

Synthesis and Characterization of Dinuclear Ni(II) Complexes with Tetraazadiphenol Macrocycle Bearing Cyclohexanes

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The dinuclear tetraazadiphenol macrocyclic nickel(II) complexes $[\text{Ni}_2(\text{[20]-DCHDC})\text{Cl}_2]$ (**I**), $[\text{Ni}_2(\text{[20]-DCHDC})(\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}]$ (**II(b)**) and $[\text{Ni}_2(\text{[20]-DCHDC})(\text{NCS})_2]$ (**III**) ($\text{[20]-DCHDC} = 14,29\text{-dimethyl-}3,10,18,25\text{-tetraazapentacyclo-[}25,3,1,0^{4,9},1^{12,16},0^{19,24}\text{]dtriacontane-}2,10,12,14,16(32),17,27(31),28,30\text{-decane-}31,32\text{-diol}$) have been synthesized by self-assembly and characterized by elemental analyses, conductances, FT-IR and FAB-MS spectra, and single crystal X-ray diffraction. The crystal structure of **II(b)** is determined. It crystallizes in the monoclinic space group $P2(1)/c$. The coordination geometries around Ni(II) ions in **I** and **II(b)** are identical and square planes. In complex **III** each Ni(II) ion is coordinated to N_2O_2 plane from the macrocycle and N atoms of NCS⁻ ions occupying the axial positions, forming a square pyramidal geometry. The nonbonded Ni...Ni intermetallic separation in the complex **II(b)** is 2.8078(10) Å. The FAB mass spectra of **I**, **II** and **III** display major fragments at m/z 635.1, 699.4 and 662.4 corresponding to $[\text{Ni}_2(\text{[20]-DCHDC})(\text{Cl} + 2\text{II})]^+$, $[\text{Ni}_2(\text{[20]-DCHDC})(\text{ClO}_4 + 2\text{II})]^+$ and $[\text{Ni}_2(\text{[20]-DCHDC})(\text{NCS}) + 6\text{II}]^+$, respectively.

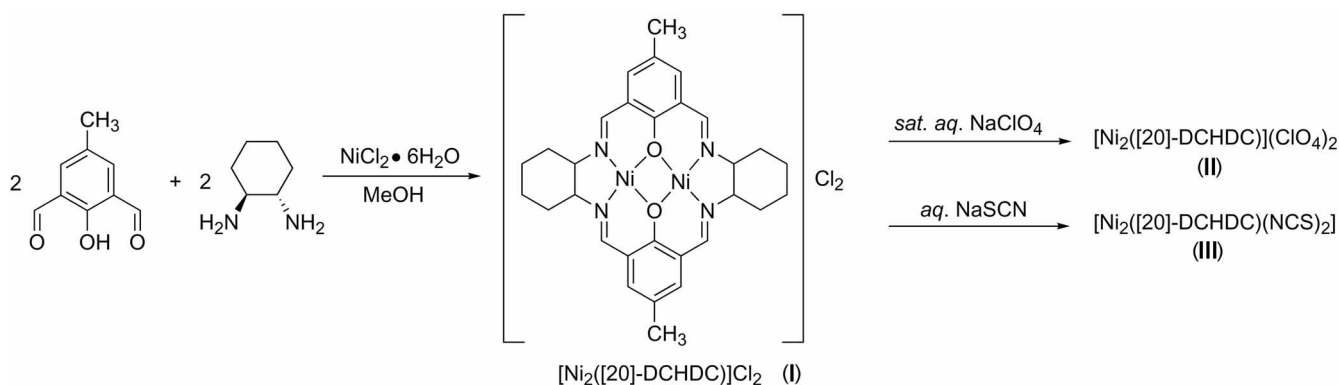
Key Words : Tetraazadiphenolic macrocycle, Macrocyclic nickel(II) complex, Crystal structure, Isothiocyanato ligand

Introduction

The tetraazadiphenol macrocycles, synthesized by the cyclocondensation between 2,6-diformyl-*p*-cresol (DFPC) and alkylenediamine, are known to exhibit an exceptionally high affinity for transition metal ions.¹⁻⁵ When the chiral precursor trans-(Δ)-1,2-diaminocyclohexane is used in these template reaction, chiral dinuclear nickel(II) complexes $[\text{Ni}_2(\text{[20]-DCHDC})(\text{ClO}_4)_2]$ ($\text{H}_2\text{[20]-DCHDC} = \text{L}_{m_2} = 14,29\text{-dimethyl-}3,10,18,25\text{-tetraazapentacyclo-[}25,3,1,0^{4,9},1^{12,16},0^{19,24}\text{]dtriacontane-}2,10,12,14,16(32),17,27(31),28,30\text{-decane-}31,32\text{-diol}$; Scheme 1) are formed. Korupoju *et al.*⁶ reported the synthesis of [2 + 2] dinuclear macrocyclic complexes resulting from cleavage and reorganization of the

[3 + 3] macrocyclic ligand during complexation.

Symmetric [2 + 2] tetraazadiphenolic macrocycles which incorporate chiral precursor 1,2-diaminocyclohexane rings in the lateral and/or head units would exhibit moderate flexibility and are the subject of wide interest owing to their application in processes, such as ion sequestration,⁷ catalysis⁸ and for biomedical uses.⁹ In particular, the transition metal complexes in a chiral macrocyclic environment are have been applied as stereoselective catalysts in reactions such as alkene epoxidation,¹⁰ epoxide carboxylation,¹¹ intramolecular reductive cyclization,¹² electrochemical annulation,¹³ and oxidation of hydrocarbons.¹⁴ All of these processes can potentially generate stereogenic centers, thus the chiral macrocycles, which can induce chirality, are of



Scheme 1. Synthetic route of the dinuclear tetraazadiphenol macrocyclic nickel(II) complexes **I**, **II(a)** and **III**.

great interest.

In the light of above discussion, we describe herein the preparation and physicochemical characterizations of the 20-membered Schiff base tetraazadiphenol macrocyclic nickel(II) complexes $[\text{Ni}_2([\text{20-DCHDC}]\text{Cl}_2)]$ (**I**), $[\text{Ni}_2([\text{20-DCHDC}])\text{(ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$ (**II(a)**) and $[\text{Ni}_2([\text{20-DCHDC}])\text{(NCS)}_2]$ (**III**) based on chiral diamine skeletons. Furthermore, crystal structure of the complex $[\text{Ni}_2([\text{20-DCHDC}])\text{(ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}]$ (**II(b)**) is determined.

Experimental Section

General methods. All chemicals were commercial analytical reagents and were used without further purification. Solvents used for electrochemical and spectroscopic studies were purified by standard procedures. DFPC was prepared with high yields by an improved oxidation method using active manganese(IV) dioxide.¹⁵

Microanalyses of C, H, and N were carried out using LECO CHN-900 analyzer. Conductance measurements of the complexes were performed in CH_3OH or DMSO at 25 ± 1 °C using an ORION 162 conductivity temperature meter. IR spectra were recorded with a Bruker FSS66 FT-IR spectrometer. FAB-MS spectra were 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 spectra were calibrated by Alkali-CsI positive.

Synthesis of $[\text{Ni}_2([\text{20-DCHDC}]\text{Cl}_2)]$ (I**).** $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (9.50 g, 40 mmol), 2,6-diformyl-*p*-cresol (4.92 g, 30 mmol), and *trans*-1,2-diaminocyclohexane (3.42 g, 30 mmol) were refluxed for 1 day in methanol (200 mL). The solution was concentrated under vacuum to approximate 50 mL and then it was on standing overnight at room temperature. The resulting dark brown precipitates were filtered, thoroughly washed with methanol, dried *in vacuo* over anhydrous calcium chloride. Yield: 43.9%. Anal. Calcd (Found) % for $\text{Ni}_2(\text{C}_{30}\text{H}_{34}\text{N}_4\text{O}_2)(\text{Cl})_2$: C, 53.71 (54.05); H, 5.11 (5.01); N, 8.35 (8.51). $\lambda_{\text{M}}(\text{CH}_3\text{OH})$: $169.3 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

Synthesis of $[\text{Ni}_2([\text{20-DCHDC}])\text{(ClO}_4)_2 \cdot 2\text{H}_2\text{O}]$ (II(a)**).** To a methanolic solution (150 mL) of $[\text{Ni}_2([\text{20-DCHDC}])\text{Cl}_2]$ (**I**) (0.670 g), a saturated aqueous NaClO_4 solution (4 mL) was added dropwise with stirring, and the mixture was refluxed for 6 h. The resulting solution was allowed to stand in a room temperature until orange precipitates formed. The precipitate was collected by filtration, thoroughly washed with methanol, and dried *in vacuo*. Yield: 67.4%. Anal. Calcd (Found) % for $\text{Ni}_2(\text{C}_{30}\text{H}_{34}\text{N}_4\text{O}_2)(\text{ClO}_4)_2$: C, 45.10 (44.83); H, 4.29 (4.30); N, 7.01 (7.04). $\lambda_{\text{M}}(\text{CH}_3\text{OH})$: $311 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

Synthesis of $[\text{Ni}_2([\text{20-DCHDC}])\text{(NCS)}_2]$ (III**).** This complex was obtained as dark brown precipitates in a way similar to that for **II(a)** using NaSCN (0.8107 g) instead of NaClO_4 . Yield: 0.6101 g (85.2%). Anal. Calcd (Found) (%) for $\text{Ni}_2(\text{C}_{30}\text{H}_{34}\text{N}_4\text{O}_2)(\text{NCS})_2$: C, 53.67 (54.53); H, 4.79 (5.05); N, 11.73 (11.86). $\lambda_{\text{M}}(\text{DMSO})$: $65.4 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

X-ray crystallography of complex. Crystal of $[\text{Ni}_2([\text{20-DCHDC}])\text{(ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}]$ (**II(b)**) suitable for X-ray diffraction study were obtained by slow evaporation of a acetonitrile solution for **II(a)**. The orange crystal of complex was attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with a graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) radiation. Crystal structure was solved by the direct methods¹⁶ and refined by full-matrix least-squares method by using the SHELXL program of the SHELXTL package,¹⁷ with 3834 of 10649 unique reflections measured. The intensity data were corrected for Lorentz and polarization effects during data reduction. All non-hydrogens atoms of the nickel(II) complex were refined on F^2 by the full matrix least-squares procedure using anisotropic displacement parameters. Hydrogen atoms were generated geometrically, assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached [$U_{\text{iso}} = 1.2U_{\text{eq}}$ (parent atom)] and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for complex **II(b)** is listed in Table 1.

Results and Discussion

Synthetic consideration. Korupoju *et al.*⁶ reported a yellow trinucleating [3 + 3] Schiff base macrocycle $\text{L}_{\text{m}3}$ from the condensation of DFPC and *trans*-1,2-diaminocyclohexane. Also dinuclear Ni(II) complex $[\text{Ni}_2\text{L}_{\text{m}2}](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$ **IV** by reaction of trinucleating macrocyclic ligand $\text{L}_{\text{m}3}$ and a mixture of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in methanol been obtained and characterized by several techniques, including X-ray

Table 1. Crystallographic data and structure refinement for complex **II(b)**

Empirical formula (M)	$\text{C}_{34}\text{H}_{40}\text{Cl}_2\text{N}_6\text{Ni}_2\text{O}_{10}$ (881.04)
Temperature	173(2) K
Crystal system / Space group	Monoclinic / $P2(1)/c$
Unit cell dimensions (Å)	$a = 9.2745(5)$, $b = 18.9687(10)$ $c = 11.0198(6)$
Volume (Å ³)	1880.06(17)
Z / D_{calc} (g cm ⁻³)	2 / 1.556
Absorption coefficient (mm ⁻¹)	1.208
$F(000)$	912
Crystal size (mm ³)	$0.40 \times 0.30 \times 0.30$
θ range (°)	2.15 to 26.37°
Index ranges	$-11 \leq h \leq 9$, $-23 \leq k \leq 21$, $-13 \leq l \leq 13$
Reflections collected / Unique	3834 / 10649 [$R(\text{int}) = 0.0392$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3834 / 0 / 245
Goodness-of-fit on F^2	1.071
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0580$, $wR_2 = 0.1507$
R indices (all data)	$R_1 = 0.0743$, $wR_2 = 0.1622$

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

diffraction. In the Korupoju's complex the nickel(II) ions lie in the plane of the N_2O_2 compartment and the cyclohexane rings are in chair conformation. And complex **IV** has two uncoordinated perchlorate anions, one methanol and an acetonitrile molecule in the crystal lattice. In contrast to the method of Korupoju *et al.*, dinuclear macrocyclic complexes obtained in this work are easily prepared by metal template condensation of suitable amines and formyl precursors. The macrocyclic mono- and polynuclear systems of the auxiliary ligands like thiocyanate or azide have been well established with strong covalent bonds. In addition, the geometry and coordination mode of NCS^- in transition metal complexes is strongly influenced by the electronic and steric effects around central atom.¹⁸ In the tetraazadiphenol macrocyclic nickel(II) complexes the Ni^{2+} ion is coordinated to isothiocyanato ligand, but the Ni^{2+} ion is uncoordinated to chloride and perchlorate anions, which suggests that interactions between the Ni^{2+} cations and NCS^- anions are strong. The NCS^- anion is thus a good competitor for Ni^{2+} cation and might also be able to form complexes with higher NCS^- to Ni^{2+} ratios.

Description of crystal structure. The ORTEP structure and labeling scheme for a dinuclear Ni(II) complex **II(b)** is depicted in Figure 1. The crystal consists of monomeric units and crystallizes in the monoclinic space group $P2(1)/c$. The molecular structure of complex **II(b)** is comprised of a centrosymmetric dinuclear cation $[Ni_2([20]-DCHDC)]^+$, two ClO_4^- counter ions and acetonitrile molecules; ClO_4^- ions and acetonitrile molecules are free from coordination and captured in the crystal lattice. The selected bond lengths and angles relevant to the nickel(II) coordination spheres are summarized in Table 2.

Complex **II(b)** adopts an essentially flat structure with the square planar nickel (II) centers similar to $[Cu_2L_m(H_2O)_2]-$

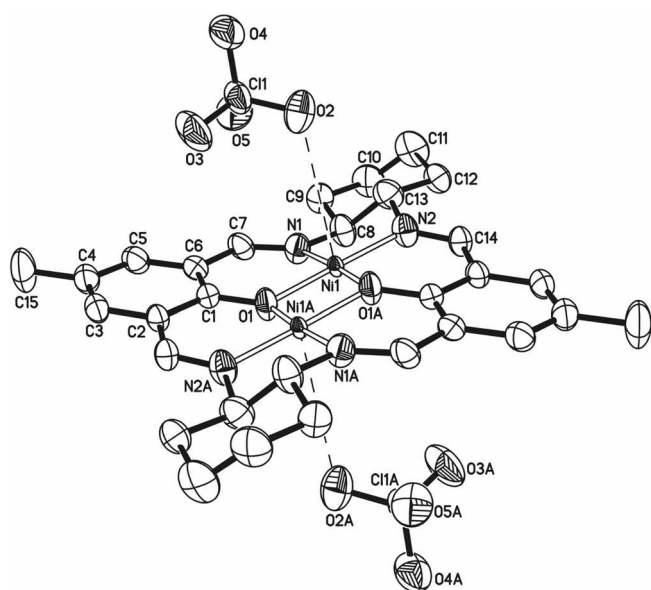


Figure 1. ORTEP view of core structure (top view) and atom labeling scheme for **II(b)** showing 50% probability thermal ellipsoids.

Table 2. Selected bond lengths (Å) and angles (°) for complex **II(b)**

Ni(1)-N(1)	1.827(3)	Ni(1)-O(1)	1.842(3)
Ni(1)-N(2)	1.828(3)	O(1)-Ni(1) ^{#2}	1.841(3)
Ni(1)-O(1) ^{#2}	1.841(3)	Ni(1)-Ni(1) ^{#2}	2.8078(10)
N(1)-Ni(1)-N(2)	89.09(15)	N(2)-Ni(1)-Ni(1) ^{#2}	135.61(11)
N(1)-Ni(1)-O(1) ^{#2}	174.76(14)	O(1) ^{#2} -Ni(1)-Ni(1) ^{#2}	40.33(8)
N(2)-Ni(1)-O(1) ^{#2}	95.30(14)	O(1)-Ni(1)-Ni(1) ^{#2}	40.31(9)
N(1)-Ni(1)-O(1)	95.03(14)	C(1)-O(1)-Ni(1) ^{#2}	128.8(3)
N(2)-Ni(1)-O(1)	175.76(14)	C(1)-O(1)-Ni(1)	129.2(3)
O(1) ^{#2} -Ni(1)-O(1)	80.64(13)	Ni(1) ^{#2} -O(1)-Ni(1)	99.36(13)
N(1)-Ni(1)-Ni(1) ^{#2}	135.27(11)		

Symmetry transformations used to generate equivalent atoms: ^{#1} -x, -y, -z+1, ^{#2} -x, -y+1, -z+1

(ClO_4)₂ (L_m = phenol-based macrocyclic compartmental ligand) and so forth.¹⁹ The coordination environment of complex **II(b)** is attributed to selectivity, inertia, high thermodynamic stability and structural rigidity of nickel(II) complex due to diaminocyclohexane rings in the lateral units of the macrocycle. In the crystal structure of **II(b)**, the two square planar nickel(II) centers are separated by 2.808(1) Å and bridged by the two phenoxide oxygen atoms with Ni-O-Ni bridge angles of 99.36(13)°, both of which are identical. The Ni-to-donor bond lengths range from 1.827(3) to 1.842(3) Å. These values are nearly similar to those reported by Korupoju's group. Such short bond lengths are characteristic of low-spin Ni(II). The Ni-O(1)A and Ni-O(1) bond lengths are long relative to the Ni-N(1) and Ni-N(2) bond lengths. The bond angles of O-Ni-O {80.64(13)°} and N-Ni-N {89.09(15)°} are smaller than 90°. The sum of the angles at the nickel basal plane (NiN_2O_2) is almost exactly 360°, indicating no planar distortion. The dihedral angle between the least-squares plane defined by N(1), O(1) and O(1)A and the plane defined by Ni(1)A, O(1) and O(1)A is 178.01°. The angle (166.55°) of C(1)-O(1)-O(1)A is smaller than the ideal value of 180°, indicating that the two phenolic mean planes are not able to achieve the flat conformation. In the crystal packing of complex **II(b)** the $Ni \cdots N(3, \text{acetonitrile})$ separation (3.256 Å) is shorter than that (4.759 Å) of $Ni \cdots O(16, \text{perchlorate ion})$ (Figure 2).

General properties. Complexes **I**, **II** and **III** are soluble in methanol, acetonitrile, DMSO and DMF. The conductivity measurements of complexes **I** ($\lambda_{M(\text{methanol})} = 169.3 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) and **II** ($\lambda_{M(\text{methanol})} = 311 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) are consistent with 2 : 1 electrolytes behavior. However, the molar conductivity of **III** suggests that complex is non-electrolyte in DMSO solvent. The non-zero value for the non-electrolyte and relatively high value for the 2 : 1 electrolyte complexes could be attributed to high polarity of solvent. The formation of binuclear Ni(II) complexes, inferable from elemental analysis and molar conductance of **I**, **II** and **III**, is evidenced by characteristic IR absorption bands and FAB mass spectra.

For complexes **I**, **II** and **III**, strong evidence that aldehyde groups had been completely converted into Schiff base residues was provided by the disappearance of the aldehydic

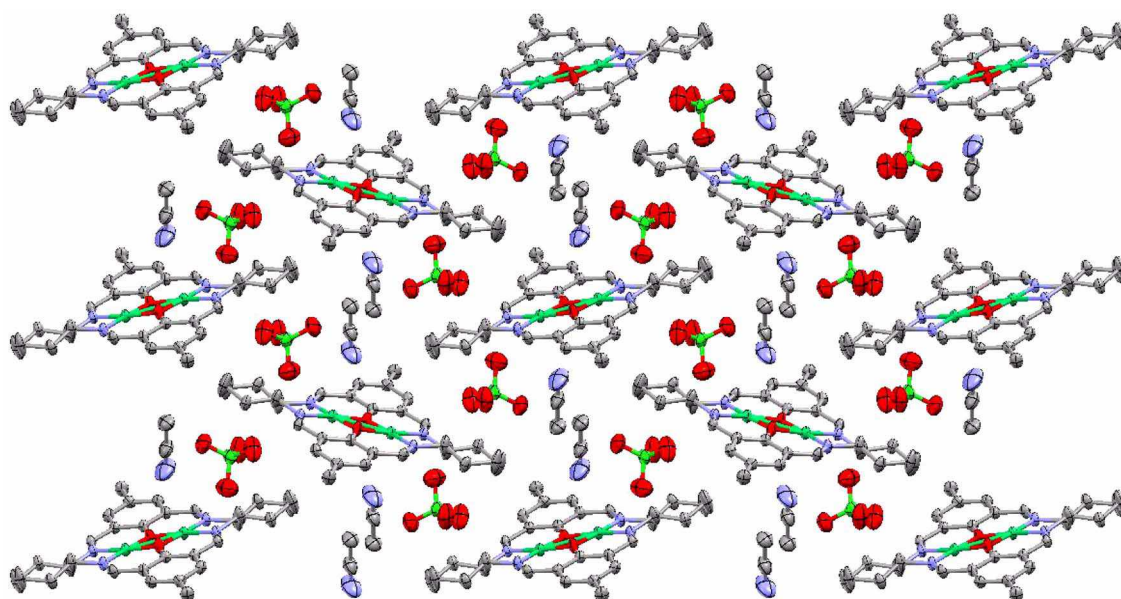


Figure 2. The molecular packing diagram for $[\text{Ni}_2([\text{20}]\text{-DCHDC})](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (**II(b)**).

C=O stretching band at 1680 cm^{-1} and the appearance of a strong band at $1624\text{--}1635\text{ cm}^{-1}$ assigned to $\nu(\text{C}=\text{N})$ stretching band.²¹ The bands that appear near $3000\text{--}2860\text{ cm}^{-1}$ and 1550 cm^{-1} are due to C-H and aromatic ring C=C stretching vibrations, respectively. The sharp absorption bands near 1240 cm^{-1} are attributed to phenolic C-O vibration. The strong ionic ClO_4^- bands are observed at approximately 1100 cm^{-1} and 620 cm^{-1} .²² The $\nu(\text{CN})$ absorption at 2044 cm^{-1} in the spectrum of **III** suggests the presence of *N*-coordinated NCS^- groups, in addition to bands near 870 cm^{-1} related to $\nu(\text{CS})$.²³

The FAB mass spectra of **I**, **II** and **III** show major fragments at m/z 635.1, m/z 699.4 and m/z 662.4 corresponding to $[\text{Ni}_2([\text{20}]\text{-DCHDC})(\text{Cl} + 2\text{H})]^+$, $[\text{Ni}_2([\text{20}]\text{-DCHDC})(\text{ClO}_4 + 2\text{H})]^+$ and $[\text{Ni}_2([\text{20}]\text{-DCHDC})(\text{NCS}) + 6\text{H}]^+$, respectively. And these complexes contain peaks attributed to $[\text{Ni}_2([\text{20}]\text{-DCHDC})]^+$ at m/z 598.1, confirming the stability of the macrocycle in the nickel(II) complexes.

With these facts in mind and in continuation of our interests^{21,23(b),24} in tetraazadiaphenol macrocyclic complexes, each Ni(II) ion in the complexes **I** and **II** is coordinated to two O atoms and two N atoms from the macrocyclic ligand having two 1,2-diaminocyclohexane rings incorporated into its backbone to form square planar environment. The structure of complex **III** shows that the two nickel centers adopt a square pyramidal geometry, each being coordinated by two imino nitrogens, two phenoxide bridging oxygens in the basal plane and *N*-coordinated NCS^- groups in the axial positions.

Supplementary data. Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC 289305). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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