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Short Communication

Synthesis, Characterization and Biological Studies of a new Cu(II) Complex Derived from 9-Anthraldehyde and 2-Aminopyridine

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Abstract

In the present study Schiff base and Cu (II) complex have been synthesized and reported. The Schiff base is prepared by condensing 2-aminopyridine and 9-anthraldehyde. The complex was synthesized by reaction of $CuCl_2.2H_2O$ with Schiff base. These compounds have been characterized byelemental analysis, magnetic measurement, molar conductance, FT-IR, UV-Vis spectra, ^1H NMR, electronic, mass and ESR spectroscopic studies. Analytical data suggests the molecular formula $[Cu(L)_2Cl_2]$ for Cu(II) complex. The IR spectral data suggest that Schiff base acts as a neutral monodentate ligand towards Cu(II) in its complex. The electronic spectral data and magnetic moment value agree with the tetrahedral geometry for the complex. The Schiff base and complex were screened for antibacterial and antifungal studies. The Cu(II) complex exhibit increased antimicrobial activity than Schiff base.

Keywords: 9-anthraldehyde, 2-aminopyridine, Schiff base, Cu(II).

Introduction

The compounds containing an azomethine group are important in elucidating the mechanism of transamination and racemization reactions in biological systems[1,2]. Schiff bases and their complexation behaviors have been studied due to the great flexibility and diverse structural aspects[3]. The development of bioinorganic chemistry has increased the interest of Schiff base complexes because of its recognition as models for biologically important species[4-6].The present study was aimed to report thesynthesis and characterisation and biological study of a new Cu(II) complex with the Schiff base derived by the condensation of 2-aminopyridine and 9-anthraldehyde. Both Schiff base and Cu(II) complex are characterized by analytical, spectral and magnetic measurements.

Materials and Methods

Synthesis of Schiff base (APY): N-(anthracene-9-ylmethylene)-pyridine-2-amine was prepared by the condensation of 9-anthraldehyde and 2-aminopyridine. A mixture of of 9-anthraldehyde and 2-aminopyridine in ethanolic solution was boiled under reflux for 3-4 hrs. After completion of reaction, the solution was cooled. The yellow precipitate obtained was collected by filtration and recrystallized from ethanol to get the purified crystal[7].

Synthesis of complex: To a hot methanol solution of APY, a hot methanol solution of $CuCl_2.2H_2O$ (0.01 mol) was added drop wise and the resulting mixture was stirred under reflux for 2 hours, when the complex gets precipitated[7]. The solid complex filtered off washed several times with methanol dried and kept in desiccator over dried silica gel.

Measurements: The elemental analysis (C, H, N) were carried out on a Vario EL-III CHN Elemental Analyzer. The ^{1}HNMR spectrum of APY recorded on a Joel GS 400 MHz FTNMR spectrometer employing TMS as internal reference and DMSO-d_6 as solvent. ESI-mass spectra of the complex was recorded on Schimadzu Biotech Axima mass spectrometer using ethanol as solvent. Molar conductance measurement was done using10^{-3} M solution of complex in methanol and DMF on a Systronics direct reading conductivity meter. The IR spectra of APY and complex were recorded in KBr medium in range 400-4000cm^{-1} on a Perkin Elmer Spectrum 65 IR Spectrophotometer. Electronic spectra were measured in range 200-900nm on a Perkin Elmer Lambda 25 UV-Vis Spectrophotometer. The magnetic moment of compound measured on a Sherwood Scientific magnetic Susceptibility at room temperature. The X-band ESR spectra obtained using Varian USA at room temperature at IIT Bombay. Antimicrobial activities of APY and complex are done at CEPC lab, Kollam. The metal content of complex was analyzed by standard methods.

Results and Discussion

Characterization of APY and complex: From microanalytical data APY and complex can be formulated as $C_{20}H_{14}N_2$ and $CuC_{40}H_{28}N_4Cl$ 'Found: C, 85.05; H, 4.96; N, 9.92%; 'molecular formula $C_{20}H_{14}N_2$' requires C, 85.10; H, 4.96; N, 9.95% and for complex 'Found: C, 68.72; H, 4.00; N, 8.03; Cu, 9.10; Cl, 10.15%; 'molecular formula $CuC_{40}H_{28}N_4Cl_2$' requires C, 68.77;

H, 4.01; N, 8.02; Cu, 9.09; Cl, 10.12%. From the elemental study it is found that Cu and APY are coordinated in 1:2 ratio.

^{1}HNMR spectra: The ^{1}H NMR spectra of APY is recorded in DMSO-d6 solution. The proton NMR spectrum of APY consists of a multiplet equivalent to aromatic protons at δ 6.9-8.1 ppm assignable to nineteen aromatic protons of aminopyridine and 9-anthraldehyde. The singlet at δ 11.5 ppm (1H) correspond to azomethine proton[8].

Mass spectra: Mass spectrum of $[Cu(APY)_2Cl_2]$ shows a molecular ion peak at m/z 698 corresponds to molecular ion species $[Cu(APY)_2Cl_2]^+$ and its stoichiometry is again confirmed by the presence of another peak at m/z 720 assignable to its (M+Na) species, which is $[Cu(APY)_2Cl_2Na]^{+.}$

Electrical Conductance: The electrical conductance of the complex measured in DMF and methanol shows the nonelectrolyte nature of Cu(II) complex.The molar conductance value of Cu(II) complex is observed in the range 5 - 14 Ω^{-1} cm^2 mol^{-1}in methanol and 2 – 10Ω^{-1} cm^2 mol^{-1}in DMF revealing their nonelectrolyte nature[9].

IR spectra: The strong band at 1442$cm^{-1}$of APY corresponds to C=N stretching vibration, gets shifted to 1406cm^{-1}in its complex $[Cu(APY)_2Cl_2]$[10]. A band observed at 420 cm^{-1}can be assigned to M-N bond in Cu(II) complex that supports the coordination to azomethine group to Cu(II) ion.

Electronic spectra: The electronic spectra of APY and $[Cu(APY)_2Cl_2]$ complex was recorded. APY shows two band maxima at 323 nm and 377 nm corresponding to n →π* and π →π* transitions respectively. In $[Cu(APY)_2Cl_2]$ complex both n →π* and π →π* bands are found shifted and appears at respectively 330 nm and 388 nm. An additional band at 444 nm can be due to d-d transition[11, 12].

ESR spectra: The ESR spectrum of $[Cu(APY)_2Cl_2]$ gives an information regarding their electronic environment[13]. The X-band spectrum at 300K in solution shows an isotropic pattern due to tumbling motion of the molecules. The complex shows absorption around 3200 G, characteristic of Cu^{2+} species and the absence of any half field absorption around 1500-1600 G rules out metal-metal interaction in these complexes[14]. The complex shows g_{avg} value 2.132. The tendency of g tensor is exhibiting isotropic nature. The ESR spectrum of $[Cu(APY)_2Cl_2]$ is shown in Figure-1.

Magnetic moment: The molar magnetic moment value of $[Cu(APY)_2Cl_2]$ is 2.4BM suggesting a tetrahedral geometry around Cu(II)ion[15].

Antimicrobial activity: The *in vitro* antimicrobial activity of synthesized APY and $[Cu(APY)_2Cl_2]$ on *Escherichia coli, Vibrio cholera, Aspergillus niger* and *Pencillium crysogenum* was carried out using disc diffusion method using DMSO as solvent. It is found that Cu(II) complex has enhanced activity compared to APY[16]. The zone of inhibition is measured for APY and $[Cu(APY)_2Cl_2]$ in cm and is tabulated in Table-1.

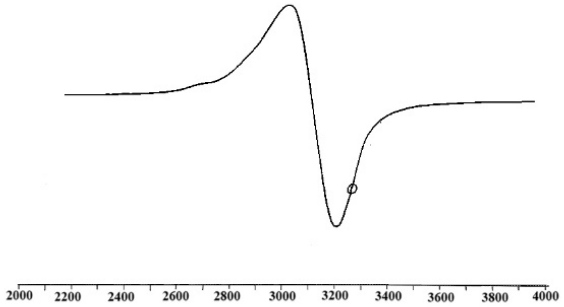

Figure-1
ESR spectrum of $[Cu(APY)_2Cl_2]$

Table-1
Antimicrobial activity of APY and $[Cu(APY)_2Cl_2]$

Compound	*E coli (cm)*	*V cholera (cm)*	*A niger (cm)*	*P crysogenum (cm)*
APY	0.7	No Zone	1.7	No Zone
$[Cu(APY)_2Cl_2]$	1.5	0.5	1.9	0.9

Conclusion

In this study a Schiff base, APY and Cu(II) complex have been prepared and characterized based on various analytical, physico-chemical and spectroscopic studies.^{1}HNMR data of APY and mass spectral data of complex supports the proposed stoichiometry. The IR spectra revealed that APY is coordinated to Cu(II) through azomethine nitrogen atom and shows neutral monodentate nature. The Cu(II) center has four coordinate tetrahedral geometry in complex. Molar conductance measurement values also support the non-electrolytic nature the complex. The tetrahedral geometry for the complex was further supported by electronic spectra and magnetic moment value. The results of antimicrobial studies show that Cu(II) complex has enhanced activity compared to APY against the studied microbes.

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