



Antimicrobial Activity of Cu(II) and Fe(III) with Pyridine Complexes as Ligands Contrary to Clinical Strains of Bacteria and Fungi Species

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In this study, green coloured Cu(II) and red coloured Fe(III) complexes of pyridine were prepared and the elemental characterization confirmed their composition. The pyridine complexes of Cu(II) and Fe(III) were found very interesting and attractive as potential candidates with antimicrobial activity. Along with this, melting point, molar conductivity measurement, magnetic moment determination, electronic and FTIR spectroscopy were also measured to characterize the prepared complexes. Pyridine acts as monodentate which resulted in formation of square planar and octahedral structure of Cu(II) and Fe(III) complexes, respectively with the nitrogen atom pyridine ring by coordination bond. For antimicrobial activity studies *Alternaria alternata*, *Bacillus cereus*, *Botrydiodia theobromal*, *Colletotrichum corcolei*, *Escherichia coli*, *Fusarium equiseti*, *Macrophomina phaseolina*, *Salmonell typhi* and *Shigella dysenteriae* were used. The prepared complexes showed inhibition against mycelial growth. Although the complexes showed satisfactory inhibition against the tested bacteria and fungi species, both of the complexes were comparatively better against bacteria than fungi compared to ligand.

Keywords: Transition metal (II) complexes, Square planar, Octahedral structure, Pyridine, Microbial activity.

INTRODUCTION

Due to the innovative design and preparation of coordination compounds, metal complexes have gained popularity in the recent past. Progress of coordination chemistry, recently undoubted because of different applications [1,2]. Mass development in different sectors of chemistry like coordination chemistry, catalysis, enzymatic reactions, magnetism and molecular architectures are hugely indebted to this current talk of the topics, coordination complexes [3-5] and in addition to this, biological activities are also unfolded by them [6-8]. Metal ions like iron

and copper show significant preface towards diverse biological activities of human [9,10].

In spite of narration of few cytotoxic nature, copper(II) based complexes can be considered to have good grounds in medicinal chemistry, while in previous work focused on the synthesis of numerous Cu(II) complexes [11-14]. Regular uptake of iron, which can be intercalated in tissues [15] and with meta-bolism, may supposed to exhibit action against cancer, which are caused by hormone because it can act as an important element of biological system with its binding capacity to protein [16,17] and hormone [18].

Pyridine is a member of cyclic aromatic molecule which due to its capabilities of σ and π -binding attracted tremendous attention and with a heap of experimental and theoretical inquiries set up that the greater portion of this type of complexes prepared from metal and pyridine are σ complexes [19-22]. This kind of complex is an important ligand found to be a versatile nucleus in the pharmaceutical field [23]. The derivatives are very much used as anticancer [24,25], antimicrobial [26-28], antiviral [29,30], antidiabetic [31] agents, *etc.* To the prolongation of previous research work, we synthesized and characterized Cu(II) and Fe(III) complexes with pyridine and also evaluated its efficiencies against some microorganisms.

EXPERIMENTAL

Analytical R grade chemicals were used throughout the experiments and procured from Sigma-Aldrich and Fluka, while the metal salts were acquired from E. Merck. Chittagong Veterinary and Animal Sciences University (CVASU), Chittagong, Bangladesh provided the micro-organism cultures studies in the present work.

Synthesis of complexes: The CuSO_4 (24.97 g, 0.1 mol) and FeCl_3 (27.03 g, 0.1 mol) were separately dissolved in 100 mL of distilled ethanol and stirred continuously. The solutions were blue and reddish-brown in colour respectively, then 8.05 mL (0.1 mol) of pyridine was added dropwise with continuous stirring in each solution. The mixtures changed instantly and became deep blue and deep brown in colour, at that time both mixtures were allowed to revolve on a magnetic stirrer at room temperature for the next 2-3 h. Then the mixtures were taken in a round bottom flask and refluxed on a water bath for about 9 and 5 h, respectively. The reaction mixtures were then allowed to stand for 24 h. A coloured precipitation was allowed to settle down for the next 24 h to assure the thorough formation of the metal complexes. The greenish coloured copper-pyridine and red coloured iron-pyridine complexes were separated by vacuum filtration. The complexes were made dry in a vacuum desiccator over the silica gel just after the washing.

The determination of melting points of all the complexes was performed by electrothermal melting point apparatus. The carbon, hydrogen, sulphur and nitrogen contents of the synthe-

sized complexes were determined using CHNS elemental analyzer (varioMICRO VI. 6.1 GmbH, Japan). On HANNA instrument with HI 8820N conductivity cell using water and chloroform as solvent, conductance values of the complexes were obtained. The measurement of magnetic susceptibility was performed for solid complexes using Sherwood Scientific magnetic susceptibility balance at room temperature. IR spectra was obtained using KBR disc in the range of 4000-400 cm^{-1} on Perkin-Elmer-883 and Shimadzu infrared spectrophotometer. A 250-500 nm was the range of electronic spectra carried out on Shimadzu UV-visible spectrophotometer (model UV-1800) using 1 cm cell.

RESULTS AND DISCUSSION

The complexes obtained were coloured, air stable, microcrystalline powders. The analytical and physical data obtained from the complexes are given in Table-1.

Molar conductance: The molar conductivity values are given in Table-1. The non-electrolytic characteristic of the complexes is supported by the molar conductance value of $0.00 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in chloroform, (colour remain intact) for both complexes. On the contrary, diaqua complex which was constructed by the complete replacement of SO_4^{2-} and Cl^- ion by H_2O molecules in aqueous solution can be proved by the molar conductivity values of 255 and $396 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in aqueous solution of the complexes corresponding to 1:1 electrolytes. So, square planar and octahedral structure are expected for Cu(II)-pyridine and Fe(III)-pyridine complexes, respectively.

IR spectral studies: The infrared spectral data are listed with the relative intensities along with tentative assignments of the various bands in Table-2. The absorption bands at 3080-3020, 1220-1145 and 1500-1400 cm^{-1} is due to the stretching vibration of C-H, C-C and C=C bond, respectively [32] in the spectrum of the complexes. The medium intensity absorption peaks at 1598-1550 cm^{-1} is due to C-N bond [31]. The strong intensity absorption peaks in 1650-1600 cm^{-1} is due to the stretching vibration of C=N.

The powerful intensity absorption peaks at 1130-1080 cm^{-1} is due to coordinated SO_4^{2-} group and the presence of bands at

TABLE-1
ANALYTICAL PHYSICAL DATA FOR COPPER AND IRON COMPLEXES

| Complex (Colour) | m.p. ($^{\circ}\text{C}$) | Elemental analysis (%): Calculated (found) | | | | | | | μ_{eff} (B.M.) | Λ_m ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) |
|---|-----------------------------|--|----------------|------------------|------------------|------------------|------------------|------------------|------------------------------|---|
| | | C | H | N | S | O | Cl | M | | |
| $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2\text{SO}_4]$ (Green) | 348 | 37.74 (37.48) | 3.19 (3.12) | 8.84 (8.71) | 10.15 (10.11) | 20.15 (19.99) | — | 19.93 (19.69) | 1.78 | 0.00 (CHCl_3) 255 (water) |
| $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3]$ (Red) | 276 | 44.99 (44.45) | 3.75 (3.71) | 10.69 (10.52) | — | — | 26.68 (26.57) | 13.89 (13.74) | 1.82 | 0.00 (CHCl_3) 396 (water) |

*Molar conductivity of about 10^{-3} molar solution in both the solvent at ambient temperature.

TABLE-2
SPECTRAL DATA FOR COPPER AND IRON COMPLEXES

| Complex | Infrared spectral assignment (cm^{-1}) | | | | | | | | | Electronic spectral band (nm) |
|--|---|--------------------|---------------------|--------------------|--------------------|---------------------|---------------------|---------------------|----------------------|-------------------------------------|
| | $\nu_{\text{C-H}}$ | $\nu_{\text{C-C}}$ | $\nu_{\text{C=C}}$ | $\nu_{\text{C-N}}$ | $\nu_{\text{C=N}}$ | $\nu_{\text{Cu-N}}$ | $\nu_{\text{Cu-O}}$ | $\nu_{\text{Fe-N}}$ | $\nu_{\text{Fe-Cl}}$ | |
| $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2\text{SO}_4]$ | 3024.38, 3039.81 | 1147.65 | 1448.40, 1489.05 | 1573.91m | 1606.7s | 542.0s, 570.9s | 443.63s, 474.49s | — | — | 300 |
| $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_3\text{Cl}_3]$ | 3076.46 | 1211.30 | 1440.83, 1483.26 | 1598.99m | 1633.71s | — | — | 609.51s | 736.81s | 490, 500, 510 |

TABLE-3
ANTIMICROBIAL STUDIES OF PYRIDINE AND ITS Cu(II) AND Fe(III) COMPLEXES

| | | Zone of inhibition (mm) | | |
|----------|----------------------------------|-------------------------|---|---|
| | | Pyridine | [Cu(C ₅ H ₅ N) ₂ SO ₄] | [Fe(C ₅ H ₅ N) ₃ Cl ₃] |
| Fungi | <i>Macrophomina Phaseolina</i> | 39.48 | 36.49 | 33.19 |
| | <i>Alternaria alternata</i> | 28.97 | 27.99 | 21.32 |
| | <i>Fusarium equiseti</i> | 34.65 | 29.91 | 19.18 |
| | <i>Collectrichums corcolei</i> | 38.22 | 36.39 | 33.46 |
| | <i>Botrgodiplodia theobromal</i> | 35.97 | 36.67 | 29.78 |
| Bacteria | <i>Salmonell typhi</i> | – | 10 | 08 |
| | <i>Shigella dysenteriae</i> | 04 | 17 | 19 |
| | <i>Escherichia coli</i> | 02 | 12 | 10 |
| | <i>Bacillus cereus</i> | 08 | 16 | 07 |

‘–’ means no inhibition.

485-410 cm⁻¹ is due to Cu-O bond [33] between Cu(II) ion and O⁻ ion of SO₄²⁻ group which indicates the bidentate mode of coordination of a sulfate group through O⁻ ion. Sharp IR bands were found in the prepared complexes at 542 and 570.9 cm⁻¹ were due to the stretching vibration of Cu-N bond, which indicates the formation of Cu(II)-pyridine complex.

In Fe(III) complex, the absorption peaks in 750-730 cm⁻¹ region is due to the stretching vibration of Fe-Cl which indicates the formation of Fe-Cl bond and the potent absorption band at 609.51 cm⁻¹ which is due to the stretching vibration of Fe-N bond [34].

Electronic spectral and magnetic moment studies: In case of Cu(II) complex, the absorption band at 300 nm in the ultraviolet region is assigned to copper-ligand charge transfer transition and also the magnetic susceptibility value of this complex is 1.78 B.M., which indicates that the complex may have square planar geometry. On the other hand, the electronic spectrum of Fe(III) complex display broad *d-d* bands at 485-520 nm in water as does the other octahedral Fe(III) complexes. However, also indicate that this complex may have octahedral geometry. The magnetic moment value is 1.82 B.M. which is in good agreement with the octahedral nature.

Antimicrobial activity: A well diffusion method was used to testify the growth of microorganisms performing Mueller Hinton Agar (MHA) and culture in nutrient broth against different kind of microorganisms [35]. A 10⁻⁴ M concentration of 4-nitro-quinoline-1-oxide and its metal chelates was fixed in the present studies. The incubation was performed of the plates at 37 °C for 24 h. The antifungal studies (Table-3) indicated the present complexes have varied amount of outcome to the resistance of mycelial growth and the formed complexes can exhibit effective part on the inhibition of mycelial growth against all the tested microorganisms.

Conclusion

The formation of chelation between pyridine and Cu(II) and Fe(III) ions can be ascertained from the physico-chemical data and spectral studies. The Fe(III) complex is more reactive in comparison to Cu(II) complex towards pyridine. The antifungal data shows that *Botrgodiplodia theobromal* is more active with Cu(II) complex. On the other hand, *Macrophomina phaseolina* is more influential in Fe(III) complex. For bacteria, *Shigella dysenteriae* is active in Fe(III) complex, while *Salmonell typhi* has very low activity against Cu(II) complex.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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