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One-pot template synthesis and properties of Ni(II) complexes of 16-membered hexaaza macrocycles

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Abstract

A new nickel(II) complex of the 16-membered hexaaza macrocyclic ligand “1,3,7,9,11,15-hexaazacyclohexadecane, (L^1); 1,9-dimethyl-, (L^2); 1,9-diethyl-, (L^3); 1,9-dibutyl^{iso}-, (L^4); 1,9-dibutyl^{sec}-, (L^5) and 1,9-dibenzyl-1,3,7,9,11,15-hexaazacyclohexadecane (L^6)” have been prepared by the one-pot template reactions of formaldehyde and propylenediamine (pn) with alkyl and benzyl amine in the presence of nickel(II) ion. The complexes of a hexaaza macrocycle have been characterized by elemental analyses, IR, UV–Vis and ^{13}C NMR spectroscopy, conductometric and magnetic measurements. The complexes of nickel(II) have square-planar coordination geometry in the solid state and in nitromethane. The spectra of $[NiL^{1-6}](ClO_4)_2$ shows that the four secondary nitrogen atoms are coordinated to the nickel(II) ion. Synthesis, characterization and solution behavior of the nickel(II) complexes of hexaaza macrocycle are reported.

Keywords: Nickel complexes; Macrocyclic complexes; Template synthesis; Hexaazacyclohexadecane

1. Introduction

Coordination geometry and properties of most transition metal complexes with 14-membered hexaaza macrocyclic ligands containing primary amine have been studied [1–4]. However, most of them were tetraaza macrocyclic ligands, and 16-membered macrocyclic ligands containing six nitrogen atoms in the fully saturated macrocyclic framework have not been reported to date. We have been interested in the synthesis of various types of polyaza macrocyclic complexes containing primary amino alkyl groups from one-pot metal template condensation reactions.

Metal template condensation reaction often provides selective routes toward products that are not obtainable in the absence of metal ions. Especially, template reactions involving formaldehyde and amines facilitate the preparation of saturated polyaza multidentate macrocyclic and macropolycyclic complexes [5–10]. The reactions are simple “one-pot reactions”, cheap and high yielding. Metal template condensation reactions involving amines and formaldehyde have been employed in the preparation of various saturated polyaza macrocyclic complexes as described in Eqs. (1)–(7), [9,11–16].

$$\mathrm{Ni(II) + dien + CH_2O \rightarrow [Ni(A)]^{2+}} \quad (1)$$

$$\mathrm{Ni(II) + H_2N(CH_2)_2NH(CH_2)_3NH_2 + CH_2O \rightarrow [Ni(B)]^{2+}} \quad (2)$$

$$\mathrm{Ni(II) + en + CH_2O + NH_3 \rightarrow [Ni(C)]^{2+}} \quad (3)$$

$$\mathrm{[Ni(C)]^{2+} + CH_2O + CH_3NH_2 \rightarrow [Ni(D)]^{2+}} \quad (4)$$

$$\mathrm{[M(en)_3]^{n+} + 6CH_2O + 2NH_3 \rightarrow [M(E)]^{n+}} \quad (5)$$

$$\mathrm{Ni(II) + trien + CH_2O + en \rightarrow [Ni(F)]^{2+}} \quad (6)$$

$$\mathrm{Ni(II) + H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2 + CH_2O + en \rightarrow [Ni(G)]^{2+}} \quad (7)$$

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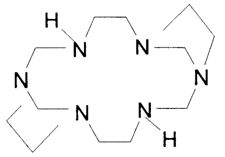

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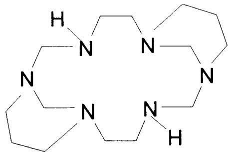

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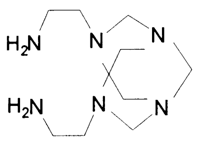

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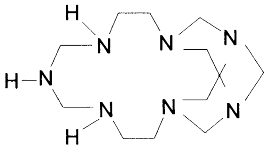

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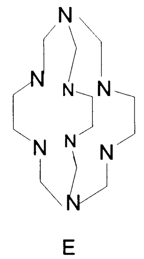

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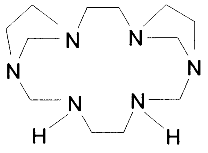

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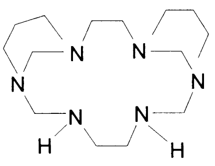

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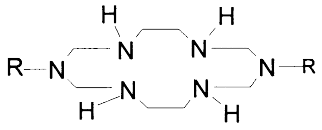

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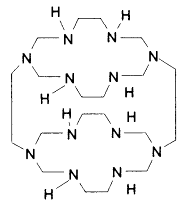
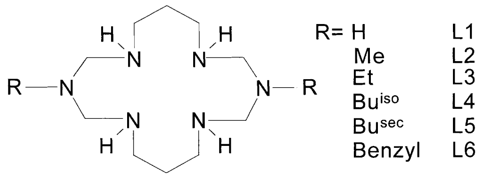


I

More recently Co(II), Pt(IV) and macrobicyclic complexes E were prepared from the condensation reaction of $[M(en)_3]^{n+}$, formaldehyde and ammonia (Eq. (5)), and also attempted to prepare the complexes of various ligands such as H and I from the condensation reaction of ethylenediamine, formaldehyde and ammonia by utilizing Ni(II) ion as a template [17–19]. In this paper, we report the synthesis, characterization and properties of the new Ni(II) complex of 1,3,7,9,11,15-hexaazacyclohexadecane, (L^1); 1,9-dimethyl-, (L^2); 1,9-diethyl-, (L^3); 1,9-dibutyl^{iso}-, (L^4); 1,9-dibutyl^{sec}-, (L^5) and 1,9-dibenzyl-1,3,7,9,11,15-hexaazacyclohexadecane (L^6); $[Ni(R_2[16]aneN_6)]^{2+}$ (Scheme 1). The mononuclear were prepared from the template condensation of propylenediamine (pn), formaldehyde and alkyl amines (Eq. (8)).

$$\mathrm{Ni(II)} + 2\mathrm{Pn} + 4\mathrm{CH_2O} + 2\mathrm{RNH_2} \rightarrow [\mathrm{Ni(R_2[16]aneN6)}]^{2+} \quad (8)$$



Scheme 1.

2. Experimental

2.1. Materials and measurements

2.1.1. Safety note

Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. For the spectroscopic measurements, water was distilled and organic solvents were purified according to the literature method [20]. For electrochemical experiments, high-purity acetonitrile was obtained from Aldrich Chemical Co. and dried over 5 Å molecular sieves. Electronic absorption spectra were obtained with a Shimadzu UV–Vis scanning spectrophotometer (Model 2101 PC), FTIR spectra with a Shimadzu Varian 4300 spectrophotometer, ^{13}C and ^{1}H NMR spectra with a Bruker AC 80 (in D_2O, CH_3CN-d_3, Me_2SO-d_6 and CH_3NO_2-d_3 as solvent) and conductance measurements with a Metrohm Herisau conductometer E 518. The elemental analysis (carbon, hydrogen and nitrogen) of complexes was obtained from Carlo ERBA Model EA 1108 analyzer. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK-1 magnetic susceptibility balance. Cyclic voltammetry was carried out with Metrohm 746. The electrochemical data were obtained in acetonitrile with 0.1 M $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte. The working electrode was a platinum disk, the auxiliary electrode was a coiled platinum wire and the reference electrode was Ag/$AgClO_4$ (0.1 M in CH_3CN), which showed +0.24 V vs. SCE. Atomic absorption spectra (AAS) were recorded on a Perkin–Elmer 4100-1319 spectrophotometer.

2.2. Preparation of $[Ni(L^2)](ClO_4)_2$

To a stirred methanol solution (100 ml) of $NiCl_2 \cdot 6H_2O$ (10.00 g, 42.07 mmol) were slowly added pn (4.98 g, 84.20 mmol), 36% formaldehyde (13 ml) and 36% methylamine (10.47 ml, 84.20 mmol). The mixture was heated at reflux for 20 h until a dark orange solution resulted. The solution was cooled to room temperature and filtered to remove nickel hydroxide. Excess perchloric acid or lithium perchlorate dissolved in methanol was added to the filtrate, and the mixture was kept in the refrigerator until yellow crystals formed. The yellow crystals were filtered, washed with methanol and air-dried. The crystals were recrystallized from hot water. Yield: ~49%. Anal. Calc. for $NiC_{12}H_{30}N_6Cl_2O_8$: C, 27.93; H, 5.86; N, 16.28; Ni, 11.37. Found: C, 27.87; H, 5.81; N, 16.36; Ni, 11.32%.

2.3. Preparation of $[Ni(L^1)](ClO_4)_2$

This compound was prepared by a method similar to that for $[Ni(L^2)(ClO_4)_2]$ except that 25% ammonia (6.3 ml, 84.20 mmol) was used instead of methylamine. Yield: ~46%. Anal. Calc. for $NiC_{10}H_{26}N_6Cl_2O_8$: C, 24.62; H, 5.37; N, 17.22; Ni, 12.03. Found: C, 24.48; H, 5.26; N, 17.35; Ni, 11.91%.

2.4. Preparation of $[Ni(L^3)](ClO_4)_2$

This complex was prepared by a method similar to that for $[Ni(L^2)](ClO_4)_2$ except that 50% ethylamine (8.72 ml, 84.20 mmol) was used instead of methylamine. Yield: ~54%. Anal. Calc. for $NiC_{14}H_{34}N_6Cl_2O_8$: C, 30.91; H, 6.30; N, 15.45; Ni, 10.79. Found: C, 30.82; H, 6.23; N, 15.56; Ni, 10.71%.

2.5. Preparation of $[Ni(L^4)](ClO_4)_2$

This complex was prepared by a method similar to that for $[Ni(L^2)](ClO_4)_2$ except that *iso*-butyl amine (8.36 ml, 84.20 mmol) was used instead of methylamine. Yield: ~41%. Anal. Calc. for $NiC_{18}H_{42}N_6Cl_2O_8$: C, 36.02; H, 7.05; N, 14.00; Ni, 9.78. Found: C, 35.91, H, 6.94; N, 14.17; Ni, 9.69%.

2.6. Preparation of $[Ni(L^5)](ClO_4)_2$

This hexaaza macrocycle complex was prepared by a method similar to that for $[Ni(L^2)](ClO_4)_2$ except that *sec*-butyl amine (8.55 ml, 84.20 mmol) was used instead of methylamine. Yield: ~38%. Anal. Calc. for $NiC_{18}H_{42}N_6Cl_2O_8$: C, 36.02; H, 7.05; N, 14.00; Ni, 9.78. Found: C, 35.82; H, 6.87; N, 14.22; Ni, 9.58%.

2.7. Preparation of $[Ni(L^6)](ClO_4)_2$

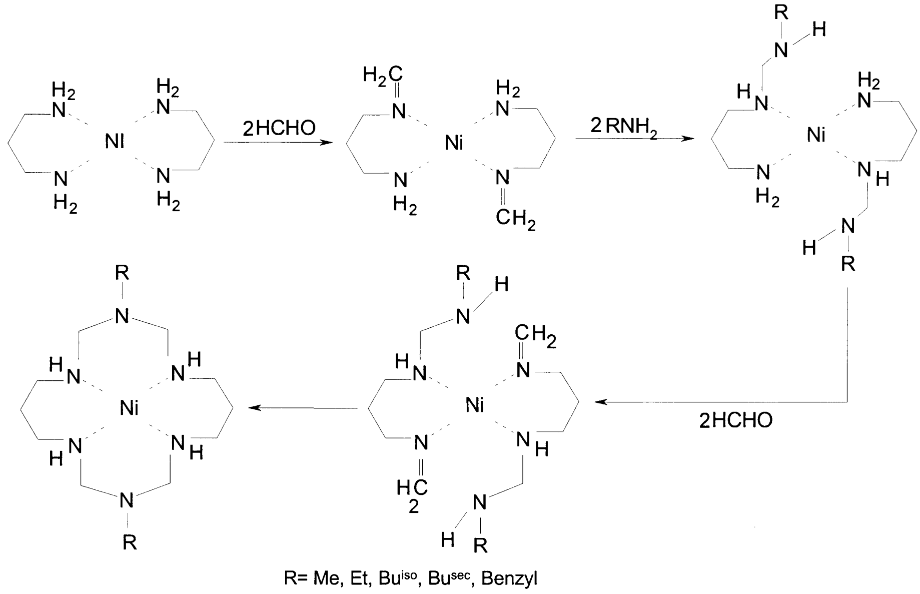
This complex was prepared by a method similar to that for $[Ni(L^2)](ClO_4)_2$ except that benzyl amine (9.20 ml, 84.20 mol) was used instead of methylamine. Yield: ~62%. Anal. Calc. for $NiC_{24}H_{38}N_6Cl_2O_8$: C, 43.14; H, 5.73; N, 12.58; Ni, 8.78. Found: C, 43.07; H, 5.65; N, 12.68; Ni, 8.69%.

2.8. Preparation of $[Ni(L^{1-6})(NCS)_2]$

To a saturated hot aqueous solution of perchlorate salt of the appropriate 16-membered hexaaza macrocycle nickel(II) "$[Ni(L^{1-6})]^{2+}$" was added excess KSCN dissolved in a minimum amount of hot water. The solution was allowed to stand at room temperature, and then the pink precipitate formed was filtered, washed with a 1:2 mixture of water and methanol and dried in vacuum. Anal. Calc. for $NiC_{12}H_{26}N_8S_2$: C, 35.57; H, 6.47; N, 27.65; Ni, 14.48. Found: C, 35.42; H, 6.31; N, 27.75; Ni, 14.37%. Anal. Calc. for $NiC_{14}H_{30}N_8S_2$: C, 38.81; H, 6.98; N, 25.86; Ni, 13.55. Found: C, 38.71; H, 6.87; N, 25.98; Ni, 13.41%. Anal. Calc. for $NiC_{16}H_{34}N_8S_2$: C, 41.65; H, 7.43; N, 24.29; Ni, 12.72. Found: C, 41.12; H, 7.34; N, 24.35; Ni, 12.61%. Anal. Calc. for $NiC_{26}H_{38}N_8S_2$: C, 53.34; H, 6.54; N, 19.14; Ni, 10.02. Found: C, 53.25; H, 6.46; N, 19.25; Ni, 9.94%.

2.9. Preparation of $[Ni(L^{1-6})](PF_6)_2$

To an acetonitrile (50 ml) suspension of $[Ni(L^{1-6})](ClO_4)_2$ (0.5 g) was added excess NH_4PF_6. $[Ni(L^{1-6})](ClO_4)_2$ went into the solution and white precipitates of NH_4ClO_4 were formed. NH_4ClO_4 was filtered off, and the filtrate was concentrated to 25 ml. Water (25 ml) was added to the solution, and the mixture was kept in a refrigerator. The yellow precipitates formed were filtered, washed with a 6:1 mixture of water and acetonitrile, and dried in vacuum. ^{13}C NMR (CD_3NO_2): $\delta = 37.80$ (N–Me), 48.5, 50.80 (N–C–C–C–N), 70.86 (N–C–N). Anal. Calc. for $NiC_{10}H_{26}N_6P_2F_{12}$: C, 20.74; H, 4.53; N, 14.52; Ni, 10.14. Found: C, 20.65; H, 4.42; N, 14.68; Ni, 10.06%. Anal. Calc. for $NiC_{12}H_{30}N_6P_2F_{12}$: C, 23.74; H, 4.98; N, 13.84; Ni, 9.67. Found: C, 23.61; H, 4.79; N, 13.98; Ni, 9.54%. Anal. Calc. for $NiC_{16}H_{38}N_6P_2F_{12}$: C, 28.98; H, 5.78; N, 12.67; Ni, 8.85. Found: C, 28.84; H, 5.71; N,



Scheme 2.

12.74; Ni, 8.78%. Anal. Calc. for $NiC_{24}H_{38}N_6P_2F_{12}$: C, 37.97; H, 5.05; N, 11.07; Ni, 7.73. Found: C, 37.81; H, 4.94; N, 11.18; Ni, 7.68%.

3. Results and discussion

3.1. Synthesis and properties

Template condensation reaction of pn with formaldehyde, in the presence of the Ni(II) ion, was expected to produce a mixture of the mononuclear 16-membered hexaaza macrocycle complex "$[Ni(R_2[16]aneN_6]^{2+}$" (Scheme 2). It was observed that the product obtained from the reactions was largely affected by the molar ratio of the reactants. The16-membered hexaaza macrocycle nickel(II) "$[NiL^n](ClO_4)_2$ ($n = 1-6$)" was readily prepared as the main product by the reaction of the Ni(II) ion, Pn, CH_2O and $R-NH_2$ in a 1:2:4:2 molar ratio, followed by the addition of a lithium perchlorate or perchloric acid. The crude product often contains small amount of uncharacterized by-products. However,

Table 1
Spectral and conductance data for 16-membered hexaaza macrocyclic nickel(II) complexes at 25 °C

Complex	IR (cm^{-1})	Electronic spectra [a] λ_{max} (nm) (ε, M^{-1} cm^{-1})	Λ_M [a] (Ω^{-1} cm^{-1} mol^{-1})
$[Ni(L^1)](ClO_4)$	ν_{N-H} 3215	447(62), 456(31) [b], 461(57) [d], 453(60) [e]	235
$[Ni(L^2)](ClO_4)$	ν_{N-H} 3210	447(59), 457(35) [b], 462(55) [d], 454(58) [e]	242
$[Ni(L^3)](ClO_4)$	ν_{N-H} 3175	446(60), 457(36) [b], 460(51) [d], 452(59) [e]	247
$[Ni(L^4)](ClO_4)$	ν_{N-H} 3165	449(61), 459(37) [b], 464(55) [d], 454(58) [e]	252
$[Ni(L^5)](ClO_4)$	ν_{N-H} 3160	449(59), 459(37) [b], 464(55) [d], 454(57) [e]	256
$[Ni(L^6)](ClO_4)$	ν_{N-H} 3218	446(61), 454(32) [b], 460(50) [d], 451(59) [e]	240
$[Ni(L^1)(NCS)_2]$	ν_{CN} 2050, ν_{CS} 780	501 [c]	–
$[Ni(L^2)(NCS)_2]$	ν_{CN} 2042, ν_{CS} 781	496 [c]	–
$[Ni(L^3)(NCS)_2]$	ν_{CN} 2031, ν_{CS} 781	497 [c]	–
$[Ni(L^6)(NCS)_2]$	ν_{CN} 2030, ν_{CS} 780	493 [c]	–
$[Ni(L^1)](PF_6)_2$	ν_{N-H} 3214	449(65), 461(23) [b], 443(59) [d]	237
$[Ni(L^2)](PF_6)_2$	ν_{N-H} 3211	447(64), 459(27) [b], 442(58) [d]	243
$[Ni(L^3)](PF_6)_2$	ν_{N-H} 3173	450(58), 464(31) [b], 447(55) [d]	250
$[Ni(L^6)](PF_6)_2$	ν_{N-H} 3218	448(60), 461(33) [b], 446(50) [d]	246

[a] In nitromethane solutions unless otherwise specified.
[b] In acetonitrile solutions.
[c] In Me_2SO solutions with excess NaSCN.
[d] In water solutions.
[e] In 3.0 M NaCl aqueous solution.

the mononuclear complex can be readily isolated by fractional recrystallization of the product from approximately 0.05 M $HClO_4$ aqueous solutions.

The yellow complexes "$[Ni(R_2[16]aneN_6)](ClO_4)_2$" readily dissolve in polar solvents such as H_2O, CH_3CN, CH_3NO_2 and Me_2SO_2. However, PF_6^- salts of the complexes readily dissolve in nitromethane and water. The nickel(II) complexes are extremely stable in the solid state and in solution, and are relatively stable against ligand dissociation even in highly acidic solutions. $[Ni(R_2[16]aneN_6)]^{2+}$ react with excess KSCN in aqueous solution to form tetragonal complexes $[Ni(R_2[16]aneN_6)(NCS)_2]$, whose IR spectra (Table 1) show that the nitrogen atoms of NCS^- ligands are coordinated to Ni(II) ion [21]. Pink complexes of thiocyanate are not soluble in most of the solvents such as CH_3CN, EtOH, DMF and in H_2O or Me_2SO to become yellow $[Ni(R_2[16]aneN_6)]^{2+}$. The IR spectra of complexes (Table 1) show a single absorption around 3200 cm^{-1}, which is attributed to ν_{N-H} of the coordinated secondary amines. A much higher ν_{N-H} value (3220 cm^{-1}) for $[Ni\{(CH_3)_2[14]aneN_6\}](ClO_4)_2$, [22], than that (3210 cm^{-1}) for $[Ni\{(CH_3)_2[16]aneN_6\}](ClO_4)_2$ indicates that the Ni–N interaction in 16-membered is much weaker than in 14-membered hexaaza complex. The molar conductance values of (242 S cm^2 mol^{-1}) measured in water correspond to 1:2 electrolytes. The magnetic moments (-0.15 to -0.6 μ_B) of the nickel(II) complexes measured in the solid state correspond to the square-planar coordination geometry of the complexes. The diamagnetic nature of the Ni(II) complex of L^2 has allowed its characterization by NMR spectrometry. ^1H NMR spectra of the Ni(II) complexes of L^n exhibit very broad peaks in D_2O, CH_3CN-d_3 and Me_2SO-d_6 but sharp resolvable peaks in CH_3NO_2-d_3. This indicates that a considerable amount of paramagnetic octahedral species of $[Ni(L^n)(solvent)_2]^{2+}$ exists in the donating solvents, whereas the Ni(II) complexes of L^n exist primarily as diamagnetic square-planar in CH_3NO_2-d_3. The ^{13}C NMR spectrum of $[Ni\{(CH_3)_2[16]aneN_6\}](PF_6)_2$ shows two carbon peaks of $N-CH_2CH_2CH_2-N$ linkages at 48.5, 50.80 and 37.8 ppm for N–Me. One peak corresponding to the $N-CH_2-N$ linkage is observed at 70.86 ppm.

The electronic spectra (Table 1) of Ni(II) complexes are comparable with those of square-planar Ni(II) complexes with saturated tetraaza macrocycles, indicating that the hexaaza ligands of this study do not differ significantly from the tetraaza ligands with respect to the ligand field strength [11–14]. Table 1 shows that the molar absorption coefficient of the ligand field transition band for complexes measured in water or acetonitrile is smaller than that in nitromethane, a non-coordinating solvent. This result is quite similar to those reported for other related polyaza macrocyclic complexes, indicating that the complex dissolves in water or acetonitrile to produce an equilibrium mixture of square-planar $[Ni\{R_2[16]aneN_6]^{2+}$ and octahedral *trans*-$[Ni\{R_2[16]aneN_6\}(solvent)_2]^{2+}$; (solvent = H_2O or MeCN) [23,24]. In general, the ligand structure, nature of the solvent and concentration of added electrolyte affect the equilibrium. The molar absorption coefficient of the ligand field transition band for $[Ni\{R_2[16]aneN_6\}]$ measured in 3.0 M NaCl aqueous solutions is somewhat higher than that in pure water (Table 1). A similar result was also observed in the solution containing NaBr, $NaNO_3$ or $NaClO_4$. This corresponds to the generally observed trend that neutral salts such as NaCl dissolved in water from their hydrate, reduce the effective concentration of free water, and then increase the concentration of square-planar species [25,26]. 14-Membered hexaaza and some tetraaza macrocyclic Ni(II) complexes exist in water as equilibrium mixture of yellow diamagnetic square-planar $[Ni(L)]^{2+}$ and blue (or violet) paramagnetic octahedral $[Ni(L)(H_2O)_2]^{2+}$ [27–30].

Cyclic voltammetric data are summarized in Table 2. Table 2 shows that oxidation and reduction potentials of

Table 2
Cyclic voltammetric data for Ni(II) complexes with 16-membered hexaaza macrocycle [a] [b]

Complexes	Oxidation potential (V) $[M(L^{1-6})]^{2+}/[M (L^{1-6})]^{+}$	Reduction potential (V) $[M(L^{1-6})]^{2+}/[M (L^{1-6})]^{3+}$	Reference
$[Ni([16]aneN_6)]^{2+}$	+0.92	−1.58	This work
$[Ni((Me)_2[16]aneN_6)]^{2+}$	+0.94	−1.57	This work
$[Ni((Et)_2[16]aneN_6)]^{2+}$	+0.93	−1.47	This work
$[Ni((Bu^{iso})_2[16]aneN_6)]^{2+}$	+0.91	−1.49	This work
$[Ni((Bu^{sec})_2[16]aneN_6)]^{2+}$	+0.91	−1.49	This work
$[Ni(benzyl)_2[16]aneN_6]^{2+}$	+0.93	−1.56	This work
$[Ni((Me)_2[14]aneN_6)]^{2+}$	+0.93	−1.55	[22]
$[Ni((Et)_2R[14]aneN_6)]^{2+}$	+0.90	−1.47	[22]
$[Ni([14]aneN_6)]^{2+}$	+0.91	−1.46	[35]
$[Ni((Me)_2[14]aneN_6)]^{2+}$	+0.92	−1.49	[35]

[a] Measured in acetonitrile solutions; 0.1 M $(n\text{-Bu})_4NClO_4$; vs. SCE.

[b] Redox potential of this work and Ref. [35] were measured against an Ag/Ag^+ (0.1 M) reference electrode and converted to the values measured against the SCE by adding +0.24 V.

the Ni(II) complexes of L^2–L^6 do not differ significantly from those of 14-membered hexaaza complexes. This suggests that macrocycles L^2–L^6 have Lewis basicities and hole size similar to those of the 14-membered hexaaza ligand in spite of the structural differences [31–34]. All efforts to obtain the free ligands from the complexes by treating the complexes with excess NaCN, H_2S gas or strong acid were unsuccessful. Free ligand L^2–L^6 must be unstable because they contain diamine moieties with secondary nitrogen.

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