ⁴T_{1g} → ⁴T_{1g} (P) and ⁴T_{1g} → ³A_{2g} (F) transitions, respectively and suggested octahedral geometry around the cobalt ions¹⁹. The cobalt(II) complexes show magnetic moment values of 4.85-4.93 BM at room temperature. These high values of the magnetic moments and the stoichiometries suggest a coordination number of six for the central cobalt(II) ion and an octahedral geometry. The

manganese(II) complex show three bands at 20491-20366, 18903-18976 and 14064-13869 cm^{-1} assignable to ${}^6A_{1g} \rightarrow {}^4A_{1g}$ ($4G$), ${}^6A_{1g}$ ($4G$) $\rightarrow {}^4T_{2g}$ and ${}^6A_{1g}$ (G) $\rightarrow {}^4T_{1g}$ transitions respectively which lie in the same range as reported for octahedrally coordinated^{20,21}. The magnetic moment for Mn(II) 4.88 is an additional evidence for an octahedral structure. On the basis of the above observations, it is tentatively suggested that all of the complexes show an octahedral geometry (Fig. 2) in which the two 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.

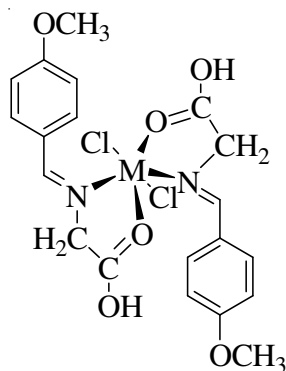


Fig. 2. Proposed structure of the metal complexes

Biological activity: The antibacterial and antifungal activity results (Figs. 3 and 4), show clearly that the newly synthesized ligand and their complexes possess good antimicrobial activity. These compounds were screened for their antibacterial activity against *S. aureus*, *B. subtilis* and *E. coli* and for antifungal activity against *F. moniliformae* and *M. phaseolina* which exhibited a markedly enhancement of activity on further coordination with the cobalt(II) ion against all the test bacteria/fungal strains. The susceptibility of bacteria towards complex compounds were tested by measuring the bacteriostatic diameter (d) and compared with parent ligand with a concentration of 2.0 $\mu\text{g}/\text{disc}$, $d \geq 20$ mm shows high sensitivity, $14 \leq d < 20$ mm shows medium sensitivity and $9 \geq d \leq 13$ shows slight sensitivity. The antibacterial activity data shows that Gram +ve bacteria, *S. aureus* and *B. subtilis* are more susceptible to test compounds than the Gram -ve bacteria, *E. coli*, which is in accordance with previous studies.

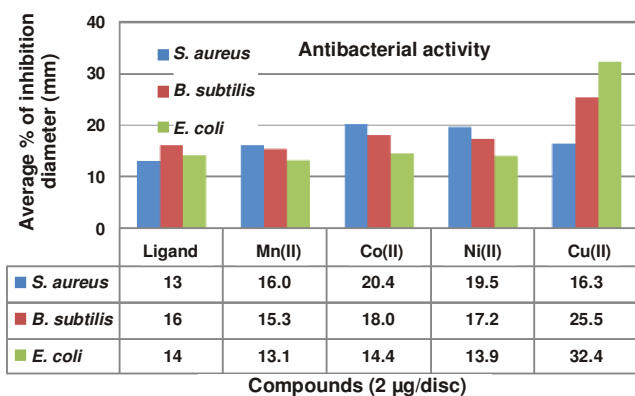


Fig. 3. Antibacterial activity of ligand and their metal complexes

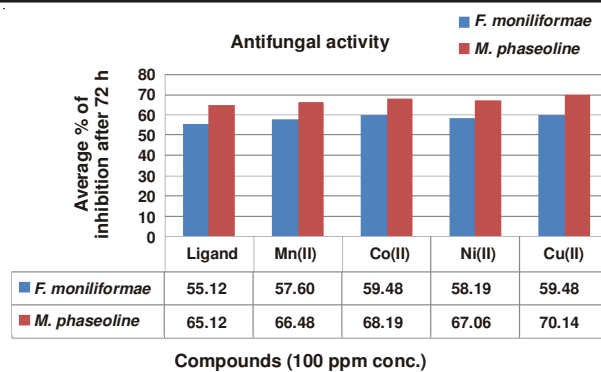


Fig. 4. Antifungal activity of ligand and their metal complexes at 100 ppm concentration

All the complexes show high activity against fungi at the lower concentration and inhibition of fungal growth has been found to be dependent on the concentration of the compound. The antifungal activity data of test compounds against *F. moniliformae* and *M. phaseolina* indicated that the test compound are more active against *M. phaseolina* than the *F. moniliformae*. It is observed among all the complexes, cobalt(II) complex has a higher activity than the free ligand.

Conclusion

In this article, all the synthesized transition metal complexes of Schiff base have been found to be octahedral geometry. The results of antimicrobial show that the metal-complexes exhibit antimicrobial properties and showed the enhanced inhibitory activity compared to parent ligand.

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