



Synthesis, molecular modeling and spectroscopic characterization of nickel(II), copper(II), complexes of new 16-membered mixed-donor macrocyclic schiff base ligand incorporating a pendant alcohol function

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ABSTRACT

Complexes of Cu(II) and Ni(II) of the composition $[M(L)X]$ [where $M = Ni(II)$, $Cu(II)$ and $X = Cl^-$, NO_3^- , CH_3COO^-] were synthesized with 1,5-dioxo-9,10-diaza-3,ol-tribenzo-(7,6,10,11,14,15) peptadecane, a N_2O_2 macrocyclic ligand. The complexes were characterized by elemental analysis, molar conductance measurements, UV–vis, IR, 1H NMR, ^{13}C NMR, EPR and molecular modeling studies. All the complexes are non-electrolyte in nature. On the basis of spectral studies, an octahedral geometry has been assigned for Ni(II) complexes and a tetragonal geometry for Cu(II) complexes.

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1. Introduction

Interest in pendant armed macrocycles is growing on account of their unique coordination and structural properties [1]. Macrocyclic ligands containing a hetero atom are important complexing agents for neutral molecules [2–5]. There is an emerging interest in the synthesis of macrocyclic complexes of transition metals and their interesting properties [6]. The formation of macrocyclic complexes depends significantly on the dimension of internal cavity, rigidity of macrocycles, nature of its donor atoms and the complexing properties of the anion involved in coordination [7,8]. Due to their resemblance with natural proteins like hemerythrin enzymes, chemical properties of macrocyclic complexes have received much attention as an active part of metalloenzyme [9–11] as biomimic model compounds [12]. A considerable number of Schiff-base complexes have potential biological interest and are used as more or less successful models of biological compounds [13,14]. Additionally, some of the salicylidene derivatives show photochromism in the solid state [15,16]. It has been suggested that the azomethine linkage is responsible for the biological activities of Schiff bases such as antitumor, antibacterial, antifungal and herbicidal activities [17–20]. Moreover metal complexes of Schiff bases derived

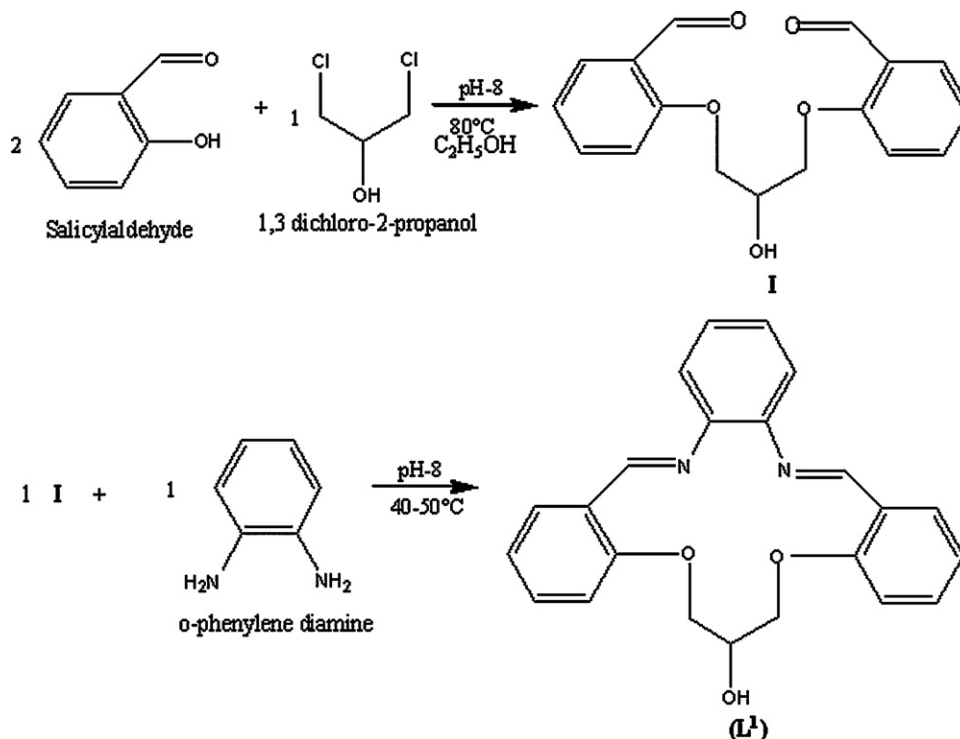
from salicylaldehyde and diamine can increase its dimensionality and can form supramolecular architectures through O–H...N and N–H...O type hydrogen bonds [21]. In this paper we report the synthesis of pentadentate Schiff base ligand, in order to investigate the coordination mode of ligand, complexes of nickel(II) and copper(II) were synthesized and characterized by UV–vis, IR, 1H NMR, ^{13}C NMR, EPR and molecular modeling studies.

2. Experimental

2.1. Chemicals and instruments

Solvents were dried and purified before being used according to published procedures [22]. Other reagents and solvents were purchased from Sigma–Aldrich and used as received. Elemental analysis of C, H and N were performed on a Carlo-Erba EA 1106 elemental analyzer. Molar conductance was evaluated on an ELICO Conductivity Bridge (Type CM82T). Magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as a callibrant. IR spectra were recorded on Perkin Elmer-137 instrument as KBr pallets. Electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrometer. 1H NMR and ^{13}C NMR (300 MHz) spectra were recorded on a Bruker Advanced DPX-300 spectrometer using $CDCl_3$ as a solvent. EPR spectra of all the complexes were recorded at room temperature (RT) and liquid nitrogen temperature (LNT) on an E4-EPR

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Scheme 1.

spectrometer using the DDPH as the g-marker. The complexes were modeled by MOPAC 2007 program in gas phase using level of theory.

2.2. Synthesis of ligand and complexes

2.2.1. Synthesis of 2-[3-(2-formyl phenoxy)-2-hydroxypropoxy] benzaldehyde (I)

2-[3-(2-Formyl phenoxy)-2-hydroxypropoxy] benzaldehyde was prepared by the method of Lindoy and Armstrong [23] with minor modification. Sodium hydroxide (8.0 g, 0.2 mol) in water (400 mL) was added to salicylaldehyde (20.98 mL, 0.2 mol) in ethanol (20 mL). The mixture was heated up to 60 °C and then 1,3 dichloro-2-propanol (9.54 mL, 0.1 mol) was added. In this mixture sufficient ethanol was added to produce a homogenous solution. The solution was refluxed for 70 h (pH ≈ 8) at 80 °C then cooled at 0 °C. The cream colored solid product was recrystallized in 2:1 ethanol–water. The resulting crystals were collected by filtration and dried in a vacuum desiccator over P₄O₁₀.

2.2.2. Synthesis of macrocyclic ligand (L¹)

To a hot ethanolic solution (20 mL) of 2-[3-(2-formyl phenoxy)-2-hydroxypropoxy] benzaldehyde (6 g, 0.02 mol), a hot solution of o-phenyldiamine (2.162 g, 0.02 mol) was added with constant stirring. The solution was heated at 40–50 °C (pH ≈ 8) for 5 h. On cooling at 0 °C, an orange colored product was precipitated out. It was filtered, washed several times with cold ethanol and dried over P₄O₁₀ (Scheme 1).

2.2.3. Synthesis of complexes

The complexes were synthesized by refluxing ethanolic solution (30 mL) of ligand (1 mmol) with an aqueous ethanolic solution (30 mL) of corresponding metal salt (1 mmol) for 8 h at 55 °C. On cooling overnight at 0 °C, the colored complex was precipitated out, which was filtered, washed with cold ethanol and dried under vacuum over P₄O₁₀ (Fig. 1).

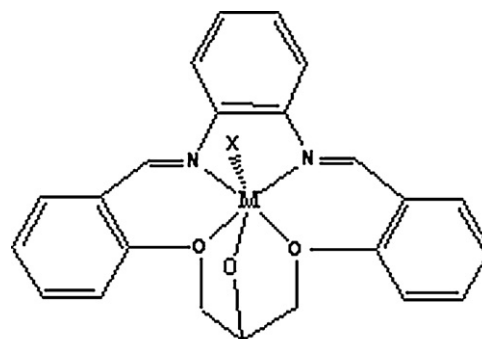
3. Result and discussion

On the basis of elemental analysis the complexes were assigned to possess the composition as shown in Table 1. The molar conductance data for Ni(II) and Cu(II) complexes revealed that these complexes behave as non-electrolytes [24]. Thus the general formula of the complexes may be given as [M(L)X] where M = Cu, Ni and X = Cl⁻, NO₃⁻, CH₃COO⁻.

3.1. IR spectra

In ligands (I) bands corresponding (OH) and C=O groups appeared at 3447 cm⁻¹ and 1636 cm⁻¹ and in ligand (L¹) bands corresponding to OH and C=N groups appeared at 3294 cm⁻¹ and 1612 cm⁻¹ respectively.

On complexation the absence of band corresponding to OH indicate the coordination of O with metal. A band corresponding to ν(C=N) shifts to the lower wave number (20–30 cm⁻¹)



Where M = Ni, Cu
X = Cl⁻, NO₃⁻, CH₃COO⁻

Fig. 1. Structure of the complexes.

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