

Synthesis and Characterization of Binuclear Ni(II)-azide Complex with 20-Membered Phenol-Based N₄O₂ Compartmental Macrocyclic Ligand

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Abstract

Binuclear Ni(II) complex, [Ni₂([20]-DCHDC)]Cl₂, with [2 + 2] symmetrical N₄O₂ compartmental macrocyclic ligand(H₂[20]-DCHDC;14,29-dimethyl-3,10,18,25-tetraazapentacyclo-[25,3,1,0^{4,9},1^{12,16},0^{19,24}]dtriacontane-2,10,12,14,16(32),17,27(31),28,30-decane-31,32-diol) containing bridging phenolic oxygen atoms was synthesized by metal template condensation of 2,6-diformyl-*p*-cresol, *trans*-1,2-diaminocyclohexane and nickel chloride hexahydrate. The reaction of [Ni₂([20]-DCHDC)] -Cl₂ with NaN₃ in methanol solution formed a new Ni(II)-azide complex, [Ni₂([20]-DCHDC)(N₃)₂]. The complexes have been elucidated by elemental analysis, molar conductance, FAB-mass, FT-IR, and electronic studies.

Key words : nickel complex, compartmental macrocyclic ligand

I. Introduction

Interest in exploring metal ion complexes with macrocyclic ligands has been continually increasing owing to the recognition of their role played by these structures in metalloproteins. Schiff base macrocycles have been of great importance in macrocyclic chemistry. They were among the first artificial metal macrocyclic complexes to be

synthesized. The metal complexes containing synthetic macrocyclic ligands have attracted a great deal of attention because they can be used as models for more intricate biological macrocyclic systems: metalloporphyrins (hemoglobin, myoglobin, cytochrome, chlorophyll), corrins (vitamin B₁₂) and antibiotics (valinomycin, nonactin). These discoveries have created supramolecular chemistry and its enormous

diversity¹⁻⁵.

Over the past decade, many studies have been focused upon metal complexes of cyclic triamines which cleaving carboxyester⁶, phosphoester⁷⁻¹¹, RNA^{12, 13}, DNA^{14, 15}, dipeptides and proteins¹⁶. To our knowledge, few papers published for the cytotoxic properties and the *in vivo* antitumor effects of triazacyclic polyamines metal complexes^{17, 18}.

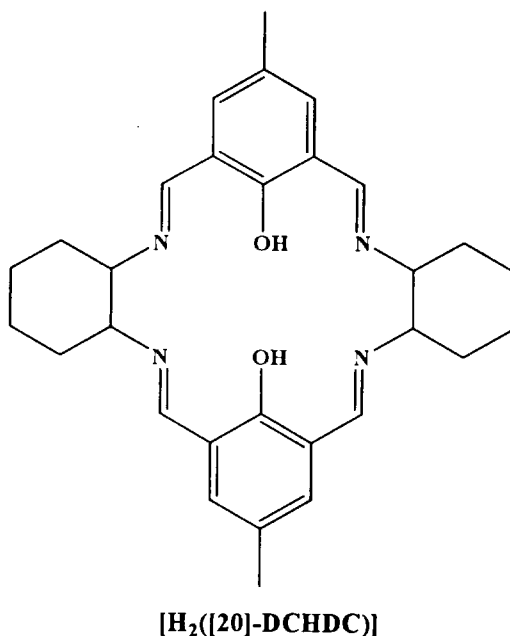
Ni(II) complexes with polyamine ligands containing binding units suited for the coordination of a single metal ion or for the dinuclear centers have proved very useful. The structure of these synthetic dioxygen carriers, the kinetics and thermo-dynamics of their formation is affected by the nature of the ligand. The use of polynucleating ligands represents an evolution in synthetic Ni(II) dioxygen carriers. These ligands contain sufficient number of oxygen and nitrogen donor atoms to coordinate more than one Ni(II) ion and can act as biomimetic models of natural non-heme types carriers, such as hemerythrin and hemocyanin¹⁹.

The Schiff base macrocyclic complexes, which form neutral or cationic complexes with the metal of interest, fulfill these requirements, because they are extremely rigid and display kinetic inertness towards metal release, whereas exocyclic ligands are labile and easy to change.

Macrocyclic Schiff bases have been widely studied because they can selectively

chelate certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of the metal center, and coordinating properties of counter ions²⁰.

This work performs synthesis, physicochemical and characterization of dinuclear Ni(II) complexes, with [2+2] symmetrical N₄O₂ compartmental macrocyclic ligand {H₂[20]-DCHDC; 14, 29-dimethyl-3,10,18,25-tetraazapentacyclo-[25,3,1,0^{4,9},1^{12,16},0^{19,24}] ditriacontane-2,10,12,14,16(32),17,27(31),28,30-decane-31,32-diol} containing bridging phenolic oxygen atoms was synthesized by condensation, in the metal ions, of 2,6-diformyl-*p*-cresol and *trans*-1,2-diaminocyclohexane.(Scheme 1)



Scheme 1. Synthesis of phenol-based macrocyclic ligand (H₂[20]-DCHDC).

II. Experimental

1. Chemicals and Physical Measurements

All chemicals were commercial analytical reagents and were used without further purification. For the spectroscopic and physical measurements, organic solvents were dried and purified according to the literature methods. Nanopure quality water was used throughout this work. Microanalyses of C, H, and N was carried out using LECO CHN-900 analyzer. Conductance measurement of the complex was performed at 25±1 °C using an ORION 162 conductivity temperature meter. IR spectrum was recorded with a Bruker FSS66 FT-IR spectrometer in the range 4000–370 cm⁻¹ using KBr pellets. Electronic absorption spectrum was measured at 25 °C on a UV-3150 UV-VIS-NIR Spectrophotometer (SHIMADZU). FAB-mass spectrum was obtained on a JEOL JMS-700 Mass Spectrometer using argon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and glycerol was used as the matrix. The mass spectrometer was operated in positive ion mode and mass spectrum was calibrated by Alkali-CsI positive.

2. Preparations of Nickel(II) complexes

The synthesis of 2,6-diformyl-*p*-cresol was prepared according to the literature methods previously reported^{21,22}.

1) Preparation of the [Ni₂([20]-DCHDC)] Cl₂

The synthesis of [Ni₂([20]-DCHDC)]Cl₂ was prepared according to the literature methods previously reported²³.

2) Preparation of the [Ni₂([20]-DCHDC) (N₃)₂]

A solution of [Ni₂([20]-DCHDC)]Cl₂ (0.670 g) in methanol (150 mL) was added dropwise of sodium azide (0.6501 g) with stirring and the mixture was refluxed for 6 h. The resulting dark brown precipitate were filtered, thoroughly washed twice with cold methanol, and dried under vacuum. % Yield : 0.3826 g (55.9 %) Anal. Calc.(Found) % for Ni₂(C₃₀H₃₄N₄O₂)(N₃)₂ C, 52.68(52.23) ; H, 5.01(5.00) ; N, 20.48(19.91) λ_M (DMSO) : 40.1 ohm⁻¹ cm² mol⁻¹

III. Results

1. IR spectra of the Nickel(II) complexes

The strong and sharp absorption bands occurring at 1620–1652 cm⁻¹ are attributed to ν(C=N) of the coordinated [20]-DCHDC ligand^{24,25}, and the absence of any carbonyl bands associated with the diformylphenol starting materials or nonmacrocyclic intermediates. The IR spectra displayed three C-H stretching vibrations from 3000 to 2800 cm⁻¹. A strong bands at near ~1550 cm⁻¹ region associated with the aromatic

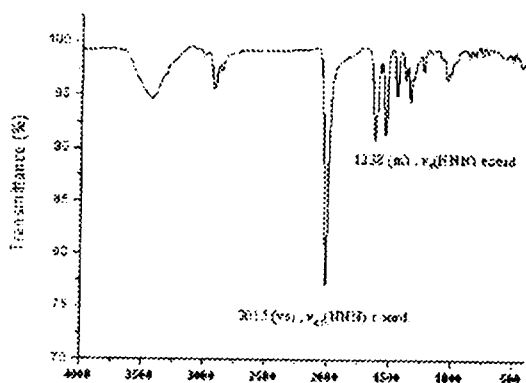


Figure 1. FT-IR spectra of $[\text{Ni}_2([\text{20}]\text{-DCHDC})(\text{N}_3)_2]$.

ring C=C vibrations. The sharp absorption bands occurring at $\sim 1230 \text{ cm}^{-1}$ regions are attributed to phenolic C-O stretching vibration. The present complexes exhibited four C-H deformation bands at 1450, 1380, 1350 and 1320 cm^{-1} regions and three out-of-plan vibration bands at 860, 820 and 770 cm^{-1} regions. In general, for azides the band due to the asymmetric N_3 stretching vibration is strong and occurs in the region 2015 cm^{-1} , while that due to the symmetric vibration is much weaker and occurs in the

region $1379\text{--}1238 \text{ cm}^{-1}$ and the band due to the deformation vibration is also weak and occurs at $680\text{--}410 \text{ cm}^{-1}$.²⁶ The absorption peak at 2015 cm^{-1} in the $[\text{Ni}_2([\text{20}]\text{-DCHDC})(\text{N}_3)_2]$ is assigned to the asymmetric stretching mode of coordinated azide. The symmetric stretching frequency of coordinated azide is observed at 1346 cm^{-1} .

2. FAB-mass spectra of the Nickel(II) complexes

Removal peaks of one nickel ion from the $[\text{Ni}_2([\text{20}]\text{-DCHDC})]^+$ ion in the formation of the fragment $[\text{Ni}([\text{20}]\text{-DCHDC})]^+$ is observed at m/z 540. The FAB mass spectra of the complexes contain peaks corresponding to the $[(\text{H}_2[\text{20}]\text{-DCHDC})]^+$ fragment ion at m/z 484 region. This indicates that the species $[\text{Ni}_2([\text{20}]\text{-DCHDC})]^+$ undergoes demetallation to give the tetraazadioxa macrocycle $\text{H}_2[\text{20}]\text{-DCHDC}$ under FAB conditions. These peaks are associated with peaks of

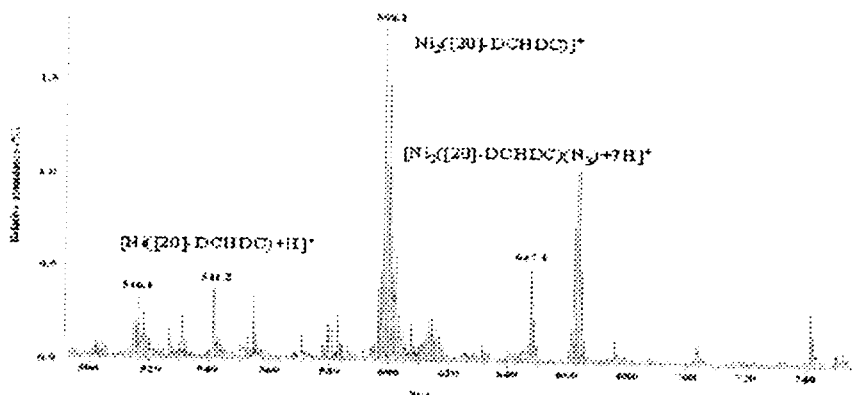


Figure 2. FAB mass spectrum of the $[\text{Ni}_2([\text{20}]\text{-DCHDC})(\text{N}_3)_2]$

mass one or two greater or less, which are attributed to protonated /deprotonated forms. Removal peaks of one exocyclic ligand resulting in the formation of the fragment $[Ni_2([20]-DCHDC)(L_a)]^+$ ($L_a = Cl^-, N_3^-$) are observed at m/z 635.1 and 647.4 respectively.

3. Electronic absorption spectrum of Ni(II) complexes

The electronic absorption spectra of Ni(II) complexes at room temperature were represented in Figure 3. Much weaker bands are found at lower energy, associated with $d-d$ transitions. However, strong absorptions at 300–450 nm are clearly associated with ligand to metal charge transfer transitions, which reflect the presence of highly delocalized π macrocyclic framework.

Complex	medium	$\lambda_{max}(\epsilon)$	medium	λ_{max}
$[Ni_2([20]-DCHDC)(N_3)_2]$	DMSO	389 (14181)	solid	463, 546sh

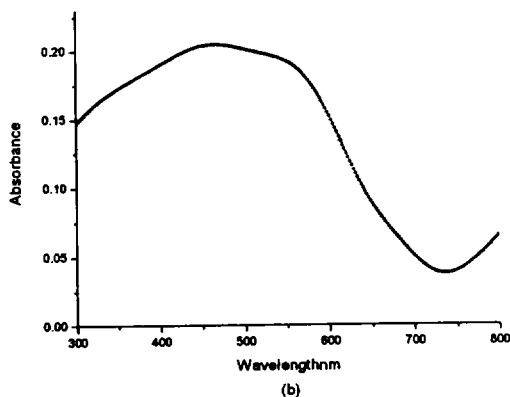
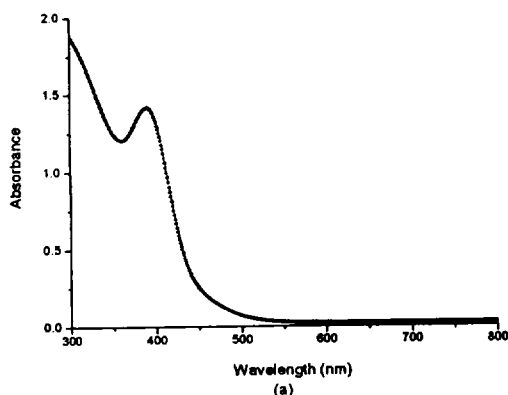


Figure 3. Electronic absorption spectrum of $[Ni_2([20]-DCHDC)(N_3)_2]$ in (a) DMSO (1.0×10^{-4} M) and (b) solid ($BaSO_4$).

IV. Discussion

Binuclear Ni(II) complex, $[Ni_2([20]-DCHDC)]Cl_2$, with [2 + 2] symmetrical N_4O_2 compartmental macrocyclic ligand containing bridging phenolic oxygen atoms was synthesized by metal template condensation of 2,6-diformyl-*p*-cresol, *trans*-1,2-diaminocyclohexane and Nickel chloride hexa-hydrate. The reaction of $[Ni_2([20]-DCHDC)]Cl_2$ with NaN_3 in methanol solution formed a new Ni(II)-azide complex, $[Ni_2([20]-DCHDC)(N_3)_2]$.

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