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Synthesis and Characterization of Binuclear Ni(II)-Isothiocyanato Complex with 20-Membered Phenol-Based N_4O_2 Compartmental Macrocyclic Ligand

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Abstract. Binuclear Ni(II) complex, [Ni_2([20]-DCHDC)]Cl_2, with [2 + 2] symmetrical N_4O_2 compartmental macrocyclic ligand {H_2[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 metal template condensation of 2,6-diformyl-*p*-cresol, *trans*-1,2-diaminocyclohexane and nickel chloride hexahydrate. The reaction of [Ni_2([20]-DCHDC)]Cl_2 with NaSCN in methanol solution formed a new Ni(II)-isothiocyanato complex, [Ni_2([20]-DCHDC)$(NCS)_2$]. The complexes have been elucidated by elemental analysis, molar conductance, FAB-mass, FT-IR, and electronic studies.

Key words : nickel complex, compartmetal 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 metalloproteines. 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 diversity.[1-5]

Over the past decade, many studies have been focused upon metal complexes of cyclic triamines which cleaving carboxyester6, phosphoeaster,[7-11] RNA,[12,13] DNA,[14,15] dipeptides and proteins.[16] 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 hemocyanin.[19]

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 ions.[20]

This work performs synthesis, physicochemical and characterization of dinuclear Ni(II) complexes, with [2+2] symmetrical N_4O_2 compartmental macrocyclic ligand {H_2[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.

II. Experimental

1. Chemicals and Physical Measurements

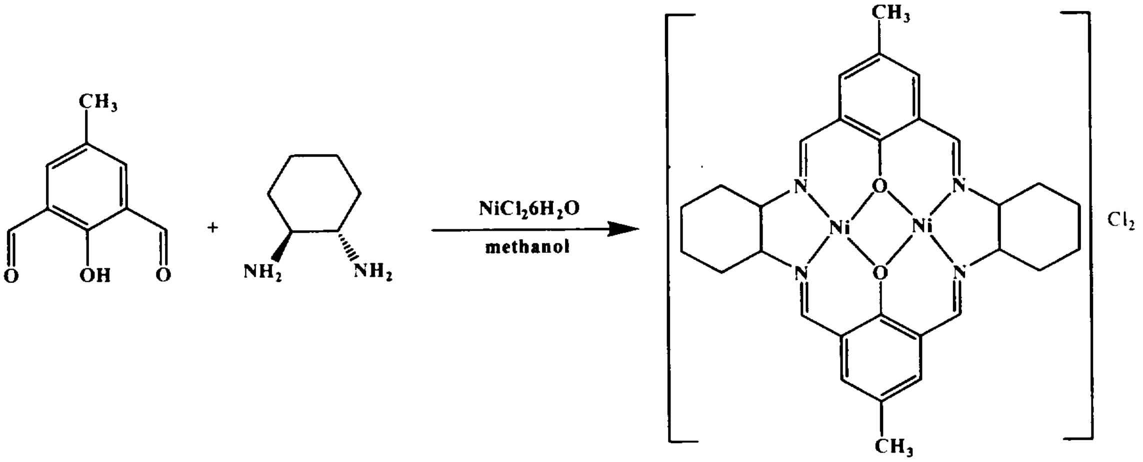
All chemicals were commercial analytical reagents and were used without further purification. For the spectroscopic and physical measurements, organic solvents were dried and purified according to the literature methods. Nanopure quality water was used throughout this work. Microanalyses of C, H, and N was carried out using LECO CHN-900 analyzer. Conductance measurement of the complex was performed at 25±1℃ 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℃ on a UV-3150 UV- VIS-NIR Spectrophotometer (SHIMADZU). FAB-mass spectrum was obtained on a JEOL JMS-700 Mass Spectrometer using argon (6kV, 10mA) 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 [Ni_2([20]-DCHDC)]Cl_2

Nickel chloride hexahydrate (9.50 g), 2,6-diformyl-*p*-cresol (4.92 g), and *trans*-1,2-diaminocyclohexane (3.42 g) in methanol (200mL) were refluxed for 1day. The solution was concentrated under rota evaporation to approximate 50 mL and then it was on standing overnight at room temperature. The resulting dark brown precipitate was filtered, thoroughly washed twice with methanol, dried under vacuum over anhydrouse calcium chloride. Yield : 4.4151 g (43.9%) Anal. Calc.(Found)% for $Ni_2(C_{30}H_{34}N_4O_2)Cl_2$ C, 53.71(54.05) ; H, 5.11(5.01) ; N, 8.35(8.51) λ_M (MeOH) : 169.3 $ohm^{-1}cm^2mol^{-1}$.



Scheme 1. Synthesis of the mononuclear nickel Ni(II) complexes of phenol-based macrocyclic ligand ([20]-DCHDC).

2) Preparation of the [Ni_2([20]-DCHDC)$(NCS)_2$]

A solution of [Ni_2([20]-DCHDC)]Cl_2 (0.670 g) in methanol (150 mL) was added dropwise of sodium thiocyanide (0.8107 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 : 0.6101g (85.2%) Anal. Calc. (Found) % for $Ni_2(C_{30}H_{34}N_4O_2)$ -$(NCS)_2$ C, 53.67(54.53); H, 4.79(5.05); N, 11.73(11.86) λ_M (DMSO) : 65.4 $ohm^{-1}cm^2mol^{-1}$

III. Results

1. IR spectra of the Nickel(II) complexes

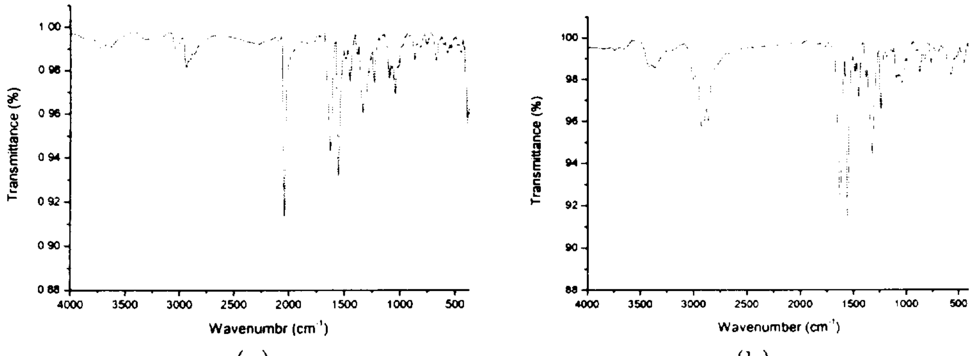
The strong and sharp absorption bands occurring at 1620~1652 cm^{-1} are attributed to ν(C=N) of the coordinated [20]-DCHDC ligand.[23,24] and the absence of any carbonyl bands associated with the diformylphenol starting materials or nonmarcrocyclic intermediates. The IR spectra displayed three C-H stretching vibrations from 3000 to 2800 cm^{-1}. A strong bands at near ~1550 cm^{-1} region associated with the aromatic ring C=C vibrations. The sharp absorption bands occurring at ~1230 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. The thiocyanate ion may act as an ambidentate ligand, bonding may occur either through the nitrogen or the sulphur atom. The bonding mode may easily be distinguished by examining the band due to the C-S stretching vibration which occurs at 730-690 cm^{-1} when the bonding occurs through the sulphur atom and at 860-780 cm^{-1} when it is through the nitrogen atom.[25] The C≡N stretching vibration of thiocyanato-complex Ga-NCS (i.e. nitrogen bound), the resulting band is strong and occurs in the region 2044 cm^{-1}. The absorption vibrations due to the N-coordinated bonded NCS^- in $[Ni_2([20]$-$DCHDC)(NCS)_2]$ appear 2044 and 871 cm^{-1}.

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

Removal peaks of one nickel ion from the $[Ni_2([20]$-$DCHDC)]^+$ ion in the formation of the fragment $[Ni([20]$-$DCHDC)]^+$ is observed at m/z 540. The FAB mass spectra of the complexes contain peaks corresponding to the $[(H_2[20]$-$DCHDC)]^+$ fragment ion at m/z 484 region. This indicates that the species $[Ni_2([20]$-$DCHDC)]^+$ undergoes demetallation to give the tetraazadioxa macrocycle $H_2[20]$-DCHDC under FAB conditions. These peaks are associated with peaks of 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^-, NCS^-) are observed at m/z 635.1 and 662.4 respectively.

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 NaSCN in methanol solution formed a new Ni(II)-isothiocyanato complex, $[Ni_2([20]$-$DCHDC)(NCS)_2]$.



(a) (b)

Figure 1. FT-IR spectra of (a) $[Ni_2([20]$-$DCHDC)]Cl_2$ and (b) $Ni_2([20]$-$DCHDC)(NCS)_2]$.

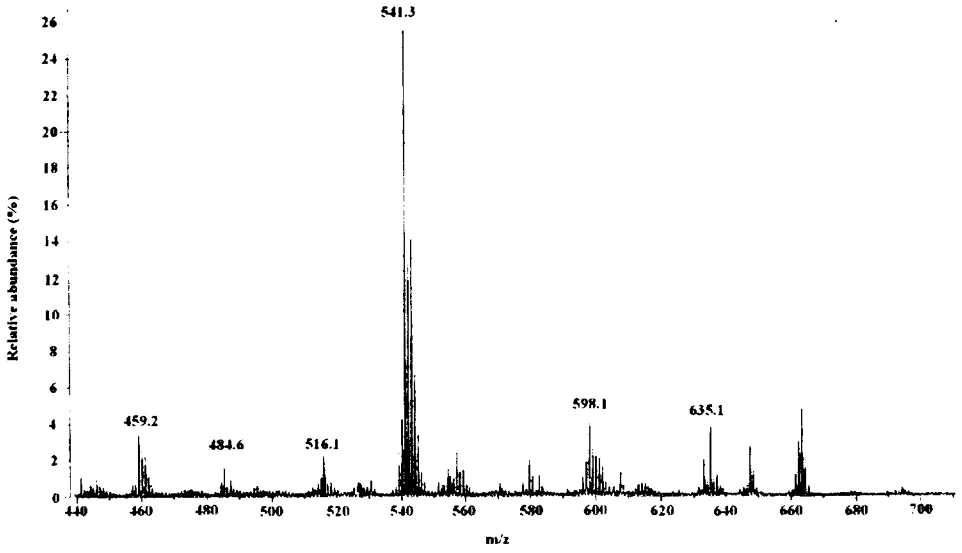
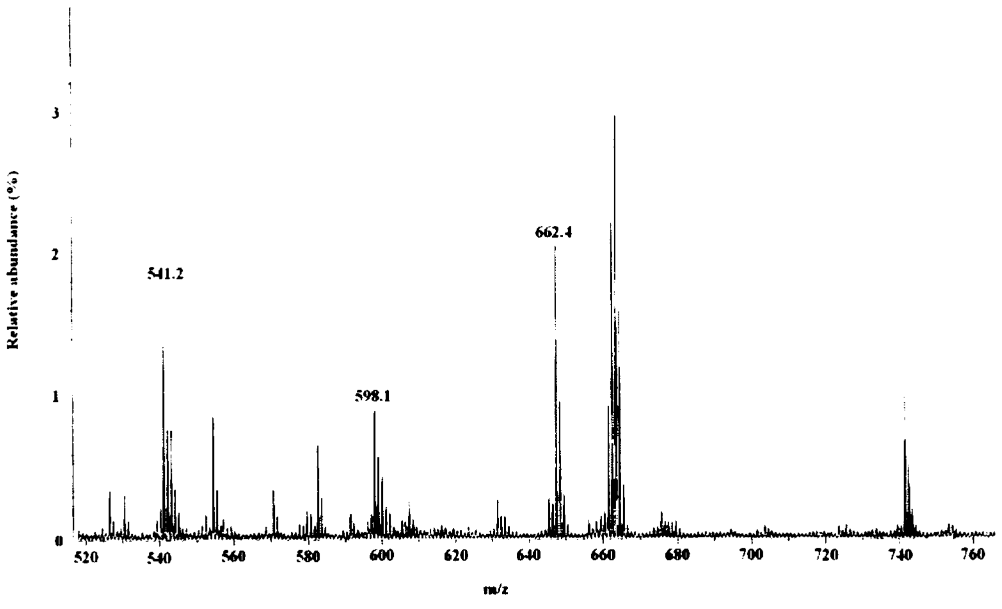


Figure 2. FAB mass spectrum of the $[Ni_2([20]\text{-DCHDC})]Cl_2$



m

a

ss **Figure 3**. FAB spectrum of the $[Ni_2([20]\text{-DCHDC})(NCS)_2]$

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