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Lateral macrobicyclic compartmental mono and binuclear nickel(II) complexes derived from phenolate ligands: Synthesis, spectral, electrochemical and kinetic studies

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Abstract

A novel macrobicyclic ditopic ligand derived from the precursor compound 3,4:10,11-dibenzo-1,13[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)benzyl}diaza]-5,9-dioxocycloheptadecane has been synthesized in the presence of metal ion via template method. Various mono and binuclear nickel(II) complexes of type $[NiL](ClO_4)$ and $[Ni_2L](ClO_4)_2$ have been synthesized in order to examine electrochemical and kinetic studies on the basis of macrocyclic ring size. Cyclic voltammetry and controlled electrolysis studies indicate that the nickel(II) complexes undergo quasireversible one electron reduction and oxidation. All the nickel(II) complexes have square planar geometry and EPR silent. The examination of kinetics of the hydrolysis of 4-nitrophenyl phosphate vindicates that the catalytic activities of the complexes are found to increase with macrocyclic ring size of the complexes. As, the macrocyclic ring size of the complexes increases, the spectral, electrochemical and catalytic studies of the complexes show remarkable variation due to distortion in the geometry around nickel(II) centre.

Keywords: Compartmental ligands; Macrobicyclic nickel(II) complexes; Chronocoulometry; Cyclic voltammetry; Kinetics; Macrocyclic ring size

1. Introduction

The design and synthesis of macrocyclic unsymmetrical ligands and their complexes have garnered increasing attention over the past decade to their potentially unique propensities [1,2]. Synthetic macrocycles [3–5] have been and still are a rapidly growing class of compounds having different molecular topologies, different set of donor atoms and then a great variety of ligational properties toward protons, metal cation and anions. The investigation [6] of the heavy metal ion chemistry of mixed donor macrocycles has been concerned with the factors influencing metal ion recognition receiving special attention. The significant thermodynamic stability and kinetic inertness associated with macrocyclic complexes is well known and continues to be of interest [7–10] especially where variation of donors leads to selectivity of metal ions into the ligand cavity. Well-organized natural or synthetic molecular receptors are at the heart of supramolecular chemistry [11]. With the development of supramolecular chemistry, there has been an increasing demand to recognize various interactions as driving forces to an anticipated aggregation state of molecules building blocks via self assembly [12,13]. The facile variety of coordination configurations around metal atoms has offered much privilege for chemists to design and synthesize particular supramolecular systems with diverse architecture and dimensions for exploring new functional materials [14,15]. In their work Nag et al. [16–19], and Okawa et al. [20–25], have

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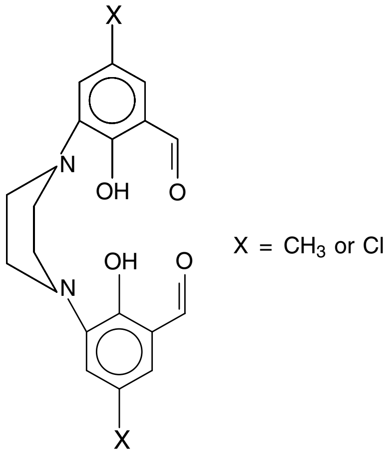
reported several macromonocyclic metal complexes, which are of interest for availing magneto-structural correlations and as useful model for electrochemical studies. Our previous works [26–30] report the magnetic and electrochemical properties of various acyclic and macromonocyclic copper(II), Mn(III) and Ni(II) complexes of the following type of ligand (**I**):



(**I**)

Our recent works [31–33] focused on synthesis and characterization of new macrobicyclic tricompartmental copper(II) complexes containing nitrogen and oxygen donor atoms. Herein we report the interesting chemistry (redox-driven translocation of reduced metal ion) observed in electrochemical studies of synthesized unsymmetrical tricompartmental macrobicyclic nickel(II) complexes and also their catalytic studies. The role of Ni(II) ion in promoting the hydrolysis of phosphate esters [34,35] has been the subject of considerable study and a great deal is now known. The mechanism of 4-nitrophenyl phosphate (NPP) hydrolysis involves the concerted binding of the substrate molecule on one metal centre and the nucleophilic attack of water or hydroxide ion at the other metal centre.

2. Experimental

Elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyzer. ^1H NMR spectra were recorded using FX-80-Q Fourier transition NMR spectrometer. Electronic spectral studies were carried out on a Hitachi 320 spectrophotometer in the range 200–800 nm. IR spectra were recorded on a Hitachi 270-50 spectrophotometer on KBr disks in the range 4000–250 cm^{-1}. The mass spectra were obtained on JEOL DX-303 mass spectrometer. The electrospray (ES) mass spectra of the complexes were obtained on a micromass Quatro II triple quadropole mass spectrometer. Molar conductivity was measured by using an Elico model SX 80 conductivity bridge using freshly prepared solution of the complex in CH_3CN. Cyclic Voltammograms were obtained on CHI600A (CHI Instruments Co., USA) electrochemical analyzer using DMF. The measurements were carried out under oxygen free condition by purging nitrogen gas, using a three electrode cell in which glassy carbon electrode was working electrode, saturated Ag/AgCl electrode was reference electrode and platinum wire was used as auxiliary electrode. Glassy carbon electrode surface was pretreated by metallographic polishing with alumina on a velvet cloth (abraded with fine grade of emery paper), followed by ultrasonic cleaning in double distilled water and washing with small amount of highly diluted acid and DMF. Two separate double step chronocoulometry experiments were carried out for the binuclear nickel(II) complexes in the first and second reduction/oxidation potential range under oxygen free condition. The plots have been corrected for background. Ferrocene/Ferrocenium (1+) couple was used as standard and $E_{1/2}$ of the Ferrocene/Ferrocenium (Fc/Fc^+) couple under the experimental condition is 470 mV in DMF and ΔE_p for Fc/Fc^+ is 70 mV. Tetra(*n*-butyl)ammonium perchlorate (TBAP) was used as supporting electrolyte. The kinetic investigation of hydrolysis of 4-nitrophenyl phosphate was carried out spectrophotometrically by choosing the strongest absorbance at 420 nm and monitoring the increase in the absorbance at this wavelength as a function of time. A plot of $\log(A_\infty/A_\infty - A_t)$ versus time was made for each complexes and the rate constant of hydrolysis of 4-nitrophenyl phosphate was calculated. All the kinetic studies were carried out in DMF solvent at room temperature (25 °C).

2.1. Materials

5-Methylsalicyladehyde [36], 3-chloromethyl-5-methylsalicylaldehyde [37] and 3,4:9,10-dibenzo-1,13-diaza-5,9-dioxacycloheptadecane [38,39] were prepared from the literature methods. TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystallised from hot methanol. [*Caution*! TBAP is potentially explosive; hence care should be taken in handling the compound.] DMF and CH_3CN were obtained from E. MERCK.

Methanol was sufficiently added to acetonitrile fractionated at high reflux until the boiling temperature rises from 60 to 80 °C and the distillate became optically clear. Sodium hydride was added and the mixture was refluxed for 15 min and then distilled rapidly.

DMF can be azeotropically distilled with benzene (10% v/v, previously dried over CaH_2) at atmospheric pressure; water and benzene distill at <80 °C. The liquid remaining in the distillation flask was dried further by adding $MgSO_4$. After the flask and its contents were shaken for 1 day, an additional amount of $MgSO_4$