

Spectral and luminescence studies on tetraazadioxo schiff base macrocyclic complex of Cu(II) metal ion

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ABSTRACT

A novel Tetraazadioxo macrocyclic metal Complex (M_2L_2) of Cu(II) have been synthesized. This complex was characterized by elemental analyses, molar conductance measurements, IR, Electronic absorption spectral and Luminescence spectral studies. The cyclic voltammograms of the macrocyclic complex shows the complex contain two metal ions. On the basis of molar conductance the complexes may be formulated as $[Cu_2(H_2L_2)(NO_3)_2(H_2O)_2].xH_2O$. The complexes are insoluble in methanol, acetonitrile, diethyl ether and chloroform but soluble in DMF, DMSO. The compound is stable both in the solid state and in solution.

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KEYWORDS

Zinc complexes;
Benzimidazole;
IR and NMR spectra.

INTRODUCTION

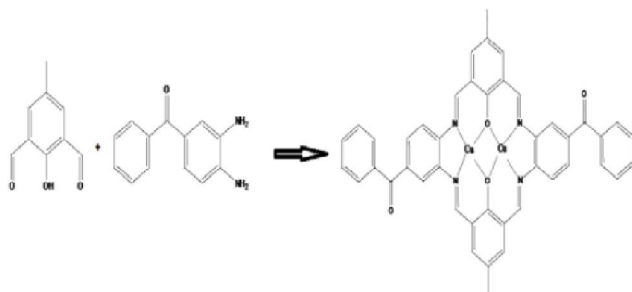
A considerable number of Schiff-base complexes have potential biological interest and are used as more or less successful models of biological compounds^[1]. The majority of radiopharmaceuticals currently available in nuclear medicine make use of metallic radioisotopes. Copper is one of the most interesting elements for various biomedical applications and its radioisotopes due to their unique properties are applied in imaging and for targeted radionuclide therapy^[2-6]. The most utilized is ^{64}Cu , which is suitable both for positron emission tomography (PET) imaging (β^+ emission) and for targeted radiotherapy (β^- emission)^[2-10]. Luminescent properties of Schiff base ligands and their metal complexes, especially Cu(II) complexes, have generated extensive interest in recent years. It is well

established that Cu(II) ion plays vital roles in numerous biological processes. Thus, Cu(II) sensing has attracted increasing interest, and a number of fluorescent probes, including Schiff base compounds. Multi – donor ligands and particularly mixed donors are important due to the presence of several potential donor centers and their flexibility to bind with biomolecules or to coordinate with various metal ions. Mixtures of two or more donors' sites have also been employed to tune selectivity and stability^[11]. In this paper, we report the synthesis, Structural and spectroscopic techniques of tetraazadioxo macrocyclic metal complex.

EXPERIMENTAL

Synthesis of schiff base macrocyclic Cu(II) complex

To a solution of 2, 6-diformyl-4-methylphenol in acetonitrile was added to Copper (II) nitrate hexahydrate in acetonitrile and another solution of 3, 4-diaminobenzophenone (DABP) in 1:1:1 mole ratio in acetonitrile. The above mixture was refluxed for 3 hours. The resultant product was filtered, washed with acetonitrile and dried over anhydrous calcium chloride (Scheme 1).



Scheme 1 : Synthesis of Cu(II) Complex

RESULT AND DISCUSSION

The complexes have been synthesized (Scheme 1) and characterized by IR, ^1H , UV-Vis spectra, Molar conductivity measurements, cyclic voltammetry and Luminescence spectral studies. The corresponding data for the complexes are presented in Figures 1-5.

Infrared spectrum

The infrared spectrum of the Cu(II) complex are recorded on a Perkin Elmer FT-IR Spectrometer in the range 4400 – 400 cm^{-1} using KBr pellets. The infrared spectrum of the Copper(II) complex shows a strong absorption at 3430 cm^{-1} due to OH stretch-

ing of phenolic OH and lattice water. The absorption at 1629 cm^{-1} is attributed to C=O stretching of the carbonyl group. A strong absorption at 1384 cm^{-1} is due to the N=O of the free nitrate group. The C-O stretching of phenolate group is observed at 1272 cm^{-1} and the C-H bending vibration of aromatic compound is observed at 719 cm^{-1} . The infrared spectrum of the complex is presented in Figure 1.

UV-Visible Spectrum

UV-Visible spectrum of the Cu(II) complex are recorded on Perkin Elmer Lambda 3B UV-Visible Spectrophotometer in the range 250-700 nm. The spectrum was recorded in DMSO at 25 $^{\circ}\text{C}$ using matched pair of Teflon stoppered quartz cell of path length 1 cm. The electronic absorption spectrum of copper(II) complex shows three absorption at 270, 284 and 424 nm. The absorption maximum at 270 nm is due to ligand centered $\pi\text{-}\pi^*$ transition, at 284 nm is due to $n\text{-}\pi^*$ and at 424 nm is due to the charge transfer transition. There is a absorption at 610 nm which may be assigned to d-d transition. The Electronic Absorption Spectrum of $[\text{Cu}_2(\text{H}_2\text{L}_2)(\text{NO}_3)_2] \cdot x\text{H}_2\text{O}$ is shown in Figure 2.

^1H NMR spectra

^1H NMR of the complexes in DMSO- d_6 solution shows that they are NMR active. The ^1H NMR spectrum of the complex showed a signal at 6.71 – 8.25 ppm is due to the aromatic proton. The signals appearing at 1.5 ppm is due to the solvent group. The ^1H NMR spectrum of the complex exhibited almost the same values as that of the ligand. The NMR

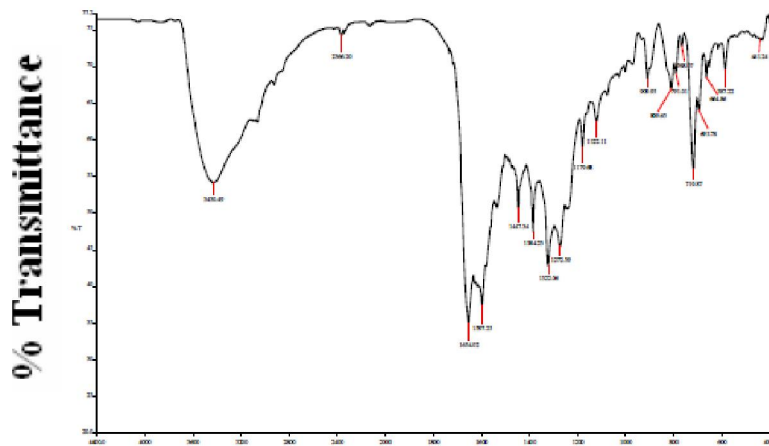
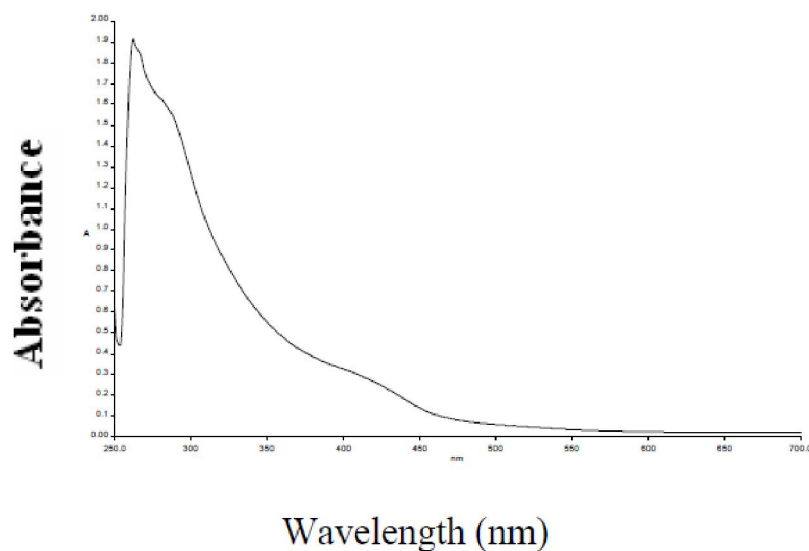
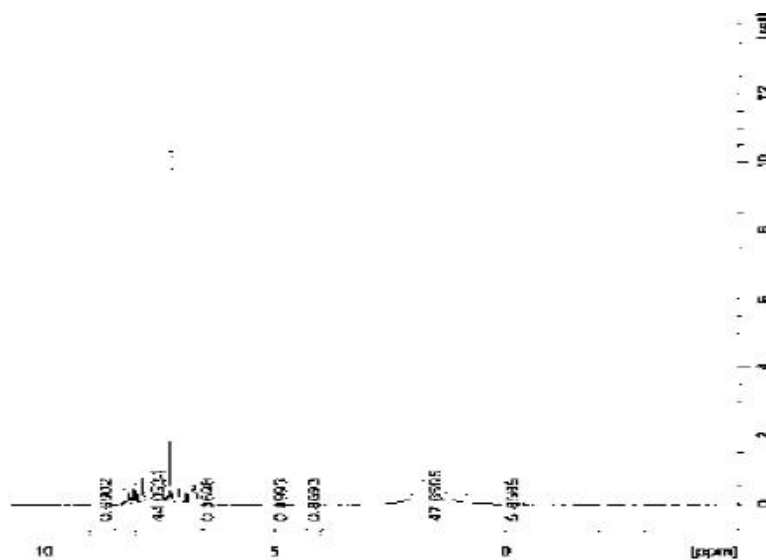
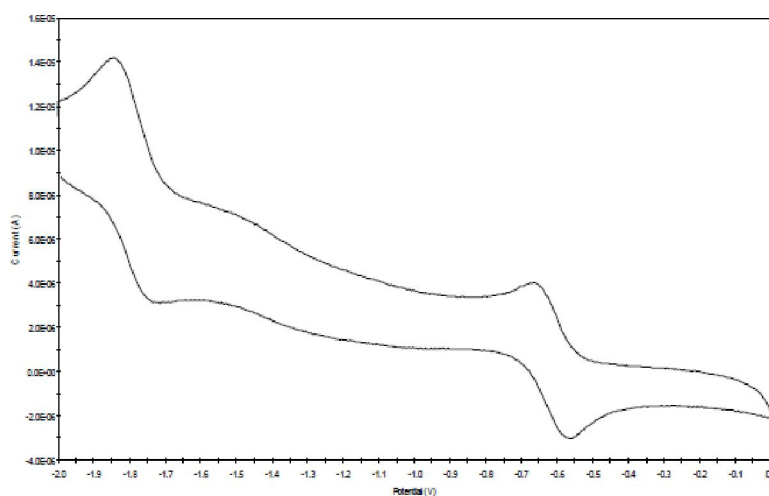


Figure 1 : Infrared Spectrum of $[\text{Cu}_2(\text{H}_2\text{L}_2)(\text{NO}_3)_2] \cdot x\text{H}_2\text{O}$

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Figure 2 : Electronic absorption Spectrum of $[\text{Cu}_2(\text{H}_2\text{L}_2)(\text{NO}_3)_2] \cdot x\text{H}_2\text{O}$ Figure 3 : ^1H NMR Spectrum of the Cu(II) complexFigure 4 : Cyclic voltammogram of $[\text{Cu}_2(\text{H}_2\text{L}_2)(\text{NO}_3)_2] \cdot x\text{H}_2\text{O}$

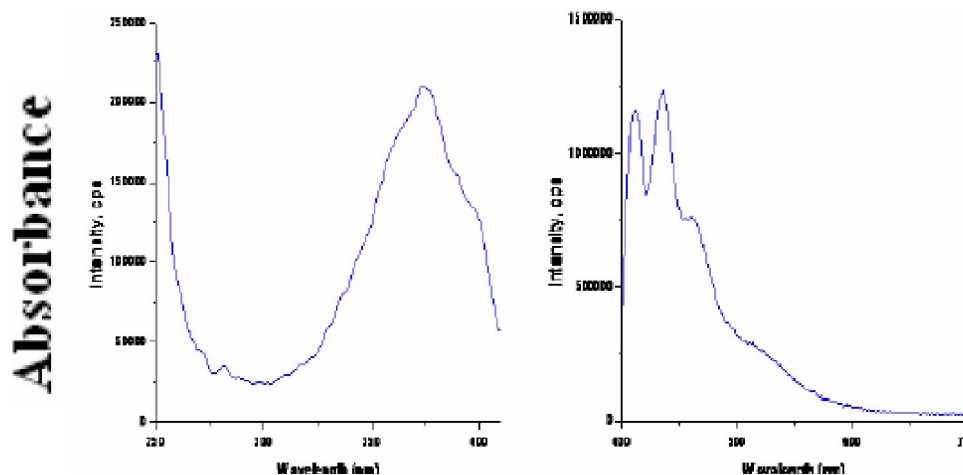


Figure 5 : Excitation and Emission spectrum of $[\text{Cu}_2(\text{H}_2\text{L}_2)(\text{NO}_3)_2] \cdot x\text{H}_2\text{O}$

spectrum of macrocyclic ligand is presented in Figure 3.

Electrochemistry

The cyclic voltammograms of Cu(II) complex are recorded using 10^{-3} M solution in DMSO with tetraethyl ammonium bromide (TEAB) was employed as the supporting electrolyte. The scan rate is fixed at 100mV/s and multiple scan is recorded. The cyclic voltammogram of copper(II) complex shows two cathodic and also two anodic peaks. The cathodic peak potentials are observed around -0.63, -1.76 V and the anodic peaks at around -0.57, -1.70 V respectively. This shows that the redox process is irreversible. These particulars shows the complex contain two metal ions. The cyclic voltammograms of macrocyclic Copper(II) complexes is shown in Figure 4.

Luminescence spectra

The luminescence property of macrocyclic complexes was standardized using 10^{-4} M solution of DMSO. The excitation spectrum of copper (II) complex shows peaks maxima at 370 nm and another peak maximum at 360 nm. The emission spectrum of copper complex shows peak maxima at 410, 440, 455 and 520 nm. The overall peak intensity was reasonably high. The excitation and emission spectra of Cu(II) complex is shown in Figure 5.

CONCLUSION

In this work, we reported the synthesis and struc-

tural Characterization of Schiff macrocyclic Cu(II) complex. The metal ions and act as tetra dentate chelate by coordinating through four nitrogen and two oxygen. The cyclic voltammograms of copper (II) complex shows two cathodic and also two anodic peaks This shows that the redox process is irreversible. These particulars shows the complex contain two metal ions. The overall peak intensity of copper complex was reasonably high.

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