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Nickel(II) Complexes with Tetra- and Pentadentate Aminopyridine Ligands: Synthesis, Structure, Electrochemistry, and Reduction to Nickel(I) Species

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A series of nickel(II) complexes with polydentate aminopyridine ligands *N*,*N*,*N*′-tris-[2-(2′-pyridyl)ethyl]ethane-1,2-diamine (**L1**), *N*,*N*,*N*′-tris-[2-(2′-pyridyl)ethyl]-*N*′-methylethane-1,2-diamine (**L2**), and *N*,*N*′-bis-[2-(2′-pyridyl)ethyl]-*N*,*N*′-dimethylethane-1,2-diamine (**L3**) were synthesized and characterized by elemental analysis and spectroscopic methods. Single-crystal X-ray diffraction studies showed that the Ni(II) ions have five-coordinate square-pyramidal geometry in [Ni**L2**]$(ClO_4)_2$, similar to that previously found in [Ni**L1**]$(ClO_4)_2\cdot CH_3NO_2$ (Hoskins, B. F.; Whillans, F. D. *J. Chem. Soc., Dalton Trans.* **1975**, 657), and square-planar geometry in [Ni**L3**]$(ClO_4)_2$. All three nickel(II) complexes are reduced by sodium borohydride or sodium amalgam in organic solvents to nickel(I) species, which were identified by highly anisotropic EPR spectra at 100 K: $g_1 = 2.239$, $g_2 = 2.199$, and $g_3 = 2.025$ for [Ni**L1**]$^+$; $g_{\|} = 2.324$ and $g_{\perp} = 2.079$ for [Ni**L2**]$^+$ and [Ni**L3**]$^+$. Cyclic voltammetry of the nickel(II) complexes in acetonitrile exhibited reversible reduction waves at –1.01 V for [Ni**L1**]$^{2+}$, –0.91 V for [Ni**L2**]$^{2+}$, and –0.83 V for [Ni**L3**]$^{2+}$ versus SCE, potentials which are significantly less negative than those of most previously characterized Ni(II) complexes with nitrogen-only donor atoms. Complexes [Ni**L1**]$^{2+}$ and [Ni**L2**]$^{2+}$ showed high catalytic activity in the electroreduction of 1,2-*trans*-dibromocyclohexane to cyclohexene.

Introduction

Nickel(II) compounds which can be reversibly reduced to nickel(I) species have been attracting attention as models of redox active nickel-containing enzymes[1,2] and as electrocatalysts.[3,4] Not every type of ligand environment can support Ni(I), and in many cases, Ni(0) is directly produced upon the reduction of a Ni(II) complex, for example, $[Ni(H_2O)_6]^{2+}$.

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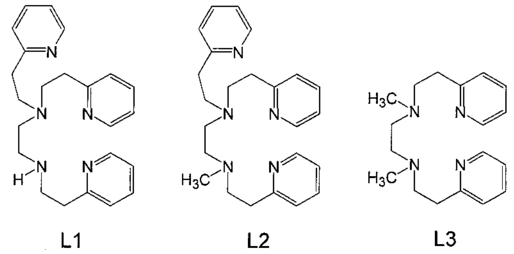
Most Ni(I) species with simple O and N ligands are thermodynamically and kinetically unstable with respect to the disproportionation into Ni(0) and Ni(II).[5,6] Another complication is that the one-electron reduction of a Ni(II) complex may lead to a Ni(II) stabilized anion radical rather than to a Ni(I) complex. EPR spectroscopy is the simplest method to distinguish such species, with monomeric Ni(I) complexes typically having highly anisotropic spectra and Ni(II) radical species having isotropic spectra with $g \approx 2.0$.[5,6]

Two successful strategies have been developed for the stabilization of Ni(I) ligation by soft donor atoms (C, P, As, S)[7−10] and by macrocycles.[11−15] Only a few Ni(I) complexes with nonmacrocyclic N ligands have been reported and characterized by spectroscopic techniques.[16−19] Sauvage and co-workers proposed to use ligands of special topology to destabilize the parent Ni(II) complex and alleviate its reduction to Ni(I) and succeeded with 2,9-disubstituted phenanthrolines, which imposed tetrahedral geometry on the metal ions.[13,17] In several other reports, the formation of Ni(I) species were proposed to account for an electrochemical reduction of Ni(II) complexes with nonmacrocyclic N ligands.[20−25] All of them contained imine donor atoms, which because of their π-acceptor ability are suitable for the stabilization of lower oxidation states. However, not all imine ligands stabilize Ni(I). A series of six-coordinated nickel(II) complexes with polydentate aminopyridines forming five-membered chelate rings showed no evidence for the electroreduction in solution within the acetonitrile window.[26] Several Ni(II) complexes with "long-armed" aminopyridines forming six-membered chelate rings were reported, but their redox properties were not studied.[27−30] Such a study could be promising, because the increased size of chelate rings was found as a factor favoring the reduction of analogous aminopyridine Cu(II) complexes to the Cu(I) state.[31] To investigate the possibility of obtaining Ni(I) complexes with aminopyridine ligands, we prepared a series of N-substituted ethylenediamines with relatively long ethylpyridine arms (Scheme 1): *N*,*N*,*N'*-tris-[2-(2'-pyridyl)ethyl]ethane-1,2-diamine (**L1**), *N*,*N*,*N'*-tris-[2-(2'-pyridyl)ethyl]-*N'*-methylethane-1,2-diamine (**L2**), and *N*,*N'*-bis-[2-(2'-pyridyl)ethyl]-*N*,*N'*-dimethylethane-1,2-diamine (**L3**). Ligand **L1** and its square-pyramidal five-coordinate Ni(II) complex were prepared earlier by Phillip and co-workers.[29,30] Recently, we proposed a simplified procedure to prepare **L1** and its methylated analogue **L2** in the form of Cu(II) complexes.[32] Ligand **L3** and its Cu(II)/Cu(I) complexes were reported by Urbach and co-workers.[31] N-methylated ligands **L2** and **L3** were chosen for this study, because methylation was found to favor lower oxidation states for several series of metal complexes with amine ligands, which was attributed to the destabilization of the parent high oxidation state complexes.[31,33] Comparison of the pentadentate **L2** with the tetradentate **L3** is important to determine the influence of ligand denticity on the stability of the reduced Ni(I) complexes.

Scheme 1. Structural Formula of the Ligands Used in This Work



In this article, we report synthesis and characterization of a series of Ni(II) complexes with "long-armed" aminopyridine ligands **L1**−**L3**, which can be reduced to relatively stable Ni(I) species, and show high catalytic activity in the electroreduction of 1,2-*trans*-dibromocyclohexane.

Experimental Section

Synthesis. One-pot synthesis and characterization of copper(II) complexes [Cu**L1**]$(PF_6)_2$ and [Cu**L2**]$(PF_6)_2$ are reported elsewhere.[32] Free ligands **L1** and **L2** and their nickel(II) complexes were obtained by a modification of the procedure reported by Phillip

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and co-workers.[29] Ligand **L3** was prepared by the method reported by Urbach and co-workers.[31] All other chemicals (reagent grade or better) were used as received. **CAUTION!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of the materials should be prepared, and these should be handled with care.

L1 ($C_{23}H_{29}N_5$). Complex [Cu**L1**]$(PF_6)_2$ (1.46 g; 2 mmol) was dissolved in 40 mL of hot water, mixed with a solution of excess $Na_2S{\cdot}9H_2O$ (0.96 g; 4 mmol) in 10 mL of water, and left overnight. The settled precipitate of CuS was filtered off, and the filtrate was made strongly alkaline by the addition of NaOH (10 g). Free amine **L1** was extracted by freshly distilled diethyl ether (3 × 100 mL). The combined ether extracts were washed with brine and dried with solid Na_2SO_4 overnight. After distilling the solvent, the yield of residual yellow oil was 0.60 g (80%). Mass spectrum (MALDI-TOF, dithranol matrix): 376.3 (**L1**H$^+$, 8%); 240.2 [$H_2C{=}N(C_2H_4C_5H_4N)_2{}^+$, 100%]. ^{1}H NMR ($CDCl_3$): δ 2.51 (t, 2H), 2.59 (t, 2H), 2.79 (m, 12H), 7.00 (m, 6H), 7.45 (m, 3H), 8.40 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 35.82, 38.39, 47.21, 49.40, 53.39, 53.95, 121.11, 121.75, 123.21, 123.48, 136.26, 136.41, 149.06, 149.17, 160.13, 160.64 (16 signals).

L2 ($C_{24}H_{31}N_5$). Free ligand **L2** was prepared as a pale yellow oil by the same procedure as **L1** starting from [Cu**L2**]$(PF_6)_2$ (1.49 g; 2 mmol) dissolved in 120 mL of hot water. Yield: 0.51 g (65%). Mass spectrum (MALDI-TOF, dithranol matrix): 390.3 (**L2**H$^+$, 10%), 281.2 [$H_2C{=}NC_2H_4N(C_2H_4C_5H_4N)_2{}^+$, 100%]. ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 3H), 2.46 (m, 2H), 2.69 (m, 4H), 2.89 (m, 10H), 7.05 (m, 6H), 7.52 (m, 3H), 8.45 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 35.92, 35.96, 42.59, 51.99, 54.46, 55.63, 58.07, 121.22, 121.28, 123.40, 123.55, 136.40, 136.51, 149.21, 149.27, 160.51, 160.67 (17 signals).

L3 ($C_{18}H_{26}N_4$). Ligand **L3** was prepared by a published procedure.[31] ^{1}H NMR ($CDCl_3$): δ 2.332 (s, 6H), 2.583 (s, 4H), 2.80 (m, 4H), 2.94 (m, 4H), 7.09 (m, 2H), 7.18 (m, 2H), 7.56 (m, 2H), 8.50 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 34.67, 41.32, 54.15, 56.86, 120.11, 122.25, 135.31, 147.93, 159.36 (9 signals).

[NiL1](ClO_4)$_2$. A solution of $Ni(ClO_4)_2{\cdot}9H_2O$ (0.37 g; 1 mmol) in water (2 mL) and a solution of ligand **L1** (0.38 g, 1 mmol) in ethanol (15 mL) were mixed together, thoroughly stirred, and left overnight in a refrigerator yielding a heavy dark blue oil. The oil was isolated by decantation and recrystallized from hot methanol yielding dark blue needle-shaped crystals of [Ni**L1**]$(ClO_4)_2$. If the crystals of the complex were small (after grinding or from fast cooling during the recrystallization), the substance appeared purple. Yield: 0.39 g (62%). IR (KBr): ν(NH), 3280m; ν($ClO_4{}^-$), 1100s(br) cm^{-1}. UV−vis diffuse reflectance spectrum (DRS) (1:2 mixture with MgO): λ_{max} 364, 565 nm. Anal. Calcd (found) for $C_{23}H_{29}Cl_2N_5NiO_8$: C, 43.63 (43.34); H, 4.62 (4.87); N, 11.06 (10.93).

[NiL2](ClO_4)$_2$. The complex was prepared as dark blue plate-shaped crystals by a procedure analogous to that for [Ni**L1**]$(ClO_4)_2$. Yield: 60%. IR (KBr): ν($ClO_4{}^-$), 1100s(br) cm^{-1}. UV−vis SDR (1:2 mixture with MgO): λ_{max} 376, 590 nm. Anal. Calcd (found) for $C_{24}H_{31}Cl_2N_5NiO_8$: C, 44.54 (44.73); H, 4.83 (4.78); N, 10.82 (10.76). For crystallographic studies, the complex was recrystallized from an ethanol−acetonitrile (9:1) mixture by slow diffusion of diethyl ether vapor.

[NiL2](ClO_4)$_2$·CH_3CN. Recrystallization of [Ni**L2**]$(ClO_4)_2$ from acetonitrile solution by diffusion of diethyl ether vapor yielded dark blue cubic crystals of the solvate [Ni**L2**]$(ClO_4)_2{\cdot}CH_3CN$. IR (KBr): ν(C≡N), 2247m; ν($ClO_4{}^-$), 1100s(br) cm^{-1}. UV−vis DRS (1:2 mixture with MgO): λ_{max} 378, 595 nm. Anal. Calcd (found) for $C_{26}H_{34}Cl_2N_6NiO_8$: C, 45.38 (45.64); H, 4.98 (5.38); N, 12.21 (12.02).

[NiL3](ClO_4)$_2$. The complex was prepared as yellow needle-shaped crystals by a procedure analogous to that for the [Ni**L1**]$(ClO_4)_2$ analogue. Yield: 50%. IR (KBr): ν($ClO_4{}^-$), 1100s(br) cm^{-1}. ^{1}H NMR (CD_3NO_2, all lines broad): δ 2.46 (2H), 2.65 (6H), 2.79 (2H), 3.34 (d, 2H), 3.62 (d, 2H), 5.31 (2H), 7.27 (2H), 7.71 (2H), 8.04 (2H). ESMS (soln in $MeNO_2$): 455 [Ni**L3**]$(ClO_4)^+$ (positive mode), 655 [Ni**L3**]$(ClO_4)_3{}^-$ (negative mode). Anal. Calcd (found) for $C_{18}H_{26}Cl_2N_4NiO_8$: C, 38.88 (38.19); H, 4.71 (4.80); N, 10.08 (9.82). Crystals suitable for X-ray diffraction study were obtained by slow recrystallization from hot methanol−ethanol (1:1) mixture.

Reduction to Ni(I) Species. A 1−2 mM solution of [Ni**L1**]$(ClO_4)_2$ or [Ni**L2**]$(ClO_4)_2$ in acetonitrile, propionitrile, or a propionitrile−2-methyltetrahydrofurane (1:2) mixture was prepared in a glovebox under argon atmosphere and shaken with an equimolar amount of sodium amalgam or 0.2 M aqueous solution of $NaBH_4$. After a deep red color fully developed in 1−2 min, the organic solution phase was decanted from the excess of the reducing material. Samples for EPR spectroscopy were put into gas-tight ampules, taken out of the glovebox, and frozen with liquid nitrogen. Room temperature UV−vis spectra of the same solutions were recorded in gas-tight cuvettes (1 mm or 1 cm optical path). The concentration of Ni(I) was determined by double integration of the EPR spectra (100 K) using the solutions of [Cu**L2**]$(ClO_4)_2$ in the same solvent as external standards.

General Methods. NMR spectra were recorded on a Bruker AM-300 spectrometer, IR spectra on a Mattison 1000 FTIR spectrometer, and EPR spectra on a Bruker EMX spectrometer. UV−vis spectra were taken on a Hitachi U-2000 spectrophotometer for solutions (350−1100 nm) and on a Hewlett-Packard spectrophotometer with a Harrick DRS cell for solid samples (350−800 nm). Mass spectra of the ligands were obtained using a Brucker BIFLEX MALDI-TOF mass spectrometer; electrosparay mass spectra of the complexes were performed by HT Laboratories (San Diego, CA). Elemental analyses were done by Desert Analytics (Tucson, AZ) and Quantitative Technologies Inc. (Whitehouse, NJ).

X-ray Diffraction Studies. Single-crystal intensity measurements for [Ni**L2**]$(ClO_4)_2$ were collected at room temperature with a Rigaku AFC5S diffractometer using Mo Kα radiation with graphite monochromator and ω-scans. Lattice parameters were obtained using least squares refinement of the angles of 24 reflections with $22° < 2\theta < 26°$. Empirical absorption correction was applied. The structure was solved by direct methods using SIR-92[34] and refined with all data by full-matrix least squares on F^2 using SHELXL-97.[35] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in idealized positions with a riding model.

Data for [Ni**L3**]$(ClO_4)_2$ were collected using a Bruker SMART CCD-based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. The crystal used for the diffraction study showed no decomposition during data collection. Cell parameters were retrieved using SMART software[36]

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Table 1. Crystallographic Data for [Ni**L2**]$(ClO_4)_2$ and [Ni**L3**]$(ClO_4)_2$

	[Ni**L2**]$(ClO_4)_2$	[Ni**L3**]$(ClO_4)_2$
chemical formula	$C_{24}H_{31}Cl_2N_5NiO_8$	$C_{18}H_{26}Cl_2N_4NiO_8$
fw	647.15	556.04
cryst syst	monoclinic	monoclinic
space group (No.)	$C2/c$ (15)	$P2_1/c$ (14)
a (Å)	40.638(19)	15.599(6)
b (Å)	7.6872(7)	9.111(4)
c (Å)	40.183(13)	16.219(6)
β (deg)	118.80(3)	97.508(9)
V (Å^3)	11000(6)	2285.5(15)
T (K)	293(2)	213(2)
λ(Å)	0.7107	0.7107
δ_{calc} (g cm^{-3})	1.563	1.616
Z	16	4
F(000)	5088	1152
abs coeff, cm^{-1}	0.957	1.135
no. of reflns collected	9743	16544
final R [$I > 2\sigma(I)$]	0.0512	0.0458
wR2	0.1688	0.1111

and refined using SAINT[37] on all observed reflections. Data reduction was performed using the SAINT software, which corrects for Lorentz polarization and decay. The structures were solved by the direct method using the SHELXS-97 program[38] and refined by least-squares method on F^2, SHELXL-97,[35] incorporated in SHELXTL V5.10.[39] The structure was solved in the space group $P2_1/c$ (No. 14) by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated by geometrical methods and refined as a riding model. The perchlorate ions were modeled with disorder.

Crystal data are summarized in Table 1.

Electrochemical Experiments. All cyclic voltammetry (CV) experiments were done under an inert gas atmosphere to protect Ni(I) species from oxidation. The CV in dimethylformamide (0.2 M n-Bu_4NBr) was done with a BAS-100B electrochemical analyzer using a three electrode cell with a pyrolytic graphite disk working electrode and referred to the aqueous saturated calomel electrode (SCE). The CV in acetonitrile (0.1 M n-Bu_4NPF_6) was performed with an EG&G PAR 273 potentiostat using a three electrode cell with a pyrolytic graphite working electrode; ferrocene was used as an internal standard, and a recently published conversion coefficient was applied to refer the potentials to SCE.[40]

All controlled-potential electrolysis experiments were done with the BAS-100B electrochemical analyzer for 1 h under constant purging with purified nitrogen gas. An H-type cell was used, with carbon cloth (2.5 × 3 cm^2) as working electrode, graphite rod as counter electrode, and saturated calomel electrode as the reference. The counter electrode chamber with KCl (1 M) was separated from the working electrode chamber by an agar/KCl bridge and a medium porosity glass frit. All experiments were done in dimethylformamide (0.2 M n-Bu_4NBr) with 18 mM *trans*-1,2-dibromocyclohexane and 1 mM nickel complex. The products of electrolysis were first purified on silica column and then analyzed by gas chromatography (HP6890, Hewlett- Packard).

Results and Discussion

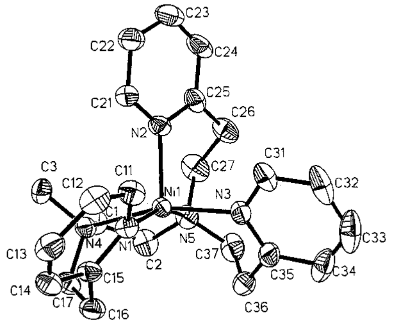

Figure 1. ORTEP drawing of complex cation [Ni**L2**]$^{2+}$. Selected bond lengths (Å) and angles (deg) for one of the two crystallographic molecules (molecule 1): Ni(1)−N(1), 2.112(4); Ni1−N2, 2.040(5); Ni(1)−N(3), 2.057(4); Ni1−N(4), 2.138(4); Ni1−N(5), 2.101(5); N(1)−Ni(1)−N(2), 102.54(19); N(1)−Ni(1)−N(3), 91.85(17); N(1)−Ni(1)−N(4), 86.72(17); N(1)−Ni(1)−N(5), 160.06(19); N(2)−Ni(1)−N(3), 95.25(18); N(2)−Ni(1)−N(4), 102.29(18); N(2)−Ni(1)−N(5), 96.90(19); N(3)−Ni(1)−N(4), 162.3(2); N(3)−Ni(1)−N(5), 90.75(19); N(4)−Ni(1)−N(5), 84.83(19).

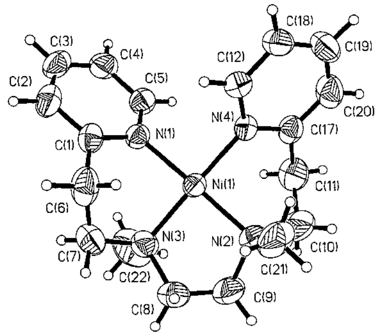

Figure 2. ORTEP drawing of complex cation [Ni**L3**]$^{2+}$. Selected bond lengths (Å) and angles (deg): Ni(1)−N(1), 1.892(2); Ni(1)−N(2), 1.949(2); Ni(1)−N(3), 1.927(3); Ni(1)−N(4), 1.907(2); N(1)−Ni(1)−N(4), 91.35(10); N(2)−Ni(1)−N(4), 90.25(10); N(2)−Ni(1)−N(3), 87.89(11); N(1)−Ni(1)−N(3), 90.63(10).

Crystal Structure of [NiL2]$(ClO_4)_2$. The asymmetric unit consists of two crystallographically independent [Ni**L2**]$^{2+}$ cations and four perchlorate anions. The two five-coordinate [Ni**L2**]$^{2+}$ cations have only slightly different geometries, in which the coordination of the Ni(II) ions can be described as a slightly distorted square pyramid (Figures 1 and S1). Geometric parameter τ, which is equal to zero for a perfect square pyramid and becomes unity for a perfect trigonal bipyramid,[41] is calculated as 0.037 and 0.087 for crystallographic molecules 1 and 2 of [Ni**L2**]$^{2+}$, respectively. The base of the square pyramid in [Ni**L2**]$^{2+}$ is formed by two ethylenediamine and two pyridine nitrogens, with the third pyridine nitrogen occupying the apex and the central Ni atom at 0.31−0.33 Å above the plane. The bond distances Ni−N (2.04−2.14 Å) are typical for complexes of high-spin Ni(II) with nitrogen donor atoms.[27] The distances between perchlorate anions and Ni^{2+} (>4.6 Å) are well beyond coordination. The molecular structure of the complex cation in [Ni**L2**]$(ClO_4)_2$ determined in this work is similar to that in [Ni**L1**]$(ClO_4)_2\cdot CH_3NO_2$ reported by Hoskins and Whillans.[30]

Crystal Structure of [NiL3]$(ClO_4)_2$. The coordination sphere of nickel(II) in this complex has a square-planar geometry (Figure 2). The bond distances Ni−N (1.89−1.95 Å) are typical for complexes of low-spin Ni(II) with nitrogen donor atoms.[27] These distances are substantially shorter than

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Table 2. Parameters of the Electronic Spectra of Ni(II) Complexes in Different Environments

environment	$[\mathrm{Ni}\mathbf{L1}]^{2+}$ $\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})	$[\mathrm{Ni}\mathbf{L2}]^{2+}$ $\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})	$[\mathrm{Ni}\mathbf{L3}]^{2+}$ $\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})
$MeNO_2$ solution	577 (45), 742 (8), 877 (7)	592 (55), 785(6.8), 880 (6.5)	450 (110)
MeCN solution	363sh (37), 571 (18), 800sh (8), 877 (11)	377 (113), 591 (46), 790sh (6), 881 (7)	366 (24), 448 (6.8), 584 (16), 800sh (4), 940 (8.2),
EtCN solution	363sh (30), 570 (15), 800sh (8), 877 (11)	377 (112), 592 (46), 790sh (8), 882 (9)	363 (28), 445sh (5), 582 (15), 800sh (4), 938 (8.8)
H_2O soultion	365 (34), 582 (16), 790sh (5), 950 (12)	377 (112), 591 (44), 790sh (5), 880 (6)	375 (17.3), 444 (6.5), 608 (9.5), 778 (2.2), 983 (9.4)
DMF solution	365sh (32), 586 (15), 795sh (6), 925 (12)	378 (39), 606 (18), 795 (3), 990 (8)	375 (23), 618 (13), 791 (2.0), 1020 (8.9)
solid $[NiL](ClO_4)_2$	364, 565	376, 590	
solid $[NiL](ClO_4)_2$·MeCN		378, 595	

the corresponding Ni−N distances in high-spin $[\mathrm{Ni}\mathbf{L1}]^{2+}$ and $[\mathrm{Ni}\mathbf{L2}]^{2+}$. Bond angles N−Ni−N are very close to 90° (Figure 2), indicating a very small degree of tetrahedral distortion. The van der Waals repulsion between 6,6′-hydrogen atoms in pyridine rings is alleviated by rotation of one of the rings away from the NiN_4 equatorial plane. A similar distorted square-planar geometry was observed in the copper(II) analogue, $[\mathrm{Cu}\mathbf{L3}](ClO_4)_2$.[32] This coordination mode, however, is somewhat atypical for aminopyridine ligands which often adopt either cis-α or cis-β configuration in the octahedral metal complexes.[42] The only structurally characterized nickel(II) complex with a linear tetradentate aminopyridine ligand bearing "short" methylpyridine arms attached to the ethylenediamine framework also displayed an octahedral geometry, with a cis-α configuration for the tetradentate ligand, and an oxalate anion completing the equatorial plane.[42] The square-planar geometry of $[\mathrm{Ni}\mathbf{L3}]^{2+}$ reported in this paper is in accord with Bosnich's analysis which predicted preferential in-plane coordination of the ligands with 656 sequence of chelate ring sizes, as opposed to the cis geometry of the 555 polychelate ligands.[43] To the best of our knowledge, $[\mathrm{Ni}\mathbf{L3}]^{2+}$ is the first structurally characterized square-planar complex of Ni(II) with a non-macrocyclic aminopyridine ligand.

Electronic Spectra of Ni(II) Complexes. The electronic spectra of the complexes with pentadentate amines **L1** and **L2** are characteristic of square-pyramidal $Ni^{II}N_5$ chromophores (Table 2).[29] The positions of the absorption maxima in the spectrum of $[\mathrm{Ni}\mathbf{L2}]^{2+}$ are very close for solids $[\mathrm{Ni}\mathbf{L2}](ClO_4)_2$ and $[\mathrm{Ni}\mathbf{L2}](ClO_4)_2 \cdot CH_3CN$ and for the solutions of $[\mathrm{Ni}\mathbf{L2}](ClO_4)_2$ in a number of solvents (nitriles, nitromethane, water), suggesting that no coordination of the solvents occurs. A similar observation can be made on the $[\mathrm{Ni}\mathbf{L1}](ClO_4)_2$ complex (Table 2), meaning that both ligands, **L1** and **L2**, form stable five-coordinate square-pyramidal complexes with Ni(II), which are not prone to add a sixth donor group. These data also suggest the same square-pyramidal geometry for the $Ni^{II}N_5$ chromophore in the solid state and in the solutions for $[\mathrm{Ni}\mathbf{L1}]^{2+}$ and $[\mathrm{Ni}\mathbf{L2}]^{2+}$.

It should be noted that coordination number five is relatively rare for Ni(II), which much more often forms either octahedral high-spin or square-planar low-spin complexes.[27] Such a property can be attributed to a smaller value of ligand field stabilization energy for the d^8 central atom surrounded by five donor atoms versus an octahedral or square-planar coordination. Ni(II) complexes with pentadentate ligands are often six-coordinate because of the addition of a solvent molecule or anion.[26,44] Five coordination can be reached with ligands having special steric properties, so that the crowding around the Ni(II) ion is large enough to prevent a sixth donor group from bonding.[45] In the cases of $[\mathrm{Ni}\mathbf{L1}]^{2+}$ and $[\mathrm{Ni}\mathbf{L2}]^{2+}$, the "bottom" of the NiN_5 square pyramid is lined by two ethylene bridges of the ethylpyridine arms, which sterically hinder the coordination of additional ligands (Figure S2). The aminopyridine ligands with shorter methylpyridine arms form six-coordinate complexes with Ni(II) and other similar 3d metal cations.[23,26,42,46]

The electronic spectrum of complex $[\mathrm{Ni}\mathbf{L3}](ClO_4)_2$ dissolved in nitromethane (Table 2) is typical of a square-planar $Ni^{II}N_4$ chromophore.[27] Successful acquisition of the ^1H NMR spectrum for $[\mathrm{Ni}\mathbf{L3}](ClO_4)_2$ dissolved in nitromethane-d_3 confirms the diamagnetic, low-spin nature of the compound in the noncoordinating solvent, CH_3NO_2. In coordinating solvents (nitriles, water, DMF), the intensity of the band at 450 nm drops dramatically (from $\epsilon = 110$ in CH_3NO_2 to $\epsilon = 5-7$ in the coordinating solvents), and several new low intensity ($\epsilon < 20$) bands typical of high-spin Ni(II) complexes appear at ∼580, 800, and 940 nm. Thus, complex $[\mathrm{Ni}\mathbf{L3}]^{2+}$ preferentially exists in a high-spin form in coordinating solvents, binding one or two solvent molecules in the apical position(s).

Chemical Reduction to Ni(I) Species and Their Characterization. Acetonitrile and propionitrile solutions of $[\mathrm{Ni}\mathbf{L1}]^{2+}$ (purple), $[\mathrm{Ni}\mathbf{L2}]^{2+}$, and $[\mathrm{Ni}\mathbf{L3}]^{2+}$ (blue) turn dark red when treated with either sodium borohydride or sodium amalgam under an inert gas atmosphere (Figure 3). The resulting solutions are extremely susceptible to air and slowly lose color even under anaerobic conditions. The reduced complex with **L1** has a half-life of about 10 min in

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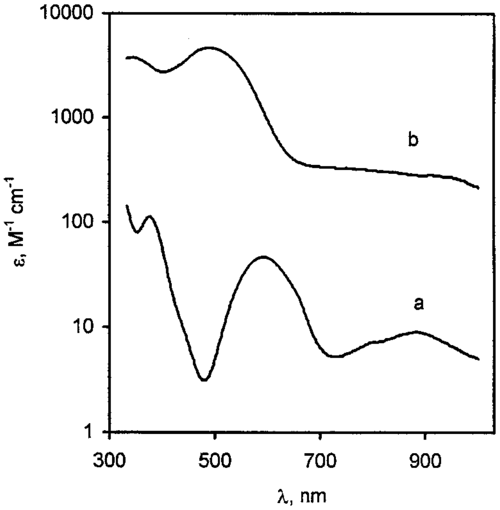

Figure 3. Electronic spectra of $[Ni^{II}\mathbf{L2}]^{2+}$ (a) and $[Ni^{I}\mathbf{L2}]^{+}$ (b) in propionitrile.

propionitrile solution at room temperature, while those with **L2** and **L3** are much more stable, decomposing only within several days. The analogous solutions prepared in acetonitrile are less stable.

EPR spectroscopy reveals that monomeric nickel(I) species are formed upon reduction of $[Ni\mathbf{L1}]^{2+}$, $[Ni\mathbf{L2}]^{2+}$, and $[Ni\mathbf{L3}]^{2+}$. All three systems give highly anisotropic spectra in frozen glasses (Figure 4), indicative of an unpaired electron localized primarily on the metal center (as opposed to a ligand anion radical). Although the signals in the spectra are rather broad, no Ni(I)−N hyperfine coupling was observed in several solvents and solvent mixtures, under a variety of concentrations and temperatures. The spectral parameters were virtually solvent independent, although a mixture of 2-methyltetrahydrofuran and propionitrile (2:1) allowed for the highest yields of the Ni(I) species along with the best quality of the glasses formed upon cooling. Quantitation of the spin concentrations shows that the yield of Ni(I) species upon reduction of Ni(II) complexes is close to 100% for **L2** and **L3** but is much lower (10−20%) for **L1**.

The EPR spectrum of complex $[Ni^{I}\mathbf{L1}]^{+}$ is rhombic (Figure 4a), with the equatorial components g_1 and g_2 being very close to each other (2.239 and 2.199), while $g_{\|}$ is substantially smaller (2.025). The spectra with $g_{\perp} > g_{\|}$ are indicative of the $(d_{z^2})^1$ ground state of Ni(I) complexes. For a d^9 metal ion in a five-coordinate environment, such a ground state is usually attributed to a trigonal-bipyramidal (TBP) coordination geometry.[47] Similar EPR spectra were observed for a few structurally characterized TBP complexes of Ni(I) with P,S ligands.[7] Simple molecular models indicated[30] that ligand **L1** is flexible and can adopt either square-pyramidal coordination (as found in the crystal structure of $[Ni^{II}\mathbf{L1}]^{2+}$) or trigonal-bipyramidal geometry (as suggested by the EPR spectrum of $[Ni^{I}\mathbf{L1}]^{+}$) without a substantial strain of natural valency angles.

The EPR spectrum of complex $[Ni^{I}\mathbf{L2}]^{+}$ (Figure 4b) is different from its nonmethylated counterpart $[Ni\mathbf{L1}]^{+}$: $g_{\|} =$ 2.324 is greater than $g_{\perp} = 2.079$ [$G = (g_{\|} - 2)/(g_{\perp} - 2) = 4.10$]. Such a spectrum is characteristic of a d^9 species (Ni^{I}) with the $(d_{x^2-y^2})^1$ ground state,[47] which could originate from either square-planar or tetragonal-pyramidal (TP) geometry of the coordination sphere. TP complexes of Ni(I) usually give rhombic EPR spectra,[5,15,48] although some examples of axial spectra were also reported.[12,48] In contrast, square-planar Ni(I) complexes normally yield axial spectra.[5,9,11,48] Consequently, square-planar geometry of $[Ni\mathbf{L1}]^{+}$ appears to be more likely, suggesting that one of the ethylpyridine pendant arms dissociates from the metal center upon reduction. This hypothesis was tested by comparison of the EPR of $[Ni\mathbf{L2}]^{+}$ to the spectrum of the Ni(I) complex with tetradentate ligand **L3**. These spectra are exactly identical in the positions of the signals (Table 3) as well as in the line width and line shape, indicating a similar square-planar coordination mode of both ligands (**L2** and **L3**).

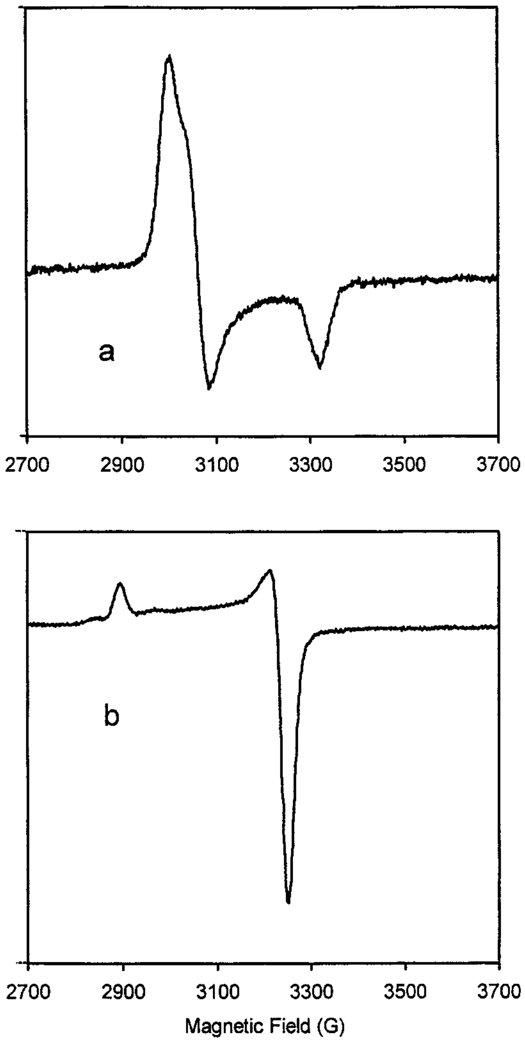

Figure 4. EPR spectra of the nickel(I) complexes in frozen propionitrile−2-methyltetrahydrofuran (1:2): (a) $[Ni^{I}\mathbf{L1}]^{+}$ and (b) $[Ni^{I}\mathbf{L2}]^{+}$ or $[Ni^{I}\mathbf{L3}]^{+}$. Conditions: microwave frequency, 9.42 GHz; temperature, 77 K.

The highly intense bands ($\epsilon \approx 4000$ M^{-1} cm^{-1}) in the UV−vis spectra of $[Ni^{I}\mathbf{L1}]^{+}$ ($\lambda_{max} = 480$ nm), $[Ni^{I}\mathbf{L2}]^{+}$ ($\lambda_{max} = 344$, 486 nm), and $[Ni^{I}\mathbf{L3}]^{+}$ ($\lambda_{max} = 357$, 480sh, 512 nm)

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Table 3. Spectroscopic Parameters of the Ni(I) Complexes

complex	$g_\perp$	$g_\parallel$	yield[a]	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[b]
[Ni**L1**]$^+$	2.239, 2.199	2.025	15 ± 5%	495 (~4000)
[Ni**L2**]$^+$	2.079	2.324	70 ± 20%	344 (3700), 486 (4500), 800sh (220), 900sh (200)
[Ni**L3**]$^+$	2.079	2.324	100 ± 5%	357 (3000), 480sh (3800), 512 (4600), 808 (210), 903 (200)

[a] The yield of Ni(I) species calculated from the double integration of the EPR spectra using [Cu**L2**]$^{2+}$ as a standard.[54] [b] Absorption coefficients were corrected for the yields determined from the EPR quantitation.

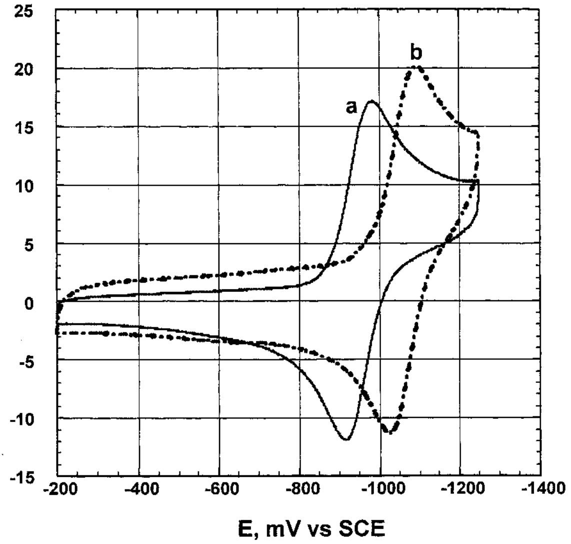

Figure 5. Cyclic voltammograms on pyrolytic graphite disk electrodes at 50 mV s^{-1} in 0.2 M TBAB in DMF: (a) 1 mM complex [Ni**L2**]$^{2+}$ and (b) 1 mM complex [Ni**L1**]$^{2+}$.

Table 4. Redox Potentials vs SCE for Selected [Ni^{II}L]$^{2+}$/[Ni^{I}L]$^+$ Couples Obtained by Cyclic Voltammetry in Acetonitrile

parent Ni(II) complex	donor atoms set	$E_{1/2}$, V	ref
[Ni**L1**]$^{2+}$	N_5	−1.01[a] (−1.06)[b]	this work
[Ni**L2**]$^{2+}$	N_5	−0.91[a] (−0.96)[b]	this work
[Ni**L3**]$^{2+}$	N_4	−0.83[a] (−0.91)[b]	this work
[Ni(dip)$_2$]$^{2+}$	N_6	−1.56	18
[Ni(tpen)]$^{2+}$	N_6	−1.88[c]	23
[Ni(salen)]	N_2O_2	−1.88[c]	22
[Ni(qpy)]$^{2+}$	N_5 or N_7[d]	−1.14	16
[Ni(cyclam)]$^{2+}$	N_4	−1.58	33
[Ni(Me$_4$cyclam)]$^{2+}$	N_4	−1.15	33

[a] Obtained with Fc as an internal standard; the potential was converted to the SCE reference using a conversion factor of +0.38 V.[40] [b] Obtained in DMF directly with the SCE reference electrode. [c] The nature of the reduced species as Ni(I) complexes was not confirmed by spectroscopic or structural studies. [d] Coordination of two acetonitrile molecules in addition to the N_5 ligand is possible.[12,16]

can be attributed to the metal-to-ligand charge-transfer bands (Table 3, Figure 3). Their positions and intensities are typical for Ni(I) complexes with imine donor atoms.[16−19] Low intensity bands at ~800 and 900 nm ($\epsilon \approx 200$ M^{-1} cm^{-1}) are observed in the spectra of [Ni^I**L2**]$^+$ and [Ni^I**L3**]$^+$, which can be attributed to the d−d transitions. The low intensity d−d transitions in the spectra of the Ni(I) complexes are usually masked by much more intense charge transfer bands, with only a few exceptions.[7,19]

Electrochemical Experiments. The electrochemical reduction of complexes [Ni**L1**]$^{2+}$ and [Ni**L2**]$^{2+}$ in DMF is reversible and diffusion controlled as evidenced by i_{pa}/i_{pc} (0.80 and 0.78), peak separation of 56 mV (±3 mV) and 62 mV (±4 mV), respectively, and linear variation of i_p with $\nu^{1/2}$ (Figures 5, S3, and S4).[49] The cyclic voltammetry of [Ni**L3**]$^{2+}$ in DMF shows a quasireversible reduction wave (peak separation of 96 mV, $i_{pa}/i_{pc} = 0.65$). All complexes undergo reversible electroreduction in acetonitrile. The Ni(II) complex with a pentadentate ligand **L2** is reduced more easily than its **L1** counterpart, at about 0.1 V less negative potential (Table 4). Higher thermodynamic stability of Ni(I) in the methylated complex (with ligand **L2**) is in agreement with its longer lifetime in solution. N-methylation has been observed to stabilize complexes of Ni(I) with tetraazamacrocyclic ligands.[33] The reduction potential of the Ni(II) complex with tetradentate ligand **L3** is even less negative that that of [Ni**L2**]$^{2+}$, indicating higher thermodynamic stability of the Ni(I) oxidation state. It appears that higher denticity of the aminopyridine ligands stabilizes the complexes of Ni(II) to a greater extent than the corresponding complexes of Ni(I), thus disfavoring the low oxidation state of nickel. An analogous trend was previously noticed for a large number of the copper(II) complexes with a variety of ligands: higher thermodynamic stability of the Cu(II) species resulted in more negative values of the Cu(II)/Cu(I) redox potentials.[50]

The potentials of the Ni^{II}/Ni^{I} redox couples for the complexes with **L1**−**L3** (ca. −0.9 V vs SCE) are significantly less negative than those obtained previously for the nickel(II) complexes with nonmacrocyclic N- or N,O-donor ligands ($E_{1/2} < -1.5$ V) (Table 4). The redox potentials less negative than −1.0 V are usually observed with ligands having soft donor atoms (P, S).[6] Pyridine nitrogen donors are softer than aliphatic amines because of π-acceptor properties of an aromatic pyridine ring, allowing for better stabilization of the low oxidation state of Ni(I). This is exemplified by a relatively high redox potential of the nickel(II) complex with a substituted quinquepyridine ligand qpy (Table 4).[16] The nature of the pyridine donor atoms alone, however, is insufficient for the stabilization of Ni(I), as can be seen from the large negative redox potential of the six-coordinate complex [Ni(tpen)]$^{2+}$, which has four short methylpyridine arms attached to the ethylenediamine framework.[23] A combination of steric and electronic factors appears to be necessary for the ability of nitrogen ligands to stabilize the Ni(I) oxidation state. Long ethylpyridine arms in **L1**−**L3** allow for greater flexibility of the ligands and, therefore, facilitate structural rearrangements upon reduction from Ni(II) to Ni(I). Additionally, the ligands with long pendant arms are expected to form thermodynamically weaker complexes with Ni(II) than their short-armed analogues,[50,51] resulting in less negative reduction potentials for the Ni(II)/Ni(I) couple.

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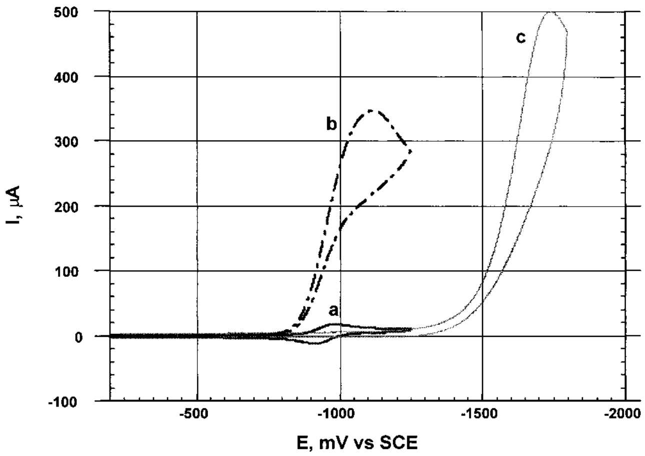
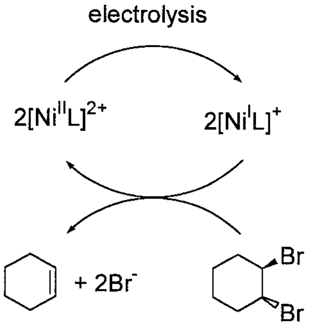


Figure 6. Cyclic voltammograms on pyrolytic graphite disk electrodes at 50 mV s^{-1} in 0.2 M TBAB in DMF of (a) 1 mM complex [Ni**L2**]$^{2+}$ alone, (b) 1 mM complex [Ni**L2**]$^{2+}$ + 12 mM 1,2-*trans*-dibromocyclohexane, and (c) 13 mM 1,2-*trans*-dibromocyclohexane alone.

Scheme 2. Proposed Pathway of the Electrocatalytic Reduction of 1,2-*trans*-Dibromocyclohexane Mediated by the Nickel Complexes



Reversible reduction of the Ni(II) complexes into Ni(I) species encouraged us to investigate their electrocatalytic properties. When 1,2-*trans*-dibromocylcohexane was added to the solutions of [Ni**L1**]$^{2+}$ and [Ni**L2**]$^{2+}$ in DMF, the reduction current greatly increased, and the reoxidation peak disappeared (Figure 6). These results are indicative of the electrocatalytic reduction of the vicinal dibromide leading to cyclohexene.[52] The large catalytic currents observed ($i_{cat}/i_D = 20$, Figure 6) are consistent with the participation of electrochemically generated Ni(I) species as mediators of the organic halide reduction.[3,22,53] Electrocatalysis carried out by nickel(II) anion radical species is known to be much less efficient.[4] Therefore, the electrochemical experiments are also consistent with the formation of nickel(I) species upon the reduction of complexes [Ni**L1**]$^{2+}$ and [Ni**L2**]$^{2+}$ (Scheme 2).

The catalytic role of the nickel complexes in the electrochemical reduction of 1,2-*trans*-dibromocyclohexane (DBCH) was confirmed by bulk electrolysis experiments, using an 18-fold excess of the substrate with respect to the metal complex. Electrochemical reduction of DBCH at a constant potential of −1300 mV and −1170 mV with [Ni**L1**]$^{2+}$ and [Ni**L2**]$^{2+}$, respectively, gave a single product, cyclohexene, in a high yield (69% and 88% based on DBCH, uncorrected for evaporation), with about ~50% current efficiency. High catalytic activity of simple, easily synthesized nickel complexes with aminopyridine ligands is promising for their applications in electrosynthesis.

Conclusions

Pentadentate aminopyridine ligands **L1** and **L2** with ethylenepyridine arms form five-coordinate square-pyramidal nickel(II) complexes both in the solid state and in solution. An analogous tetradentate ligand **L3** forms a low-spin square-planar Ni(II) complex in the solid state and in noncoordinating solvent (nitromethane), while in coordinating solvents it preferentially exists in a high-spin state. The nickel(II) complexes with all three ligands (**L1**−**L3**) can be reversibly reduced to relatively stable ERP-active nickel(I) species in solution. Identical EPR spectra of [Ni**L2**]$^{+}$ and [Ni**L3**]$^{+}$ indicate a similar coordination environment of Ni(I) in these two complexes, suggesting dissociation of one of the ethylpyridine arms upon reduction of [Ni**L2**]$^{2+}$. The half-wave Ni(II)/Ni(I) potentials increase in the series [Ni**L1**]$^{2+}$ > [Ni**L2**]$^{2+}$ > [Ni**L3**]$^{2+}$. The nickel(I) complexes with ligands **L2** and **L3** are also substantially more stable kinetically than the complex with **L1**, showing that N-methylation in the ligand system stabilizes the lower oxidation state. The nickel(II) complexes with **L1** and **L2** show high catalytic activity in the electroreduction of 1,2-*trans*-dibromocylcohexane into cyclohexene.

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Supporting Information Available: Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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