

Oxidative Dehydrogenation of Hexaaza Macrocyclic Nickel(II) Complexes Bearing Two *N*-Alkyl Pendant Arms: Preparation of New Complexes Containing Imidoamidinate Linkages

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Metal-promoted reactions of coordinated organic compounds, such as oxidative dehydrogenation reactions,¹⁻⁹ have attracted particular attention because of their potential applications in organic chemistry, catalysis, and biochemistry. The saturated tetraaza macrocyclic nickel(II) complex $[\text{NiL}^5]^{2+}$ is known to react with HNO_3 to yield $[\text{NiL}^6]^{2+}$ containing four isolated imino groups.⁵ The reaction of $[\text{NiL}^7]^{2+}$ with HNO_3 produces $[\text{NiL}^8]^{2+}$ and $[\text{NiL}^9]^{2+}$ containing only one or two imino groups in the six-membered chelate ring(s).⁶ On the other hand, $[\text{NiL}^{10}]^{2+}$ reacts with H_2O_2 to produce the dinuclear complex $[\text{Ni}_2\text{L}^{11}]^{4+}$, in which two unsaturated macrocyclic units are linked together by a C=C bond.⁷ Literature up to date clearly shows that the number and position of the imino groups in the product is strongly influenced by the structural characteristics of the macrocycle.³⁻⁹

In this work, we attempted the oxidative dehydrogenation

of the hexaaza macrocyclic complexes $[\text{NiL}^1]^{2+}$ and $[\text{NiL}^2]^{2+}$ bearing two *N*-alkyl groups and prepared $[\text{NiL}^3]^{2+}$ ($\text{L}^3 = 1,8$ -dimethyl-1,3,6,8,10,13-hexaazacyclotetradeca-2,6,9,13-tetraene) and $[\text{NiL}^4]^{2+}$ ($\text{L}^4 = 1,8$ -dibenzyl-1,3,6,8,10,13-hexaazacyclotetradeca-2,6,9,13-tetraene) containing two imidoamidinate ($-\text{N}=\text{CH}-\text{N}(\text{R})-\text{CH}=\text{N}-$) linkages. Interestingly, $[\text{NiL}^4](\text{ClO}_4)_2$ consists of two stable conformational isomers and forms a 2D supramolecular structure. Synthesis and chemical properties of $[\text{NiL}^3]^{2+}$ and $[\text{NiL}^4]^{2+}$ are reported.

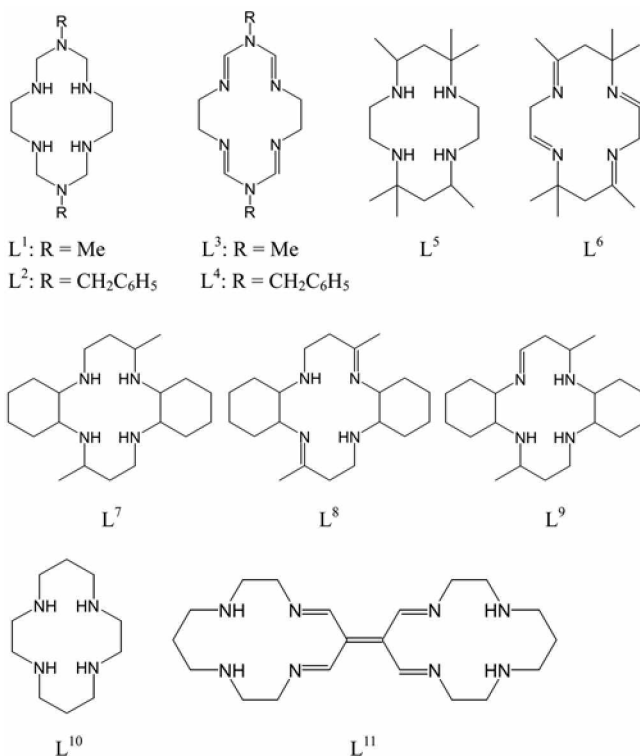
Imidoamidinates are widely used as precursors for the synthesis of various organic compounds and polymers, exhibiting useful properties.^{10,11} Recently, some nickel(II) complexes of imidoamidinates ($\text{HN}=\text{CR}-\text{NH}-\text{CR}=\text{NH}$; R = alkyl group) have been also prepared and characterized.¹⁰⁻¹³ However, $[\text{NiL}^3]^{2+}$ and $[\text{NiL}^4]^{2+}$ are rare examples of 14-membered hexaaza macrocyclic complexes that contain two imidoamidinate linkages.

Experimental Section

Materials and Measurements. All chemicals used in syntheses were of reagent grade. The complexes $[\text{NiL}^1](\text{ClO}_4)_2$ and $[\text{NiL}^2](\text{ClO}_4)_2$ were prepared as described previously.^{14,15}

Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer, electronic absorption spectra with an Analytikjena Specord 200 UV/Vis spectrophotometer, ¹³C-NMR spectra with a Varian Mercury 300 NMR spectrometer, and conductance measurements with a Metrohm Herisau Conductometer E518. Elemental analyses and mass spectral analysis were performed at the Korea Basic Science Institute, Daegu, Korea. Cyclic voltammograms were recorded using a BAS-100 B/W auto cyclic volt/ampere meter. The electrochemical measurements were conducted in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solutions at 20 °C. The working and counter electrodes were platinum, and the reference electrode was saturated calomel electrode (SCE).

Preparation of $[\text{NiL}^3](\text{ClO}_4)_2$. To a warm water-acetonitrile (1:1) solution (30 mL) of $[\text{NiL}^1](\text{ClO}_4)_2$ (1.0 g) was added H_2O_2 (0.5 mL). The solution was stirred for >10 h at room temperature. After the addition of 60% HClO₄ (ca. 0.5 mL), the resulting mixture was stored in an open beaker at



room temperature to form a pale yellow solid. The product was filtered, washed with methanol, and recrystallized from hot acetonitrile-water (1:1) solution (yield: ~70%). Anal. Calcd for $C_{10}H_{18}N_6NiCl_2O_8$: C, 25.04; H, 3.78; N, 17.51%. Found: C, 24.95; H, 3.65; N, 17.38%. FAB mass (m/z): 381 ($[NiL^3 + ClO_4]^-$), 281 ($[NiL^3 - H]^-$). IR (cm^{-1}): 1680 (N=C-N(Me)-C=N), 1605 (N=C-N(Me)-C=N), 1100 (νClO_4).

Preparation of $[NiL^4](ClO_4)_2$. This complex was prepared by a method similar to that of $[NiL^3](ClO_4)_2$, except that $[NiL^2](ClO_4)_2$ (1.0 g) was reacted in a water-acetonitrile (1:2) solution (30 mL). The product was recrystallized from hot water-acetonitrile (1:2) solution (yield: ~70%). Anal. Calcd for $C_{22}H_{26}N_6NiCl_2O_8$: C, 41.80; H, 4.11; N, 13.30%. Found: C, 41.89; H, 4.05; N, 13.40%. IR (cm^{-1}): 1670 (N=C-N(CH₂C₆H₅)-C=N), 1640 (N=C-N(CH₂C₆H₅)-C=N), 1600 (N=C-N(CH₂C₆H₅)-C=N), 1100 (νClO_4).

Preparation of $[NiL](PF_6)_2$ ($L = L^3$ or L^4). To a warm acetonitrile (*ca.* 10 mL) solution of $[NiL](ClO_4)_2$ (*ca.* 0.5 g) was added an excess of NH_4PF_6 . A white solid (NH_4ClO_4) formed was removed by filtration, and water (10 mL) was added to the filtrate. A yellow solid was filtered, washed with water, and dried in air. Yield: ~90%.

$[NiL^3](PF_6)_2$. Anal. Calc. for $C_{10}H_{18}N_6NiP_2F_{12}$: C, 21.04; H, 3.18; N, 14.72%. Found: C, 20.98; H, 3.12; N, 14.90%. ¹H NMR (CD_3NO_2): δ 3.65 (*s*, Me), 3.80 (*s*, N-CH₂-CH₂-N), and 7.86 (*s*, N-CH=N) ppm. ¹³C NMR (CD_3NO_2): 40.8 (Me), 57.3 (N-CH₂-CH₂-N), and 153.5 (N-CH=N) ppm. **$[NiL^4](PF_6)_2$.** Anal. Calc. for $C_{22}H_{26}N_6NiP_2F_{12}$: C, 36.54; H, 3.62; N, 11.62%. Found: C, 36.70; H, 3.74; N, 11.73%. FAB mass (m/z): 579 ($[NiL^4 + PF_6]^-$), 433 ($[NiL^4 - H]^-$). ¹³C NMR (CD_3NO_2): 51.1 (CH₂), 55.3 (CH₂), 56.6 (CH₂), 57.4 (CH₂), 57.7 (CH₂), 57.8 (CH₂), 58.3 (CH₂), 129.0 (C₆H₅), 129.1 (C₆H₅), 129.2 (C₆H₅), 129.9 (C₆H₅), 130.2 (C₆H₅), 130.3 (C₆H₅), 130.4 (C₆H₅), 130.5 (C₆H₅), 135.7 (C₆H₅), 136.1 (C₆H₅), 152.8 (N=CH-N), 153.1 (N=CH-N), 153.2 (N=CH-N), and 159.6 (N=CH-N) ppm.

Crystal Structure Determination. A single crystal of $[NiL^4](ClO_4)_2$ suitable for X-ray study was grown from acetonitrile-water-ethanol. Intensity data were collected with an Enraf-Nonius CAD4 diffractometer using monochromated Mo $K\alpha$ radiation at 20 °C. The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 and SHELXL-97.¹⁶ Anisotropic displacement parameters were determined for all non hydrogen atoms.

Crystal and Refinement Data: $C_{22}H_{26}Cl_2N_6NiO_8$, $M = 632.10$, monoclinic, $C2/m$, $a = 11.826(2)$, $b = 15.201(3)$, $c = 14.689(3)$ Å, $\beta = 101.17(2)^\circ$, $V = 2590.6(9)$ Å³, $Z = 4$, $D_{calc} = 1.621$ g cm⁻³, $\mu = 10.15$ cm⁻¹. Goodness-of-fit on $F^2 = 1.100$. Final $R_1 = 0.0636$, $wR_2 = 0.1736$ ($I > 2\sigma(I)$), $R_1 = 0.0850$, $wR_2 = 0.1888$ (all data), Largest diff. peak and hole = 0.711 and -0.454 eÅ⁻³.

Results and Discussion

Synthesis. The only product prepared from the reaction of the hexaaza macrocyclic complex $[NiL^1]^{2+}$ or $[NiL^2]^{2+}$ with

H_2O_2 was $[NiL^3]^{2+}$ or $[NiL^4]^{2+}$ containing two imidoylamine linkages. The position and/or number of the imino groups in the product are quite different from those prepared from the oxidative dehydrogenation reaction of various tetraaza macrocyclic complexes, such as $[NiL^5]^{2+}$, $[NiL^7]^{2+}$, and $[NiL^{10}]^{2+}$.^{5,7} It is expected that the metal-promoted ligand dehydrogenation reaction begins with the oxidation of nickel(II) to nickel(III) state which then oxidizes the macrocyclic ligand.²⁻¹⁰ However, any intermediate such as the nickel(III) state could not be isolated as a solid in the present experimental conditions.

Crystal Structure of $[NiL^4](ClO_4)_2$. The crystallographic asymmetric unit of $[NiL^4](ClO_4)_2$ contains two crystallographically independent cations (1 and 2) and four perchlorate anions ($Z = 4$) (Figs. 1 and 2). Figure 1 shows that the cation 1 has a square-planar coordination polyhedron with an inversion center at the metal ion and a two-fold rotational axis through the midpoint of the ethylene group in each five-membered chelate ring. The ClO_4^- anion is not involved in coordination. Two phenyl groups of 1 are *anti* with respect to the macrocyclic plane. Selected bond distances and angles of the cation 1 are listed in Table 1. The Ni(1)-N(1) distance (1.846(4) Å) is comparable with the Ni-N(imine) distances (1.849(9) and 1.851(8) Å) of $[Ni_2L^{11}](ClO_4)_4$.⁷ The C(2)-N(1) bond distance (1.268(8) Å) is comparable with the C=N distances of $[NiL^9](ClO_4)_2$ (1.291(9) Å) and $[Ni_2L^{11}](ClO_4)_4$ (1.290(13) and 1.303(12) Å).^{6,7} The C(2)-N(2) distance (1.375(8) Å) is considerably shorter than the C(1)-N(1) bond distance (1.461(7) Å) and, furthermore, the C-N(2)-C bond angles sum to 360° within experimental error. This indicates an in-plane sp^2 -like hybridization of the N(2) atom. The N-Ni(1)-N angles are consistent with the observation that the metal ion is placed in the N₄ plane. The bond angles and distances involving the nitrogen (N(1) and N(2)) and carbon (C(2)) atoms strongly indicate that all the atoms

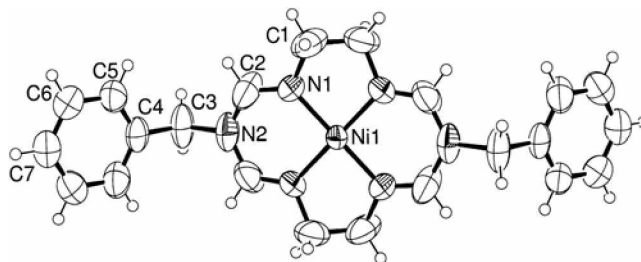


Figure 1. ORTEP Drawing of the cation 1 of $[NiL^4](ClO_4)_2$.

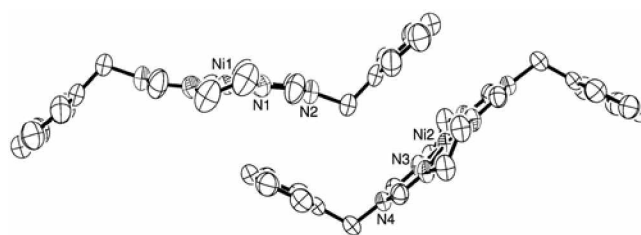


Figure 2. Perspective view of the cations 1 (upper left) and 2 (lower right) of $[NiL^4](ClO_4)_2$.

Table 1. Bond distances [Å] and angles [°] for $[\text{NiL}^4](\text{ClO}_4)_2$

Cation 1		Cation 2	
Ni(1)-N(1)	1.846(4)	Ni(2)-N(3)	1.841(4)
C(1)-N(1)	1.461(7)	C(8)-N(3)	1.474(6)
C(2)-N(1)	1.268(8)	C(9)-N(3)	1.280(6)
C(2)-N(2)	1.375(8)	C(9)-N(4)	1.365(5)
N(1)#1-Ni(1)-N(1)	93.8(3)	N(3)#1-Ni(2)-N(3)	93.0(2)
N(1)#1-Ni(1)-N(1)#2	86.2(3)	N(3)#4-Ni(2)-N(3)	87.0(2)
N(1)-C(2)-N(2)	123.4(6)	N(3)-C(9)-N(4)	123.9(5)
N(2)-C(3)-C(4)	114.1(7)	N(4)-C(10)-C(11)	113.7(6)
C(2)-N(1)-C(1)	120.3(5)	C(9)-N(3)-C(8)	119.7(4)
C(2)-N(1)-Ni(1)	126.8(5)	C(9)-N(3)-Ni(2)	127.2(3)
C(1)-N(1)-Ni(1)	112.7(4)	C(8)-N(3)-Ni(2)	113.0(3)
C(2)#1-N(2)-C(2)	124.4(7)	C(9)-N(4)-C(9)#1	123.7(5)
C(2)-N(2)-C(3)	117.7(4)	C(9)-N(4)-C(10)	118.1(3)

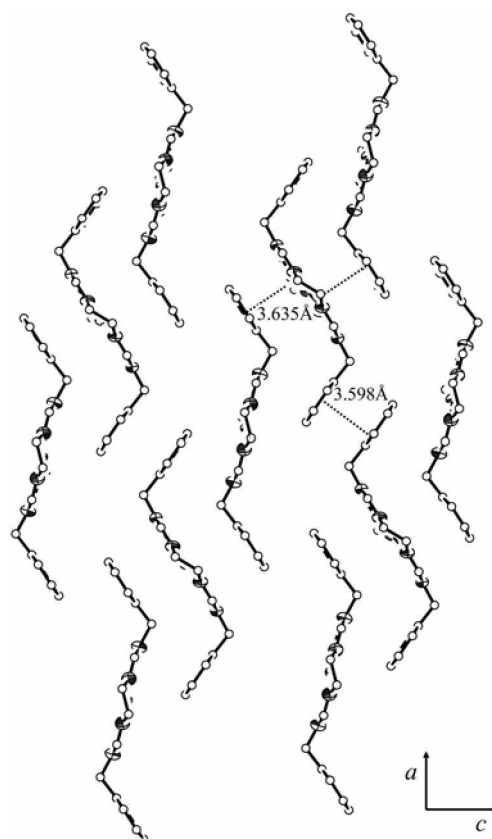
Symmetry transformations used to generate equivalent atoms: #1 $x, -y, z$; #2 $-x-1, -y, -z-1$; #3 $-x-1, y, -z-1$; #4 $-x, y, -z$; #5 $-x, -y, -z$

in each six-membered chelate rings are almost coplanar. Therefore, the macrocyclic unit of the complex may be regarded as a plane, except the twisting of the $-\text{CH}_2-\text{CH}_2-$ bonds in the five-membered chelate rings.

The bond distances and angles (Table 1) of the cation 2 are not quite different from those of the cation 1. However, Figure 2 clearly shows that the cation 2 is a conformational isomer of the cation 1: the carbon-carbon bonds in the five-membered chelate rings of the cation 2 are nearly perpendicular to the planes of the pendant benzyl groups, whereas those of 1 parallel with the planes of the pendant arms.

Figure 3 shows that the crystal structure of $[\text{NiL}^4](\text{ClO}_4)_2$ consists of 2D supramolecular network in the ac plane constructed by various intermolecular interactions of the cations, such as $\pi-\pi$ stacking interactions. Each phenyl group of the cation 2 is involved in an intermolecular face-to-face $\pi-\pi$ interaction with the other phenyl group of a neighboring cation: the two phenyl groups are anti-parallel to each other with the separation of 3.598 Å. Such $\pi-\pi$ interactions between the cations (2) extend to form 1D chain. Figure 3 also shows that the six-membered chelate rings of the cation 2 also interacts with the phenyl groups of the neighboring cation 1 to form 2D network along the ac plane. The distance between each six-membered chelate ring of the cation 2 and the nearest phenyl ring of the cation 1 is *ca.* 3.635 Å, indicating that the cations 1 and 2 are also involved in intermolecular $\pi-\pi$ interactions. A cell view (Fig. 4) along the a -axis shows the parallel packing of the 2D sheets. The ClO_4^- anions fill the interstitial spaces between the sheets.

Spectra and Properties. The complexes $[\text{NiL}^3](\text{ClO}_4)_2$ and $[\text{NiL}^4](\text{ClO}_4)_2$ are relatively stable even in low or high pH: visible spectra of complexes (2.0×10^{-3} M) measured in 0.1 M NaOH or 0.1 M HClO_4 acetonitrile-water (1:1) solutions showed that only less than 2% of the complexes were decomposed in 5 h at room temperature. The molar conductance values for the complexes in acetonitrile are 235-250 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$, indicative of 1:2 electrolytes. The infrared

**Figure 3.** A 2D sheet (ac plane) of $[\text{NiL}^4](\text{ClO}_4)_2$, showing intermolecular interactions.

spectrum of $[\text{NiL}^3](\text{ClO}_4)_2$ shows $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{N})$ of the $-\text{N}=\text{C}-\text{N}(\text{Me})-\text{C}=\text{N}-$ linkages at 1680 and 1605 cm^{-1} , respectively; no band around 3200 cm^{-1} corresponding to $\nu(\text{N}-\text{H})$ was observed. In the spectrum of $[\text{NiL}^4](\text{ClO}_4)_2$, several peaks of $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ are observed at 1680-1580 cm^{-1} . The ^{13}C -NMR spectrum of $[\text{NiL}^3](\text{PF}_6)_2$ measured in CD_3NO_2 solution shows only three carbon peaks at 40.8, 57.3, and 153.5 ppm, which are corresponding to the ligand structure. However, unexpectedly, the spectrum of $[\text{NiL}^4](\text{PF}_6)_2$ shows 21 carbon peaks (*see* Experimental section); the number is three times that expected from the ligand structure. This strongly indicates that the complex exists as a mixture of more than two conformational isomers in the solution.

The electronic absorption spectra (Table 2) of $[\text{NiL}^3](\text{ClO}_4)_2$ measured in various solvents show a d-d transition band at *ca.* 445 nm ($\epsilon = 60-70 \text{ M}^{-1}\text{cm}^{-1}$). The molar absorption coefficient in each solvent is somewhat larger than that of $[\text{NiL}^1](\text{ClO}_4)_2$.¹⁴ The spectra of $[\text{NiL}^4](\text{ClO}_4)_2$ are not quite different from those of $[\text{NiL}^3](\text{ClO}_4)_2$. However, the d-d band for $[\text{NiL}^4](\text{ClO}_4)_2$ is much broader than that for $[\text{NiL}^3](\text{ClO}_4)_2$. This observation as well as the infrared and ^{13}C -NMR spectra correspond to the suggestion that $[\text{NiL}^4]^{2+}$ exists as a mixture of several conformational isomers in various solvents.

The cyclic voltammograms of the complexes measured in acetonitrile solutions showed one-electron reduction peak

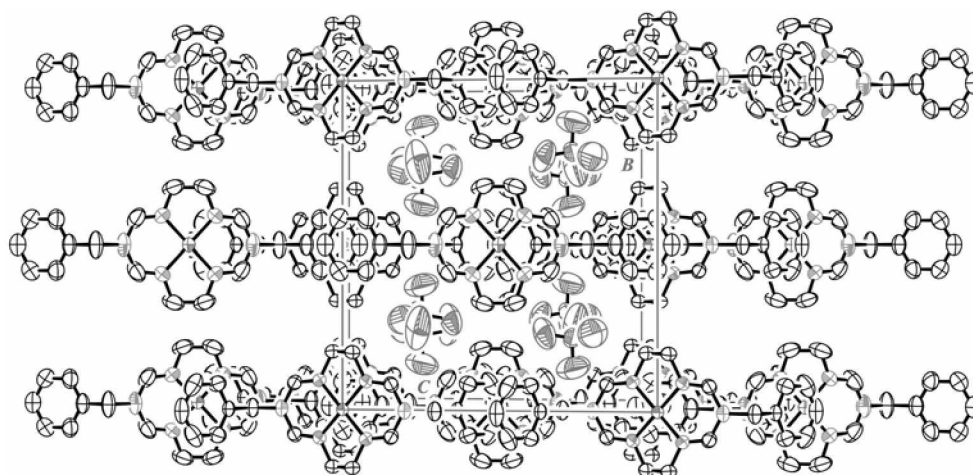


Figure 4. View of the unit cell of $[\text{NiL}^4](\text{ClO}_4)_2$ along the a axis, showing the parallel packing of the 2D sheet.

Table 2. Electronic spectral Data for the Nickel(II) Complexes

Compound	λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) ^a
$[\text{NiL}^1](\text{ClO}_4)^b$	449(56) 460(32) ^c 446(40) ^d
$[\text{NiL}^2](\text{ClO}_4)_2^c$	447(69) 450(34) ^c 446(54) ^d
$[\text{NiL}^3](\text{ClO}_4)_2$	444(70) 445(63) ^c 446(60) ^d
$[\text{NiL}^4](\text{ClO}_4)_2$	430-450(90) 430-450 (93) ^e

^aIn nitromethane at 20 °C unless otherwise specified. ^bRef. 14. ^cIn acetonitrile. ^dIn water. ^eRef. 15.

corresponding to Ni(II)/Ni(I) process. The reduction potentials of $[\text{NiL}^3](\text{ClO}_4)_2$ and $[\text{NiL}^4](\text{ClO}_4)_2$ are -1.36 and -1.34 V vs. SCE, respectively. The potentials are considerably lower than those of $[\text{NiL}^1](\text{ClO}_4)_2$ (-1.54 V vs. SCE) and $[\text{NiL}^2](\text{ClO}_4)_2$ (-1.51 V vs. SCE).^{14,15} This can be attributed to the relatively low electron density on the metal ion of the unsaturated complexes due to the π -accepting property of the macrocycles.

Summary

The unsaturated hexaaza macrocyclic nickel(II) complexes $[\text{NiL}^3]^{2-}$ and $[\text{NiL}^4]^{2-}$ can be prepared by the reaction of $[\text{NiL}^1]^{2-}$ or $[\text{NiL}^2]^{2-}$ with H_2O_2 . The macrocyclic backbones of the complexes containing two imidoylamidine units are almost planar. In the solid state, $[\text{NiL}^4](\text{ClO}_4)_2$ exists as a 1:1 mixture of two conformational isomers, **1** and **2**, and forms 2D supramolecular network constructed by 1-2 and 2-2 intermolecular π - π interactions.

Supplementary Material. Crystallographic data for $[\text{NiL}^4](\text{ClO}_4)_2$ have been deposited with the Cambridge Crystallographic Data Center. CCDC number 640115. Copies of the data may be obtained free of charge, on application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (<http://www.ccdc.cam.ac.uk>, or e-mail: deposit@ccdc.cam.ac.uk).

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