WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 6.805
Volume 5, Issue 4, 887-891. Research Article ISSN 2277– 7105

SYNTHESIS, SPECTRAL EVALUATION AND BIOLOGICAL STUDIES OF COPPER (II) CONTAINING MIXED LIGANDS SCHIFF BASE (4-BROMO- (2-CARBOXYPHENYL)-PYRIDINE-2-YL ETHYLENE AMINE) AND 1,10 PHENANTHROLINE

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Article Received on
24 Jan 2016,
Revised on 15 Feb 2016,
Accepted on 11 Mar 2016
DOI: 10.20959/wjpr20164-5866

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ABSTRACT

Copper (II) complex having general formula [CuL(phen)BF $_4$]BF$_4$ was prepared by using Schiff base, 4-bromo-(2-carboxyphenyl)-Pyridine-2-yl ethylene amine, secondary ligand 1,10-Phenanthroline and copper tetrafluoroborate salt with 1:1:1 molar ratio. Distorted octahedron structure was elucidated on the basis of elemental analyses, IR, electronic spectra, magnetic susceptibility measurements, molar conductivity. We report synthesis and spectral evaluation of copper (II) complex of mixed ligands Schiff base, 4-bromo-(2-carboxyphenyl)-pyridine-2-yl ethylene amine and 1,10-Phenanthroline .

KEYWORDS: Synthesis, Spectral evaluation, Schiff base, 4-bromo-(2-carboxyphenyl)-pyridine-2-yl ethylene amine, 1,10-phenanthroline, copper (II) complex.

INTRODUCTION

Schiff bases have recently been focused by the coordination chemist and can act as important organic ligands and useful blockers/chelators due to their ease of preparation, structural varieties and varied denticities and subtle steric and /or electronic effects on their framework.[1-12] Tetrafluoroborate are also suitable terminal/bridging units which in combination with Schiff bases and metal (II) may result in different molecular architectures through their versatile ligational mode. Schiff bases and their metal complexes perform very important role in bioinorganic chemistry since they have significant biological activities. Metal complexes containing diimine ligands such as 1,10 – phenanthroline have gained

importance because of their versatile roles as binding blocks for the synthesis of metallo – dendrimers and as molecular scaffolding for supramolecular assemblies and in analytical chemistry, catalysis, electrochemistry, ring opening metathesis polymerization and biochemistry. Recently the medicinal application of metal complexes has also been a subject of great interest.

Transition metal ions are known to play very important role in biological processes in the human body. For example, copper (II) ion are found either at the active sites or as structural components in number of enzymes. For instance, to name among others, 1,10 – phenanthroline and its copper complexes have been reported to exert a range of biological activities, such as antitumour, anti-candida, antimycobacterial and antimicrobial effects.[13-14]

Hence, this field has attracted the attention of several medicinal chemists to investigate further in view of the growing resistance to chemotherapy by cancer cells. Research on anticancer activity of Schiff bases are well known in the prior arts.

In the present paper, we report the synthesis and spectral evaluation of copper (II) complex of mixed ligand Schiff base, 4–bromo (2-carboxyphenyl)-pyridine-2-yl ethylene amine and 1, 10-phenanthroline.

EXPERIMENTAL SECTION

Materials

All chemicals used were of the analytical reagents grade (AR) and of highest purity available. 2-amino-5 -bromobenzoic acid, 2-acetylpyridine (Lanchester) was purchased from the respective concerns and was used as received.

Methods

Copper was analyzed by titrimetric method. Elemental analysis (C, H and N) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Infrared spectra were recorded on Perkin Elmer FT-IR spectrometer as KBr pellets in the 4000-400 cm^{-1} spectral range. ^{1}H NMR spectra of ligands were recorded on Bruker 400 MHz spectrometer using DMSO as a solvent. Electronic spectra were recorded on a Shimadzu UV-visible NIR spectrophotometer. Molar Conductance (Λ_M) was measured on the ELICO (CM-185) conductivity bridge using 10^{-3} M solution in DMF. Magnetic susceptibility was measured on Gouy balance at room temperature using Hg $[Co(SCN)_4]$ as calibrant.

Synthesis of ligand (4- bromo-(2-carboxyphenyl)-pyridine-2-ylethyleneamine (L)

The Schiff base ligand, 4-bromo(2-carboxyphenyl)-pyridine-2-ylethyleneamine (L) synthesized by mixing a solution of 2-acetylpyridine (0.121 g, 1 mmol) in 10 ml of ethanol with solution of 2-amino-5-bromobenzoic acid (0.137 g, 1mmol) which was dissolved in 10 ml of absolute ethanol. The resulting mixture was refluxed at 80°C until the completion of reaction (checked by TLC). The resultant brown colored liquid was concentrated to give dark brown colored solid and purified by crystallization to give product. (Yield: 70%; M.P.: 173^0C; elemental analysis, calcd (found) (%) $C_{14}H_{11}Br\ N_2\ O_2$: C, 52.69 (51.70), H, 3.47 (3.60), N, 8.78 (8.90); IR (cm^{-1}) in KBr: 1610, 1668, 669; ^{1}H NMR (DMSO)(400MH_Z) δ 2.4 (s, H_3C-C=N), δ 6.5-8.5 (m, Ar H); UV-VIS (λ_{max}) (nm): 272, 332, 410.

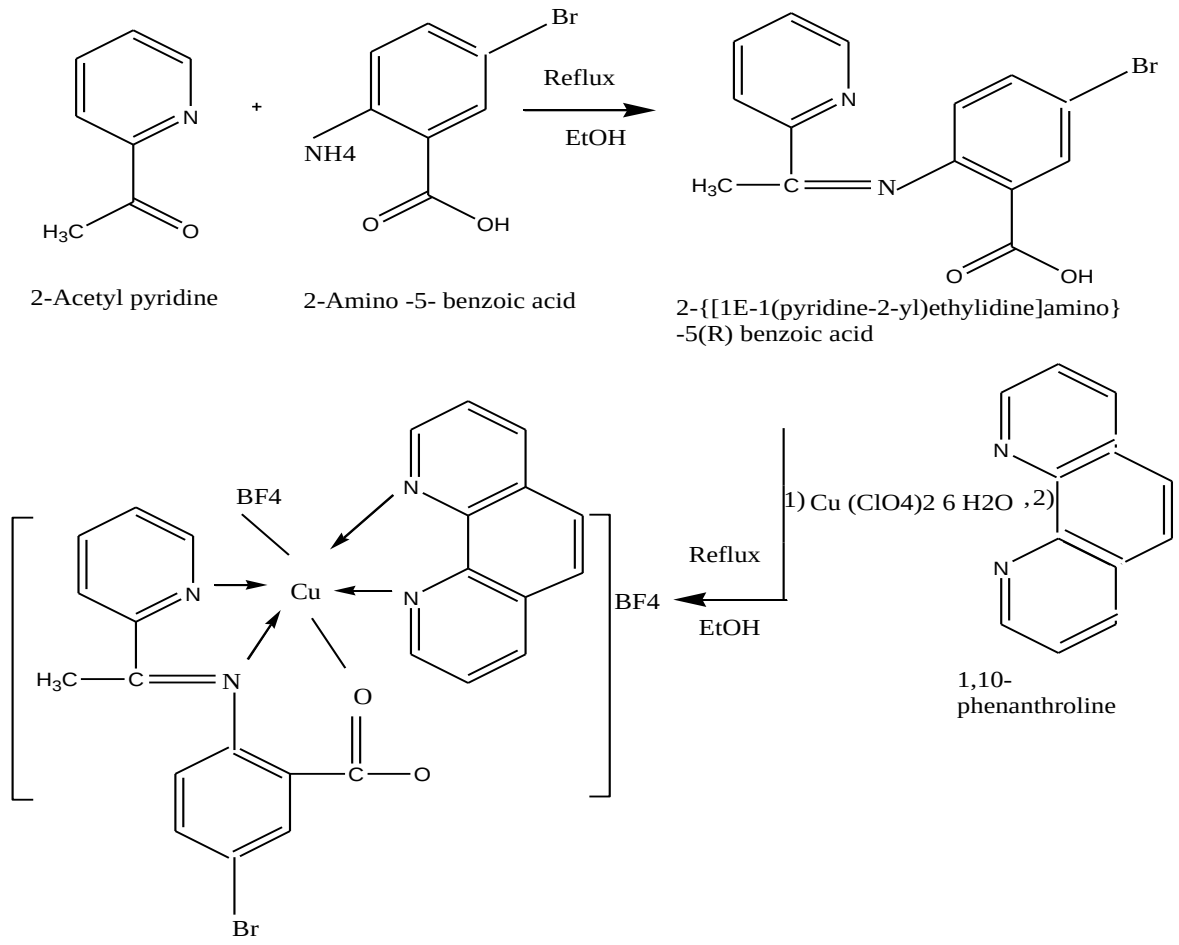
Synthesis of Cu (II) complex [CuL(phen)BF $_4$]BF_4

To a ethanolic solution of $Cu(NO_3)_2.6H_2O$ (0.241g,1 mmol), a ethanolic solution of Schiff base ligand (L) (0.285g, 1 mmol) was added followed by 1,10-phenanthroline (0.181g ,1 mmol) as secondary ligand then the ethanolic solution of sodium tetrafluoroborate (0.076g ,1 mmol) added with constant stirring. Resulting solution refluxed for 2 hr. The resulting solid green product was filtered, washed with ethanol and dried over $CaCl_2$. (Yield: 65%; M.P.: 300^0C; elemental analysis, calcd (found) (%) $C_{26}H_{19}N_4O_2\ Br\ F_8\ B_2\ Cu$: Cu, 8.62 (8.61), C, 42.40 (41.99), H, 2.60 (2.41), N, 7.60 (7.51); IR (cm^{-1}) in KBr: 1614, 1590, 1372, 1534, 1432, 897, 736, 1091, 730, 633; UV-VIS (λ_{max}) (nm): 252, 257, 410, 618, 723; Λ_M ($\Omega^{-1}cm^2mol^{-1}$): 114.0; μ_{eff} (B.M.) = 1.73.

RESULTS AND DISCUSSION

Analytical data for copper (II) complex conform to $C_{26}H_{19}N_4O_2\ Br\ F_8\ B_2\ Cu$. The Complex is soluble in DMF and DMSO. The spectroscopic evaluation of the synthesized complex involved elemental analysis, IR, UV-Visible spectral investigations and the results are matched the proposed structure. Copper (II) complex was obtained by the reaction of the ligands Schiff base 4-bromo-(2-carboxyphenyl)-pyridine-2-ylethyleneamine and 1,10-phenanthroline with $Cu(BF_4)_2$ in ethanol (**Scheme 1**). The high yield (65 %) obtained for copper (II) complex can be attributed to the solvent effect of ethanol. The IR spectrum of free ligand show bands at 1610 cm^{-1}, 1668 cm^{-1} and 669 cm^{-1} which is assigned due to C=N, COO^- and Py-N respectively. The IR spectrum of complex show bands at 1614 cm^{-1}, 1590 cm^{-1}, 1372 cm^{-1} and 633 which is assigned due to C=N, COO^-, Py-N respectively. The bands at 1534 cm^{-1}, 1432 cm^{-1}, 897 cm^{-1} and 736 cm^{-1} which is assigned for 1,10-phenantroline.

The bands at 1091 cm^{-1} and 730 cm^{-1} which is assigned due to BF_4^-. The shift in band takes place due to formation of complex of metal with ligands. ^1H -NMR spectrum of the ligand exhibited δ 2.4 (s, H_3C-C=N), δ 6.5-8.5 (m, Ar H). The UV-Visible spectra of the complex shows two weak bands at 252 nm - 257 nm and 410 nm which are assigned to the n→π, π→π* transitions respectively. The small shift is observed in the UV-visible spectra of complex and free ligand. The broad band centered at 618 nm - 723 nm appearing as an envelope in the copper (II) complexes assigned to the ^2Eg and ^2T_2g transition reveals the octahedral geometry. The ^2Eg and ^2T_2g states of the octahedral copper (II) (d^9) split under the influence of tetrahedral distortion and distortion can be such as to cause three transition $^2B_1g \rightarrow {}^2B_2g$; $^2B_1g \rightarrow {}^2Eg$ and $^2B_1g \rightarrow {}^2A_1g$ to remain unresolved in the spectra. Molar conductance (Λ_M) of complex obtained was 114.0 $\Omega^{-1}cm^2mol^{-1}$ which is in the range of characteristic of the non-electrolytic nature suggesting the complex is neutral. The magnetic susceptibility (μ_{eff}) value of complex obtained was 1.73 B.M. The octahedral geometry of copper (II) ion in the complex is confirmed by the measured magnetic moment value which is in harmony with the reported value.



Scheme 1: Synthesis of $[CuL(phen)BF_4]BF_4$

CONCLUSION

In the present work, the copper (II) complex containing mixed ligands, Schiff base, 4 bromo (2-carboxyphenyl)-pyridine-2-ylethyleneamine and 1,10-phenanthroline as secondary ligand was synthesized, characterized and the coordination chemistry is described. The Schiff base ligand act as monobasic tridentate, coordinated to the metal ions in a tridentate manner with ONN donor sites of the carbonyl oxygen, azomethine nitrogen, and pyridine nitrogen along with anion and two nitrogen of 1, 10-phenanthroline in the complex formation and in ligands, the coordination mode of carboxylate group is unidentate mode, correlating the experimental data, one can suggest the octahedral geometry for the prepared metal complex.

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