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Template Condensation Reactions of Formaldehyde with Tetraamines and Ethylenediamine: Preparation, Properties, and Structures of Nickel(II) and Copper(II) Complexes of Hexaaza Macrotricyclic Ligands 1,3,6,8,11,14-Hexaazatricyclo[12.2.1.1^{8,11}]octadecane and 1,3,6,8,12,15-Hexaazatricyclo[13.3.1.1^{8,12}]eicosane

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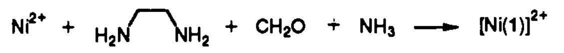
Square-planar Ni(II) and Cu(II) complexes of macrotricyclic ligands 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1^{8,11}]octadecane (A) and 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}]eicosane (B) have been prepared from the simple template condensation reactions of formaldehyde and ethylenediamine with 2,2,2-tet and 3,2,3-tet, respectively, in the presence of metal ion. Infrared and UV/vis spectra indicate that complexes $[M(B)]^{2+}$ containing 1,3-diazacyclohexane small-ring moieties fused to the hexaaza macrocyclic framework exert weaker M–N interactions and weaker ligand field strengths than complexes $[M(A)]^{2+}$ containing 1,3-diazacyclopentane ring moieties fused to the macrocycle. $[Ni(A)](ClO_4)_2$ (A = $C_{12}H_{26}N_6$) crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.502$ (7) Å, $b = 9.476$ (9) Å, $c = 13.491$ (5) Å, $\beta = 93.14$ (4)°, and $Z = 4$. The structure was solved by direct methods and refined anisotropically to R values of $R = 0.055$ and $R_w = 0.057$ for 2692 observed reflections with $F \geq 2\sigma(F)$ measured with Mo Kα radiation on a CAD-4 diffractometer. $[Ni(B)](ClO_4)_2 \cdot {}^1/_2H_2O$ (B = $C_{14}H_{30}N_6$) crystallizes in the monoclinic space group $C2/c$ with $a = 32.569$ (15) Å, $b = 9.577$ (4) Å, $c = 14.400$ (6) Å, $\beta = 111.31$ (4)°, and $Z = 8$. The structure was solved by Patterson methods and refined to R values of $R = 0.038$ and $R_w = 0.048$ for 3334 observed reflections measured with Mo Kα radiation on a CAD-4 diffractometer. The X-ray structures indicate that two 1,3-diazacyclopentane ring moieties in $[Ni(A)](ClO_4)_2$ and two 1,3-diazacyclohexane ring moieties in $[Ni(B)](ClO_4)_2 \cdot {}^1/_2H_2O$ are located oppositely and almost perpendicularly to the plane of the ruffled 14-membered macrocycle. The average Ni–N bond distances are 1.923 (8) Å for $[Ni(A)](ClO_4)_2$ and 1.951 (13) Å for $[Ni(B)](ClO_4)_2 \cdot {}^1/_2H_2O$. The fusion of the 1,3-diazacyclopentane ring forces more acute angles within the six-membered chelate, accounting for the slight contraction. The Ni(II) complexes of A and B exhibit equilibria between square-planar and octahedral species in aqueous solutions. The equilibrium constant for square-planar/octahedral conversion is much larger for $[Ni(B)]^{2+}$ than for $[Ni(A)]^{2+}$. Cyclic voltammetry indicates that both oxidation and reduction of Ni(II)/Ni(III) and Ni(II)/Ni(I) are significantly easier for $[Ni(B)]^{2+}$ than for $[Ni(A)]^{2+}$.

Introduction

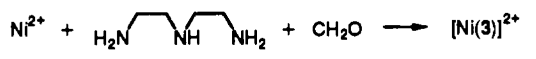
Metal template syntheses often provide selective routes toward products that are not obtainable in the absence of metal ions. Especially, template reactions involving formaldehyde and amines facilitate the preparation of saturated polyaza multidentate, macrocyclic, and macropolycyclic complexes.[1-6] The reactions are simple ("one-pot reactions"), cheap, and high yielding.

Previously, the Ni(II) complexes of **1–4** were prepared in our laboratory from the template condensation reactions as described in eqs 1–4.[4,6]

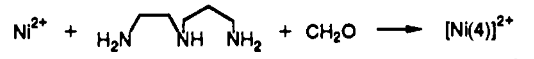


$$Ni^{2+} + H_2NCH_2CH_2NH_2 + CH_2O + NH_3 \longrightarrow [Ni(1)]^{2+} \quad (1)$$

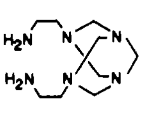
$$[Ni(1)]^{2+} + CH_2O + CH_3NH_2 \longrightarrow [Ni(2)]^{2+} \quad (2)$$



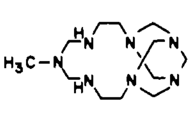
$$Ni^{2+} + H_2NCH_2CH_2NHCH_2CH_2NH_2 + CH_2O \longrightarrow [Ni(3)]^{2+} \quad (3)$$



$$Ni^{2+} + H_2NCH_2CH_2NHCH_2CH_2CH_2NH_2 + CH_2O \longrightarrow [Ni(4)]^{2+} \quad (4)$$



1



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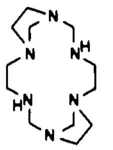

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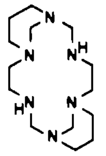
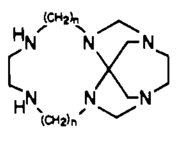
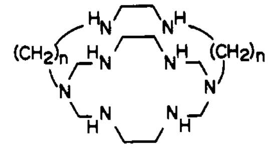


4

For the Ni(II) complexes of **1** and **2**, N–N bite distances involving tetraazabicyclononane were unusually short and the complexes exhibit interesting spectroscopic properties.[4] Therefore, we have attempted to synthesize complexes of **5** from the reactions of tetramine, formaldehyde, and ethylenediamine in the presence of Ni(II) or Cu(II) ion to see how the spectroscopic properties and structures of the complexes are influenced by having an ethylene moiety substituted for a methylene moiety linking two uncoordinated nitrogens. We also expected that complexes of **6** might be formed from the reaction because the molecular models for the complexes of **6** showed no strain.



5



6 (n=2or3)

However, the reaction yielded complexes of A and B (A = $C_{12}H_{26}N_6$ = 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1^{8,11}]octadecane; B = $C_{14}H_{30}N_6$ = 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}]eicosane) instead of **5** or **6**. The macrocyclic ligands A and B resemble those of **3** and **4**, respectively, although the position of the small-ring moieties is different.

This paper presents the synthesis and structures of Ni(II) and Cu(II) complexes of A and B. Comparisons of the spectroscopic and electrochemical properties of these two complexes are made as well as with the complexes of **3** and **4**. The complexes of A and B contain fully saturated hexaaza macrotricyclic ligands that have rarely been reported.[5,6] Furthermore, this report reveals, for the first time to the best of our knowledge, that the size of the small-ring moieties fused to the macrocyclic ligand significantly affects the metal–donor distances as well as the spectroscopic and electrochemical properties of the complexes. This report also shows that equilibria between square-planar and octahedral species of

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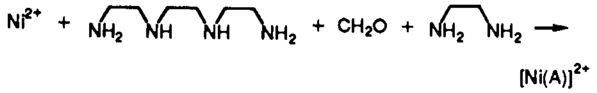
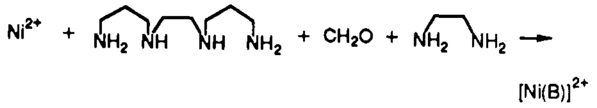
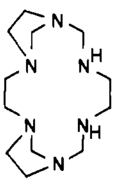
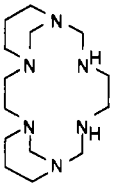

(5)


(6)


A


B

Ni(II) complexes in aqueous solutions are also greatly influenced by the small-ring moieties fused to the macrocyclic ligand.

Experimental Section

Reagents. 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.[7]

Measurements. Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer. Conductance measurements were performed by using a Metrohm Herisau E518 conductometer and RC-216B$_2$ conductivity bridge. ^1H and ^{13}C NMR spectra were recorded on a Bruker WP80 FT NMR spectrometer. Electronic absorption spectra were obtained on a Shimadzu 260 UV/vis spectrophotometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Equilibrium constants were calculated from UV/vis spectra. For variable-temperature measurements, the temperature was controlled to within ±0.1 °C by using a thermostated cell holder, connected to a Shimadzu TB-85 circulating thermobath. The concentration of the complexes was made (2.9–5.1) $\times 10^{-3}$ M in 0.07 M $NaClO_4$ aqueous solutions.

Cyclic voltammetry was carried out with CV-1B cyclic voltammograph coupled with a Hewlett Packard 7015A X-Y recorder. 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 a SCE.

Synthesis. Safety Note. *Caution*! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

$[Ni(A)](ClO_4)_2$ (A = $C_{12}H_{26}N_6$). To a stirred methanol solution (50 mL) of $NiCl_2 \cdot 6H_2O$ (11.9 g) were added 82% diethylenetriamine (8.9 g), 36% aqueous formaldehyde (16.2 mL), and then ethylenediamine (3 g). The mixture was heated at reflux for 12 h until a dark orange solution resulted. The solution was filtered to remove insoluble material and cooled to room temperature. A saturated methanol solution of excess $LiClO_4 \cdot 3H_2O$ (2 g) was added to the filtrate, and the solution was allowed to stand in a refrigerator until orange crystals formed. The crystals were filtered out, washed with methanol, and recrystallized from hot water. The single crystals for X-ray crystallographic work were obtained by dissolving the crystals in a warm (~50 °C) 10:1 acetonitrile–ethanol mixture and allowing the solution to stand at room temperature. Yield: ~70%. Anal. Calcd for $NiC_{12}H_{26}N_6Cl_2O_8$: C, 28.15; H, 5.12; N, 16.41. Found: C, 28.14; H, 4.98; N, 15.89. ^{13}C NMR (CD_3CN) for $[Ni(A)](PF_6)_2$: δ 47.8, 48.8, 55.8, 55.9, 70.7, 76.1.

$[Ni(B)](ClO_4)_2 \cdot {}^1/_2H_2O$ (B = $C_{14}H_{30}N_6$). To a stirred methanol solution (50 mL) of $NiCl_2 \cdot 6H_2O$ (11.9 g) were added *N*,*N'*-bis(3-aminopropyl)ethylenediamine (8.7 g), 36% aqueous formaldehyde (16.2 mL), and then ethylenediamine (3 g). The mixture was heated at reflux for 6 h. The solution was filtered hot and cooled to room temperature. A saturated methanol solution of excess $LiClO_4 \cdot 3H_2O$ (2 g) was added to the solution, and the solution was allowed to stand in a refrigerator until reddish orange crystals formed. The crystals were filtered out, washed with methanol, air-dried, and then recrystallized from hot water. The single crystals for X-ray crystallographic work were obtained by dissolving the crystals in a warm (~50 °C) 10:1 acetonitrile–ethanol mixture and allowing the solution to stand at room temperature. Yield: ~80%. Anal. Calcd for $NiC_{14}H_{31}N_6Cl_2O_{8.5}$: C, 30.63; H, 5.69; N, 15.31. Found: C, 30.93; H, 5.81; N, 15.61. ^{13}C NMR (CD_3NO_2) for $[Ni(B)](PF_6)_2$: δ 24.3, 48.4, 49.3, 57.0, 58.2, 71.0, 74.8.

Table I. Crystal Data for $[Ni(C_{12}H_{26}N_6)](ClO_4)_2$ and $[Ni(C_{14}H_{30}N_6)](ClO_4)_2 \cdot {}^1/_2H_2O$

emp formula	$NiC_{12}H_{26}N_6Cl_2O_8$	$NiC_{14}H_{31}N_6Cl_2O_{9.5}$
fw	511.99	549.06
cryst system	monoclinic	monoclinic
a, Å	15.502 (7)	32.569 (15)
b, Å	9.476 (9)	9.577 (4)
c, Å	13.491 (5)	14.400 (6)
β, deg	93.14 (4)	111.31 (4)
V, Å^3	1979 (3)	4185 (5)
space group	$P2_1/c$	$C2/c$
Z	4	8
D(calcd), g/cm^3	1.69	1.75
D(exptl), g/cm^3	1.72	1.74
μ, mm^{-1}	1.31	1.25
T_{max}, T_{min}	0.97, 0.95	0.96, 0.93
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
temp, K	295–300	295–300
R, R_w, %	5.5, 5.7	3.8, 4.8
GOF	0.98	1.12

$[Cu(A)](ClO_4)_2$. This compound was prepared by a method similar to that for $[Ni(A)](ClO_4)_2$ except that $Cu(OAc)_2 \cdot H_2O$ (10 g) was used instead of $NiCl_2 \cdot 6H_2O$. The red crystals of square-planar complexes were filtered out, which were mixed with a trace amount of five-coordinated violet crystals. The products were recrystallized from hot water. Yield: ~60%. Anal. Calcd for $CuC_{12}H_{26}N_6Cl_2O_8$: C, 27.89; H, 5.07; N, 16.26. Found: C, 27.76; H, 5.08; N, 15.59.

$[Cu(A)Cl]ClO_4$. This compound was synthesized by a method similar to that for $[Cu(A)](ClO_4)_2$ except that $CuCl_2 \cdot 2H_2O$ (8.5 g) was used instead of $Cu(OAc)_2 \cdot H_2O$. The violet crystals formed were filtered out, washed with methanol, and air-dried. Yield: ~60%. Anal. Calcd for $CuC_{12}H_{26}N_6Cl_2O_4$: C, 31.83; H, 5.78; N, 18.56. Found: C, 31.52; H, 5.63; N, 18.73.

$[Cu(B)](ClO_4)_2$. This compound was prepared by a method similar to that for $[Ni(B)](ClO_4)_2 \cdot {}^1/_2H_2O$ except that $CuCl_2 \cdot 2H_2O$ (8.5 g) was used instead of $NiCl_2 \cdot 6H_2O$. The red crystals of square-planar complexes were obtained, which were mixed with some violet crystals. The products were recrystallized from hot water. Yield: ~50%. Anal. Calcd for $Cu_{14}H_{30}N_6Cl_2O_8$: C, 30.86; H, 5.55; N, 15.42. Found: C, 30.33; H, 5.55; N, 15.07.

X-ray Diffraction Measurements. The crystallographic data collection and refinement details are summarized in Table I and supplementary material Tables S1 and S2. The intensity data were measured on a CAD-4 Enraf-Nonius Diffractometer (Mo radiation, monochromated, θ–2θ scans). No absorption correction was necessary in view of the uniform crystal dimensions.

$[Ni(A)](ClO_4)_2$. A total of 3855 reflections were measured for $2\theta \leq 50°$, of which 2692 were considered to be observed [$F \geq 2\sigma(F)$]. The structure was solved by direct methods with MULTAN 78[8] and refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atom parameters were calculated by assuming idealized geometry. Hydrogen atom contributions were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices were $R = 5.5\%$ and $R_w = 5.7\%$ for the 2692 observed reflections. The final difference Fourier map was essentially featureless with the largest peaks, 0.5 e Å^{-3}, in the vicinity of the perchlorate oxygen atoms.

$[Ni(B)](ClO_4)_2 \cdot {}^1/_2H_2O$. A total of 4007 unique reflections were measured for $2\theta \leq 50°$, of which 3334 were considered to be observed [$F \geq 2\sigma(F)$]. The nickel and two chloride atoms were located with the aid of a Patterson map; the remainder were located from least-squares difference Fourier techniques. Some disorder was observed in the perchlorate anions. This was accommodated by the anisotropic thermal parameters for six of the oxygen atoms. Each of the two remaining perchlorate oxygen atoms gave rise to split peaks on difference Fourier syntheses and were refined isotropically, at multiplicities of 0.5 each. In the final refinement anisotropic thermal parameters were used for all atoms, except two of the perchlorate oxygen atoms and the hydrogen atoms. Hydrogen atom parameters were calculated by assuming ideal-

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Table II. Spectral and Conductance Data for Hexaaza Macrocyclic Nickel(II) and Copper(II) Complexes

complex	IR: ν_{NH}, cm^{-1}	electronic spectra: λ_{max}, nm (ϵ, M^{-1} cm^{-1})	conductance: Λ_M,[a] Ω^{-1} cm^{-2} M^{-1}
$[Ni(A)](ClO_4)_2$	3170	458 (84),[a] 456 (89)[b]	231
$[Ni(B)](ClO_4)_2\cdot{}^1/_2H_2O$	3215	477 (50),[a] 471 (90)[b]	245
$[Cu(A)](ClO_4)_2$	3165	506 (155),[a] 485 (138)[b]	260
$[Cu(B)](ClO_4)_2$	3225	527 (122),[a] 501 (112)[b]	209
$[Ni(\mathbf{3})](ClO_4)_2$[c]	3180	443 (72),[a] 447 (80)[b]	
$[Ni(\mathbf{4})](ClO_4)_2$[c]	3259	468 (58),[a] 465 (95)[b]	
$[Cu(\mathbf{3})](ClO_4)_2$[d]	3212	535 (185),[a] 486 (151)[b]	
$[Cu(\mathbf{4})](ClO_4)_2$[d]	3268	529 (142),[a] 505 (122)[b]	

[a] Measured in aqueous solutions at 20 °C. [b] Measured in $MeNO_2$ solutions. [c] Reference 6. [d] Reference 30.

Table III. Atomic Coordinates of Non-Hydrogen Atoms for $[Ni(C_{12}H_{26}N_6)](ClO_4)_2$[a]

atom	*x*	*y*	*z*
Ni	0.24199 (5)	0.03074 (8)	0.16353 (5)
Cl1	0.3928 (1)	0.3769 (2)	0.1254 (1)
Cl2	0.9158 (1)	0.1510 (2)	0.3273 (1)
O1	0.3156 (3)	0.2995 (6)	0.1051 (4)
O2	0.4035 (5)	0.4813 (7)	0.0578 (5)
O3	0.4580 (4)	0.2867 (8)	0.1309 (11)
O4	0.3940 (7)	0.4428 (10)	0.2155 (6)
O5	0.9728 (4)	0.0656 (7)	0.2763 (5)
O6	0.9204 (8)	0.2898 (8)	0.3035 (8)
O7	0.8323 (4)	0.1075 (9)	0.3072 (7)
O8	0.9327 (8)	0.1458 (13)	0.4261 (6)
N1	0.3316 (4)	−0.0997 (6)	0.1299 (4)
N2	0.2901 (3)	0.0248 (5)	0.2977 (4)
N3	0.1953 (3)	0.0507 (5)	0.0300 (4)
N4	0.1465 (3)	0.1438 (5)	0.2027 (3)
N5	0.2124 (3)	0.2064 (5)	0.3673 (3)
N6	0.2878 (4)	−0.1398 (6)	−0.0342 (4)
C1	0.3665 (5)	−0.1637 (8)	0.2229 (6)
C2	0.3761 (5)	−0.0469 (8)	0.2982 (5)
C3	0.2994 (4)	0.1686 (7)	0.3422 (4)
C4	0.1617 (4)	0.2535 (7)	0.2809 (4)
C5	0.1011 (4)	0.2043 (8)	0.1130 (5)
C6	0.1034 (4)	0.0931 (8)	0.0342 (4)
C7	0.2067 (5)	−0.0692 (7)	−0.0442 (5)
C8	0.2983 (5)	−0.2109 (7)	0.0584 (5)
C9	0.2284 (5)	−0.0448 (7)	0.3628 (5)
C10	0.1805 (5)	0.0763 (7)	0.4106 (5)
C11	0.3640 (6)	−0.0494 (8)	−0.0373 (6)
C12	0.3988 (5)	−0.0346 (8)	0.0702 (7)

[a] Esd's in the least significant digits are shown in parentheses.

ized geometry. Hydrogen atom contributions were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices were $R = 3.8\%$ and $R_w = 4.8\%$ for the 3334 observed reflections. The final difference Fourier map was essentially featureless with no peaks greater than 0.35 e $Å^{-3}$ in the vicinity of the perchlorate oxygen atoms.

Results

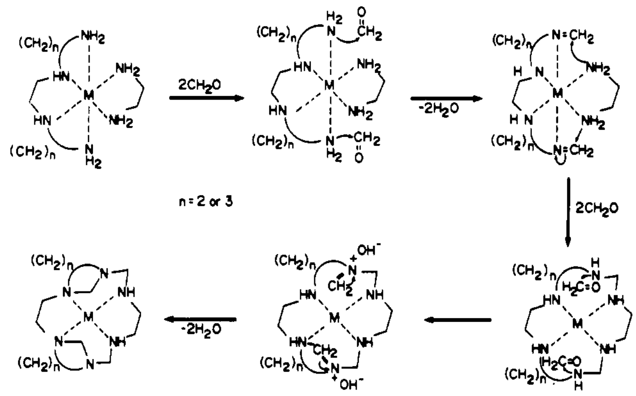
New hexaaza macrotricyclic complexes $[M(A)](ClO_4)_2$ and $[M(B)](ClO_4)_2$ (M = Ni, Cu) with square-planar geometry were prepared in high yield (50–80%) by the simple template condensation reactions of tetraamine (2,2,2-tet for A and 3,2,3-tet for B), ethylenediamine, and formaldehyde in the presence of the metal ion. The spectra and conductance of the complexes were measured, and the data are summarized in Table II. The structure studies for $[Ni(A)](ClO_4)_2$ and $[Ni(B)](ClO_4)_2$ were undertaken, whose results are presented in Tables III–VI. Non-hydrogen atom coordinates are listed in Tables III and IV, and the bond lengths and angles are listed in Tables V and VI. Thermodynamic data for the equilibrium between square-planar and octahedral species of Ni(II) complexes of A, B, **3**, and **4** were measured in aqueous solutions (I = 0.07 M ($NaClO_4$)), and the results are presented in Table VII. Finally, electrochemical studies were undertaken for the Ni(II) complexes, whose results are presented in Table VIII. These will be introduced at appropriate places in the sections that follow.

Table IV. Atomic Coordinates of Non-Hydrogen Atoms for $[Ni(C_{14}H_{30}N_6)](ClO_4)_2\cdot{}^1/_2H_2O$[a]

atom	*x*	*y*	*z*
Ni	0.13164 (1)	0.20768 (3)	0.05153 (2)
Cl1	0.05711 (2)	0.14849 (8)	0.45484 (5)
Cl2	0.29520 (3)	0.10462 (8)	0.36682 (5)
O1A	0.29231 (22)	−0.0402 (6)	0.3557 (5)
O1B	0.28325 (20)	−0.0416 (6)	0.3630 (4)
O2	0.34022 (10)	0.1321 (4)	0.3831 (3)
O3	0.28525 (13)	0.1566 (4)	0.4472 (2)
O4	0.26855 (10)	0.1732 (3)	0.2790 (2)
O5	0.06718 (13)	0.2614 (4)	0.4045 (3)
O6	0.09411 (9)	0.0550 (3)	0.4850 (2)
O7A	0.04651 (23)	0.1714 (10)	0.5344 (4)
O7B	0.05014 (24)	0.2169 (7)	0.5321 (4)
O8	0.01983 (10)	0.0837 (3)	0.3855 (3)
O9	0.00000 (0)	0.4071 (4)	0.2500 (0)
N1	0.08460 (7)	0.3211 (2)	−0.0435 (2)
N2	0.16231 (7)	0.1795 (2)	−0.0404 (2)
N3	0.10376 (7)	0.2404 (2)	0.1488 (2)
N4	0.17864 (7)	0.0964 (2)	0.1435 (1)
N5	0.14313 (8)	0.0597 (2)	0.2671 (2)
N6	0.12395 (8)	0.3688 (2)	−0.1548 (2)
C1	0.10358 (10)	0.4299 (3)	−0.0925 (2)
C2	0.16495 (9)	0.3028 (3)	−0.1033 (2)
C3	0.20719 (9)	0.1241 (3)	0.0159 (2)
C4	0.20192 (9)	0.0197 (3)	0.0879 (2)
C5	0.16725 (10)	−0.0023 (3)	0.2122 (2)
C6	0.10061 (9)	0.1103 (3)	0.2045 (2)
C7	0.05813 (9)	0.2884 (3)	0.0898 (2)
C8	0.06184 (10)	0.3930 (3)	0.0155 (2)
C9	0.05011 (9)	0.2428 (3)	−0.1267 (2)
C10	0.06711 (10)	0.1822 (3)	−0.2027 (2)
C11	0.09208 (11)	0.2912 (3)	−0.2377 (2)
C12	0.12586 (10)	0.3509 (3)	0.2252 (2)
C13	0.16956 (11)	0.3067 (3)	0.2996 (2)
C14	0.16694 (11)	0.1631 (4)	0.3431 (2)

[a] Esd's in the least significant digits are shown in parentheses.

Scheme I



Discussion

Synthesis and Properties. A possible route for the formation of hexaaza macrotricyclic complexes $[M(A)](ClO_4)_2$ and $[M(B)](ClO_4)_2$ (M = Ni, Cu) is presented in Scheme I. In this reaction, a metal ion coordinates a tetraamine and an ethylenediamine in octahedral fashion, and formaldehyde links two cis-coordinated amine moieties for the cyclization, yielding methylenediamine linkages. Because of the characteristic properties of methylenediamine linkages,[4–6,9] uncoordinated secondary amines involving methylenediamine linkages react further with formaldehyde to become tertiary. The resulting macrocyclic ligands contain six nitrogen atoms, of which four nitrogens are tertiary and either coordinated or uncoordinated, while the remaining two are secondary and coordinated to the metal ion.

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Table V. Bond Distances (Å) and Angles (deg) for $[Ni(C_{12}H_{26}N_6)](ClO_4)_2$

(a) Bond Distances

Ni–N1	1.933 (4)	Ni–N2	1.920 (4)
Ni–N3	1.913 (4)	Ni–N4	1.925 (4)
N1–C1	1.470 (7)	N1–C8	1.501 (6)
N1–C12	1.485 (7)	N2–C2	1.495 (7)
N2–C3	1.493 (6)	N2–C9	1.488 (7)
N3–C6	1.485 (7)	N3–C7	1.531 (7)
N4–C4	1.491 (6)	N4–C5	1.482 (6)
N5–C3	1.452 (6)	N5–C4	1.441 (6)
N5–C10	1.462 (6)	N6–C7	1.425 (8)
N6–C8	1.421 (7)	N6–C11	1.462 (8)
C1–C2	1.505 (8)	C5–C6	1.498 (8)
C9–C10	1.529 (8)	C11–C12	1.527 (9)

(b) Bond Angles

N1–Ni–N2	87.4 (2)	N1–Ni–N3	94.7 (2)
N1–Ni–N4	173.9 (2)	N2–Ni–N3	175.9 (2)
N2–Ni–N4	91.3 (2)	N3–Ni–N4	86.9 (2)
Ni–N1–C1	107.4 (3)	Ni–N1–C8	111.9 (3)
Ni–N1–C12	113.4 (3)	C1–N1–C8	110.9 (4)
C1–N1–C12	113.4 (5)	C8–N1–C12	99.8 (4)
Ni–N2–C2	108.5 (3)	Ni–N2–C3	112.1 (3)
Ni–N2–C9	109.8 (3)	C2–N2–C3	110.3 (4)
C2–N2–C9	113.4 (4)	C3–N2–C9	102.6 (4)
Ni–N3–C6	107.8 (3)	Ni–N3–C7	119.4 (3)
C6–N3–C7	111.8 (4)	Ni–N4–C4	119.2 (3)
Ni–N4–C5	109.2 (3)	C4–N4–C5	111.0 (4)
C3–N5–C4	111.1 (4)	C3–N5–C10	103.0 (4)
C4–N5–C10	113.8 (4)	C7–N6–C8	111.4 (4)
C7–N6–C11	115.6 (4)	C8–N6–C11	104.4 (5)
N1–C1–C2	106.9 (5)	N2–C2–C1	106.1 (4)
N2–C3–N5	104.4 (4)	N4–C4–N5	114.5 (4)
N4–C5–C6	106.2 (4)	N3–C6–C5	106.1 (4)
N3–C7–N6	114.8 (4)	N1–C8–N6	104.5 (4)
N2–C9–C10	105.0 (4)	N5–C10–C9	106.4 (4)
N6–C11–C12	105.7 (5)	N1–C12–C11	104.7 (5)

Table VI. Bond Distances (Å) and Angles (deg) for $[Ni(C_{14}H_{30}N_6)](ClO_4)_2\cdot{}^1/_2H_2O$

(a) Bond Distances

Ni–N1	1.969 (2)	Ni–N2	1.945 (2)
Ni–N3	1.952 (2)	Ni–N4	1.939 (2)
N1–C1	1.511 (3)	N1–C8	1.484 (3)
N1–C9	1.511 (3)	N2–C2	1.510 (3)
N2–C3	1.488 (3)	N3–C6	1.504 (3)
N3–C7	1.491 (3)	N3–C12	1.507 (3)
N4–C4	1.483 (3)	N4–C5	1.509 (3)
N5–C5	1.431 (3)	N5–C6	1.435 (3)
N5–C14	1.471 (3)	N6–C1	1.421 (3)
N6–C2	1.419 (3)	N6–C11	1.467 (3)
C3–C4	1.495 (4)	C7–C8	1.503 (4)
C9–C10	1.510 (4)	C10–C11	1.518 (4)
C12–C13	1.498 (4)	C13–C14	1.527 (4)

(b) Bond Angles

N1–Ni–N2	93.78 (8)	N1–Ni–N3	87.87 (8)
N1–Ni–N4	178.90 (8)	N2–Ni–N3	176.92 (8)
N2–Ni–N4	85.16 (8)	N3–Ni–N4	93.18 (8)
Ni–N1–C1	111.0 (1)	Ni–N1–C8	106.4 (1)
Ni–N1–C9	116.4 (1)	C1–N1–C8	108.8 (2)
C1–N1–C9	106.5 (2)	C8–N1–C9	107.6 (2)
Ni–N2–C2	117.1 (1)	Ni–N2–C3	108.9 (1)
C2–N2–C3	110.3 (2)	Ni–N3–C6	112.9 (1)
Ni–N3–C7	105.5 (1)	Ni–N3–C12	114.4 (2)
C6–N3–C7	108.2 (2)	C6–N3–C12	107.5 (2)
C7–N3–C12	108.2 (2)	Ni–N4–C4	109.6 (1)
Ni–N4–C5	118.1 (2)	C4–N4–C5	109.8 (2)
C5–N5–C6	113.0 (2)	C5–N5–C14	116.4 (2)
C6–N5–C14	111.6 (2)	C1–N6–C2	114.8 (1)
C1–N6–C11	111.6 (2)	C2–N6–C11	116.9 (2)
N1–C1–N6	112.0 (2)	N2–C2–N6	114.5 (2)
N2–C3–C4	106.2 (2)	N4–C4–C3	104.7 (2)
N4–C5–N5	114.7 (2)	N3–C6–N5	112.2 (2)
N3–C7–C8	106.9 (2)	N1–C8–C7	106.5 (2)
N1–C9–C10	113.8 (22)	C9–C10–C11	111.0 (2)
N6–C11–C10	112.6 (2)	N3–C12–C13	113.7 (2)
C12–C13–C14	111.6 (2)	N5–C14–C13	113.2 (2)

Table VII. Thermodynamic Data for the Equilibrium[a]

$$[Ni(L)]^{2+} + 2H_2O \rightleftharpoons [Ni(L)(H_2O)_2)]^{2+}$$

L	$K_{25\,°C}$	$-\Delta H°$, kJ mol^{-1}	$-\Delta S°$, kJ mol^{-1}	ref
A	0.0398	31.5	132	this work
	0.0707^b	12.9^b	65.4^b	
B	0.297	34.1	124	this work
	0.646^b	24.6^b	86.1^b	
3	0.0511	24.5	106	this work
	0.0538^b	21.4^b	96.2^b	
4	*c*	*c*	*c*	this work
	0.772^b	20.9^b	72.4^b	
$Me_2[14]aneN_6$	0.17^d	36^d	136^d	
	0.44^b	17^b	64^b	5
$Et_2[14]aneN_6$	0.23^d	19^d	75^d	
	0.36^b	10^b	43^b	5

[a] I = 0.07 M ($NaClO_4$) and T = 25 °C unless otherwise specified. [b] Measured in pure water. [c] Data can not be measured in I = 0.07 M ($NaClO_4$) because of insolubility of the complex. [d] I = 0.1 M ($NaClO_4$). [e] Abbreviations: $Me_2[14]aneN_6$ = 1,8-dimethyl-1,3,6,8,12,13-hexaazacyclotetradecane, $Et_2[14]aneN_6$ = 1,8-diethyl-1,3,6,8,10,13-hexaazacyclotetradecane.

Table VIII. Cyclic Voltammetry Data (V) for Ni(II) Complexes with Hexaaza Macrocycles[a,b]

complex	$E_{ox}([Ni(L)]^{2+}/[Ni(L)]^{3+})$	$E_{red}([Ni(L)]^{2+}/[Ni(L)]^{+})$
$[Ni(A)](ClO_4)_2$	+1.43 (i)	−1.25
$[Ni(B)](ClO_4)_2$	+1.25	−1.14
$[Ni(3)](ClO_4)_2$	+1.50 (i)	−1.28
$[Ni(4)](ClO_4)_2$	+1.34	−1.20 (qr)
$[Ni(Me_2[14]aneN_6)](ClO_4)_2$^{c}	+0.93^c	−1.55^c
$[Ni(Et_2[14]aneN_6)](ClO_4)_2$^{c}	+0.90^c	−1.47^c

[a] Measured in acetonitrile solutions, 0.1 M $(n\text{-}Bu)_4NClO_4$, volts vs SCE. [b] i = irreversible; qr = quasi-reversible. [c] Reference 5.

The complexes contain two 1,3-diazacyclopentane or 1,3-diazacyclohexane small-ring moieties fused to the macrocyclic ligands. The formation of such rings in macrocyclic ligands have been rarely reported.[10,11] The complexes of **3** and **4** that were synthesized previously in our laboratory contain such small-ring moieties.[6]

Ni(II) and Cu(II) complexes (~5 × 10^{-3} M) of A and B are stable in acidic aqueous solutions (0.15 M) against decomposition. The spectra showed that only a few percent of the complexes were decomposed in 24 h. The molar conductance values (Table II) of the complexes indicate that the complexes are 1:2 electrolytes. The infrared spectra (Table II) of the complexes show ν_{N-H} bands for the secondary amines of the ligands at 3170–3225 cm^{-1}. The values of ν_{N-H} are much higher for the Ni(II) and Cu(II) complexes of B than those for the complexes of A. This indicates that the metal–nitrogen interactions are weaker for the complexes with macrotricyclic ligand containing 1,3-diazacyclohexane ring moieties than the complexes with the ligand containing 1,3-diazacyclopentane ring moieties. The electronic absorption spectra (Table II) indicate that the Ni(II) and Cu(II) complexes have square-planar Ni(II)–N_4 and Cu(II)–N_4 chromophores. Maximum absorptions of the Ni(II) and Cu(II) complexes of B appear at ca. 15 nm longer wavelengths than those of A, indicating that macrotricyclic ligand containing 1,3-diazacyclohexane ring moieties exerts a much weaker ligand field than that containing 1,3-diazacyclopentane ring moieties. Similar observations were made for the Ni(II) complexes of **3** and **4**.[6] The spectra also indicate that the complexes of macrocyclic ligands A and B absorb at longer wavelengths than the complexes of macrocyclic ligands **3** and **4**, respectively. This shows that the macrocyclic ligand containing both two small-ring moieties on only one side of the

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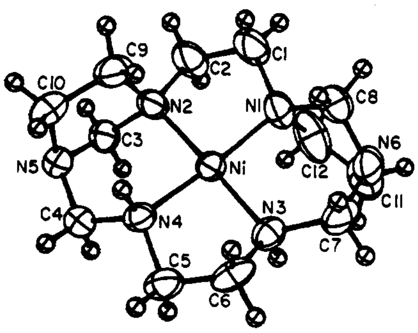

Figure 1. ORTEP drawing and the atomic labeling scheme of $[Ni(C_{12}H_{26}N_6)](ClO_4)_2$.

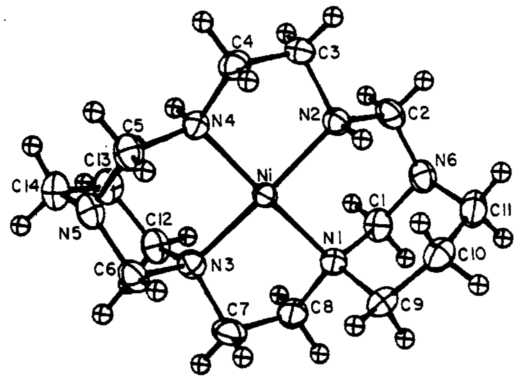

Figure 2. ORTEP drawing and the atomic labeling scheme of $[Ni(C_{14}H_{30}N_6)](ClO_4)_2 \cdot {}^1/_2H_2O$.

ligand exerts weaker ligand field than that containing two small-ring moieties oppositely.

^{13}C NMR spectra of PF_6 salts of $[Ni(A)]^{2+}$ and $[Ni(B)]^{2+}$ show six and seven unique carbon peaks, respectively, as summarized in the Experimental Section. These are consistent with the ligand structures of A and B.

Description of the Structures. ORTEP plots of the $[Ni(A)]^{2+}$ and $[Ni(B)]^{2+}$ cations with the atomic numbering schemes are presented in Figures 1 and 2. Each structure consists of an $S = 0$, Ni(II) complex of a 14-membered hexaaza macrocyclic ligand. The six-membered chelate rings of each macrocycle have an amino function at the bridgehead position. One of the macrocycles has two 1,3-diazacyclopentane rings fused to each of the six-membered chelate rings. The other macrocycle has 1,3-diazacyclohexane rings fused to the six-membered chelate rings. These five- and six-membered diaza rings have envelope and chair conformations, respectively, and are nearly perpendicular (98 and 95°) to the coordination plane. In each ligand, the fused diaza rings are attached to cis-nitrogen atoms in the coordination sphere and to bridgehead nitrogen atoms of the six-membered chelate rings. The fused rings are anti with respect to the macrocyclic plane. The nitrogen atom configurations are the same as that of *trans*-$[Ni(cyclam)Cl_2]$ and permit each of the rings to adopt the optimum chair or gauche conformations.[12]

Coordination Geometry. The coordination geometry is best understood by comparisons with other saturated 14-membered ring nickel(II) cyclam derivatives. These consist of several series having various numbers of $-CH_3$ or $-CH_2CH_3$ groups attached to the carbon atoms of the six-membered chelate rings.[13-16] The average Ni-N bond distance of $[Ni(A)](ClO_4)_2$ is 1.923 (4) Å and is similar to that commonly observed for $S = 0$, saturated 14-membered tetraaza macrocyclic Ni(II) complexes (1.86-1.94 Å) as well as close to those of $[Ni(3)]Cl_2 \cdot H_2O$ (1.920 Å). However, the average Ni-N bond distance in $[Ni(B)](ClO_4)_2 \cdot {}^1/_2H_2O$ is 1.951 (2) Å, significantly longer than that for the former complex. This lengthening is consistent with the weaker Ni-N interaction, as indicated by ν_{NH} values and the weaker ligand field strength of the complex as shown from the d-d spectra. In each complex the nickel atoms are nominally in the coordination plane, displaced by 0.020 Å for $[Ni(A)](ClO_4)_2$ and 0.025 Å for $[Ni(B)](ClO_4)_2$ from the N_4 coordination plane. The deviations of the donor N atoms from this least-squares plane are much larger for $[Ni(A)]^{2+}$, 0.08 Å for each nitrogen atoms vs only 0.02 Å for $[Ni(B)]^{2+}$.

Analysis of the Effects of the Diaza-Fused Rings. The replacement of the bridgehead carbon of the six-membered chelate rings with nitrogen atoms shortens the N-to-center distances slightly. In both structures, the N-C distances (at the six-membered-ring bridgehead positions) are significantly shorter (average of eight N-C distances for the two structures is 1.429 Å) than normal aliphatic N-C distances, which are typically 1.52 Å. Since there are four such bonds per macrocycle, a modest contraction of the ring compared to that of cyclam would be predicted. This prediction is not borne out by the observed Ni-N distances and rather suggests the existence of compensating factors, such as an inherent decrease in field strength (basicity) of the donor nitrogen atoms caused by the bridgehead nitrogen atoms.

Comparisons with related structures show that there is no significant difference between the C-N-C angles of the complexes described herein compared to C-C-C angles in six-membered rings of cyclam derivatives.

The fusion of the five-membered 1,3-diazacyclopentane ring moieties causes an additional contraction of the macrocyclic ring that is not observed with the fused six-membered 1,3-diazacyclohexane ring moieties as demonstrated from the Ni-N distance, 1.923 Å vs 1.951 Å. This small contraction has an obvious explanation in that the interior angles of a five-membered ring are constrained to be smaller (average of 104.5 (4)° of the N-C-N fragment fused onto the five-membered ring) whereas the analogous segments in the six-membered ring have nearly tetrahedral angles, 112.1°. The more acute angle of the five-membered ring segment leads to a shortening of the N2-N5 and N1-N6 distances (average = 2.31 Å vs an average of 2.44 Å in the six-membered ring).

Variations of the Ni-N distances between the secondary and tertiary nitrogen atoms are probably not chemically significant. Larger Ni-N variations (1.966 (4) and 1.916 (4) Å) have been reported for chemically equivalent bonds involving only secondary nitrogen atoms in an $S = 0$, $[Ni(Me_4[14]ane)](ClO_4)_2$ complex.[15]

In both complexes the Ni-O(ClO_4) distances are nonbonding, consistent with the $S = 0$ observation. For $[Ni(A)]^{2+}$ the closest contacts with ClO_4^- anions are 2.917 and 3.445 Å for O1 and O6, respectively. In $[Ni(B)]^{2+}$, the closest ClO_4^- contacts are 3.360 and 2.809 Å for O1A and O6, respectively. It is interesting that the structure of (2,5-diethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) diperchlorate is reported to be paramagnetic, consistent with the average Ni-N distance of 1.988 Å with a long axial Ni-O(ClO_4) distance (2.758 Å). This is only about 0.1 Å shorter than observed Ni-O(ClO_4) for diamagnetic, solid $[Ni(B)](ClO_4)_2$.[16]

Equilibrium between Square-Planar and Octahedral Species of Ni(II) Complexes in Water. Some macrocyclic Ni(II) complexes are known to exist in water as equilibrium mixtures of yellow diamagnetic square-planar $[Ni(L)]^{2+}$ and blue (or violet) paramagnetic octahedral $[Ni(L)(H_2O)_2]^{2+}$ species.[5,17-25]

$$[Ni(L)]^{2+} + 2H_2O \rightleftharpoons [Ni(L)(H_2O)_2]^{2+} \qquad (7)$$

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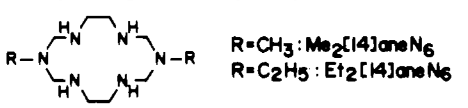
The equilibrium constant K in eq 7 is decreased by increasing either the concentration of supporting electrolyte (e.g. $NaClO_4$) or the temperature. As shown in Table II, the extinction coefficients at λ_{max} measured in water for $[Ni(L)]^{2+}$, where L = A, B, 3, and 4, are smaller than those measured in nitromethane, indicating that some of the square-planar species are converted to the octahedral species in water. The equilibrium constants were obtained from the ratio $K = (\epsilon_{lim} - \epsilon)/\epsilon$, where ϵ_{lim} and ϵ represent limiting values of molar extinction coefficient for the square-planar species and the apparent molar extinction coefficient in 0.07 M $NaClO_4$, respectively. For the Ni(II) complexes of A, a value of ϵ_{lim} was obtained at a supporting electrolyte concentration of 0.07 M and T = 50 °C because of the limited solubility of the complexes at higher concentration of electrolyte. For the Ni(II) complexes of B, 3, and 4, values of ϵ_{lim} were assumed to be same as that measured in nitromethane. The equilibrium constants were determined at different temperatures, and $\Delta H°$ values were obtained from a ln K vs $1/T$ plot, and $\Delta S°$ values from $\Delta G° = \Delta H° - T\Delta S°$.

As shown in Table VII, the formation constants of octahedral species for $[Ni(A)]^{2+}$ and $[Ni(3)]^{2+}$ at room temperature are very small, but those for $[Ni(B)]^{2+}$ and $[Ni(4)]^{2+}$ are much larger (ca. 10 times) and comparable to the data for hexaaza monocyclic $Me_2[14]aneN_6$ or $Et_2[14]aneN_6$ complexes.[5] The Ni–N bond distances in octahedral species are longer than those in square-planar species.[21,26,27] In addition, as discussed previously, the X-ray structure showed that the ligands containing six-membered 1,3-diazacyclohexane ring moieties have larger hole size than the ligands containing five-membered 1,3-diazacyclopentane ring moieties. Therefore, the ligands B and 4 having larger macrocyclic hole sizes accommodate the larger octahedral Ni(II) ion better. The data also indicate that macrotricyclic ligands B and 4 are as flexible as monocyclic ligands $Me_2[14]aneN_6$ and $Et_2[14]aneN_6$ to control the hole sizes of the ligands to accommodate larger Ni(II) octahedral ion, while macrotricyclic ligands A and 3 have rigid hole sizes and hardly accept the larger Ni(II) octahedral ion.



The negative values of $\Delta H°$ indicate that the endothermic effect due to the in-plane Ni–N bonds weakening on the formation of the octahedral species is exceeded by the exothermic effect resulting from the formation of the two axial $Ni–OH_2$ bonds. The values of $\Delta S°$ nearly correspond to those expected for the loss of freedom of two water molecules in the octahedral species (30–40) × 2 J K^{-1} mol^{-1}.[28] However, larger negative $\Delta S°$ values observed for the Ni(II) complexes of B and 3 suggest that square-planar/octahedral conversion involves the immobilization of more than two water molecules, probably due to the interaction of solvent molecules with axially coordinated water molecules of the octahedral species through the second-sphere hydrogen bonding.

Electrochemistry. Cyclic voltammetric data in Table VIII show that both oxidation and reduction potentials for the macrotricyclic Ni(II) complexes of A, B, 3, and 4 are much more anodic than the Ni(II) complexes of related monocyclic ligands $Me_2[14]aneN_6$ and $Et_2[14]aneN_6$. Although the main macrocyclic framework of A, B, 3, 4, and $R_2[14]aneN_6$ are similar, A, B, 3, and 4 contain two tertiary and two secondary nitrogen donors while $R_2[14]aneN_6$ contains four secondary nitrogen donors. It has been reported that N-alkylation of cyclam type ligands results in anodic shift for both oxidation and reduction of the Ni(II) complexes, and the extent of anodic shift depends on the number of alkyl group introduced to the ligand.[24,29] Therefore, the anodic shift of oxidation and reduction potentials for the Ni(II) complexes of A, B, 3, and 4 compared with those of $Me_2[14]aneN_6$ and $Et_2[14]aneN_6$ is attributed to the tertiary amine donors of the former ligands, in accordance with the previous reports. Table VIII also shows that both oxidation and reduction of Ni(II) complexes are more difficult for the ligand systems of A and 3 than for the ligand systems of B and 4. This may be attributed to the better ring size fitness of the Ni(II) ion in the complexes of A and 3 than in the complexes of B and 4. As discussed previously, the macrocyclic holes in the Ni(II) complexes of B and 4 are much larger and more flexible than those of A and 3 and thus make attainment of both Ni(I) and Ni(III) states easier.

Conclusion

This study shows, for the first time to the best of our knowledge, that spectroscopic properties as well as the Ni–N bond distances are greatly affected by small-ring moieties fused to a macrocyclic ligand even though the same macrocyclic frameworks are retained. The complexes containing 1,3-diazacyclohexane small-ring moieties fused to hexaaza macrocyclic ligands exhibit weaker M–N interactions and weaker ligand field strengths than the complexes containing 1,3-diazacyclopentane because of the longer M–N distances. A thermodynamic study for the square-planar and octahedral conversion and the electrochemistry for the Ni(II) complexes indicate that macrotricyclic ligands B and 4 containing 1,3-diazacyclohexane ring moieties have more flexible macrocyclic cavities than macrotricyclic ligands A and 3 containing 1,3-diazacyclopentane ring moieties.

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Supplementary Material Available: Tables S1–S8, giving complete details of crystal data and the structure determination, anisotropic thermal parameters, hydrogen atom positions, and complete bond distances and angles for $[Ni(C_{12}H_{26}N_6)](ClO_4)_2$ and $[Ni(C_{14}H_{30}N_6)](ClO_4)_2 \cdot {}^1/_2H_2O$ (15 pages); Tables S9 and S10, listing structure factors (27 pages). Ordering information is given on any current masthead page.

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