2544 *Inorg. Chem.* **1988**, *27*, 2544–2546

Notes

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Synthesis and Properties of Nickel(II) and Copper(II) Complexes of 14-Membered Hexaaza Macrocycles, 1,8-Dimethyl- and 1,8-Diethyl-1,3,6,8,10,13-hexaazacyclotetradecane

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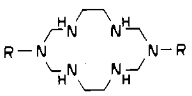
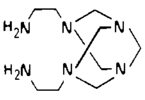
Received November 12, 1987

A large number of 14-membered macrocyclic ligands and their complexes have been synthesized and studied. However, most of them were tetraaza macrocyclic ligands, and 14-membered macrocyclic ligands containing six nitrogen atoms in the fully saturated macrocyclic framework have not been reported to date.

We attempted the synthesis of 14-membered hexaaza macrocyclic ligand A by the condensation reaction of ethylenediamine, formaldehyde, and ammonia in the presence of Ni(II) ion. However, we obtained the complexes of D, E, and F instead.[2,3]


A : R=H
B : R=CH$_3$
C : R=C$_2$H$_5$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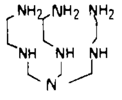
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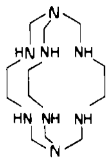
F

$$Ni^{2+} + en + CH_2O + NH_3 \rightarrow [Ni(D)]^{2+}, [Ni(E)]^{2+}, [Ni(F)]^{2+} \quad (1)$$

Similarly, it was reported that condensation of $[Co(en)_3]^{3+}$ with formaldehyde and ammonia produced the Co(III) complex of F.[4] In these reactions, formaldehyde links two amine moieties, forming methylenediamine linkages ($-N-CH_2-N-$). The methylenediamine linkages are unstable when they contain primary and secondary amines, and thus secondary nitrogens of methylenediamines in the Ni(II) complexes of E and F are stabilized by the coordination to the metal ion. The failure to synthesize the complexes of A was ascribed to the instability of methylenediamine linkages containing uncoordinated secondary nitrogens.

In this paper, we report the new Ni(II) and Cu(II) complexes of the 14-membered hexaaza macrocycles 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane (B) and 1,8-diethyl-1,3,6,8,10,13-hexaazacyclotetradecane (C). The complexes were prepared from the template condensation of ethylenediamine, formaldehyde, and alkylamines.

$$M^{2+} + 2en + 4CH_2O + 2RNH_2 \rightarrow [M(B)]^{2+}, [M(C)]^{2+} \ (M = Ni, Cu) \quad (2)$$

$$R = Me \text{ for B}; R = Et \text{ for C}$$

Ni(II) complexes of B and C gave equilibrium mixtures of square-planar and octahedral species in aqueous solutions, and the corresponding equilibrium processes were investigated.

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.[5]

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. ^{1}H NMR spectra were obtained on a Varian EM 360 60-MHz NMR spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP 80 FT NMR spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. In equilibrium studies, temperature was controlled to within ±0.1 °C by using a water circulator. Cyclic voltammetry was carried out with a Princeton Applied Research Corp. (PARC) 173 potentiostat coupled with a PARC 175 universal programmer and Watanabe 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 Ag/AgClO$_4$ (0.1 M in CH$_3$CN), which showed +0.24 V vs SCE.

Synthesis. ***Caution!*** Some of the compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

[Ni(B)](ClO$_4$)$_2$. To a stirred methanol solution (50 mL) of NiCl$_2$·6H$_2$O (11.5 g) were slowly added 99% ethylenediamine (6.8 mL), 36% formaldehyde (20 mL), and 40% methylamine (8.6 mL). The mixture was heated at reflux for 24 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: ~50%. Anal. Calcd for NiC$_{10}$H$_{26}$N$_6$Cl$_2$O$_8$: C, 24.61; H, 5.37; N, 17.22. Found: C, 24.93; H, 5.51; N, 17.30.

[Ni(B)](PF$_6$)$_2$. To an acetonitrile (20 mL) suspension of [Ni(B)](ClO$_4$)$_2$ (0.3 g) was added excess NH$_4$PF$_6$. [Ni(B)](ClO$_4$)$_2$ went into the solution, and white precipitates of NH$_4$ClO$_4$ were formed. NH$_4$ClO$_4$ was filtered off, and the filtrate was concentrated to 15 mL. Water (10 mL) was added to the solution, and the mixture was kept in a refrigerator. The yellow precipitates formed were filtered, washed with a 5:1 mixture of water and acetonitrile, and dried in vacuo. ^{13}C NMR (CD$_3$NO$_2$): δ 38.3 (N-Me), 48.6 (N-C-C-N), 70.7 (N-C-N).

[Ni(C)](ClO$_4$)$_2$. This compound was prepared by a method similar to that for [Ni(B)](ClO$_4$)$_2$ except that 33% ethylamine (17 mL) was used instead of methylamine. Yield: ~40%. Anal. Calcd for NiC$_{12}$H$_{30}$N$_6$Cl$_2$O$_8$: C, 27.93; H, 5.86; N, 16.29. Found: C, 28.07; H, 5.87; N, 16.09.

[Ni(C)](PF$_6$)$_2$. This complex was prepared from [Ni(C)](ClO$_4$)$_2$ by a method similar to that for [Ni(B)](PF$_6$)$_2$. ^{13}C NMR (CD$_3$NO$_2$): δ 13.3 (N-C-*C*), 45.5 (N-*C*-C), 48.6 (N-C-C-N), 68.7 (N-C-N).

[Ni(B)(NCS)$_2$] and [Ni(C)(NCS)$_2$]. To a saturated hot aqueous solution of perchlorate salt of the appropriate complex ion 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 vacuo. Anal. Calcd for NiC$_{12}$H$_{26}$N$_8$S$_2$: C, 35.56; H, 6.46; N, 27.65; Ni, 15.82. Found: C, 35.48; H, 6.44; N, 27.46; Ni, 15.60. Calcd for NiC$_{14}$H$_{30}$N$_8$S$_2$: C, 38.81; H, 6.98; N, 25.86. Found: C, 38.10; H, 6.94; N, 24.94.

[Cu(B)](ClO$_4$)$_2$. To a methanol solution (50 mL) of CuCl$_2$·2H$_2$O (8.5 g) were added 99% ethylenediamine (6.8 mL), 36% formaldehyde (20 mL), and 40% methylamine (8.6 mL). The solution was heated at reflux for 24 h until a deep blue-violet solution resulted. The solution was filtered to remove insoluble materials, and excess perchloric acid or lithium perchlorate dissolved in methanol was added to the filtrate. The

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

complex	IR, cm^{-1}	electronic spectra[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	Λ_M,[a] Ω^{-1} cm^{-2} M^{-1}
$[Ni(B)](ClO_4)_2$	ν_{NH} 3220	446 (40), 449 (56)[b]	225
$[Ni(C)](ClO_4)_2$	ν_{NH} 3185	445 (47), 449 (64)[b]	252
$[Ni(B)(NCS)_2]$	ν_{NH} 3222 ν_{CN} 2056, ν_{CS} 783	500, 338[c]	
$[Ni(C)(NCS)_2]$	ν_{NH} 3210 ν_{CN} 2060, ν_{CS} 781	485[c]	
$[Cu(B)](ClO_4)_2$	ν_{NH} 3212	495 (70), 486 (73)[b]	240
$[Cu(C)](ClO_4)_2$	ν_{NH} 3232	497 (79), 485 (77)[b]	245
$[Ni(5,7\text{-}Me_2[14]aneN_4)](PF_6)_2$[11]		441 (62)	
$[Ni([14]macN_4L_c)]^{2+}$[12,d]		450	
$[Ni([14]aneN_4)]^{2+}$[13]		445 (46)	
$[Cu(5,12\text{-}Me_2[14]4,11\text{-}dieneN_4)]^{2+}$[15]		508 (87)	
$[Cu(\mathit{ms}\text{-}Me_6[14]4,11\text{-}dieneN_4)]^{2+}$[16]		501 (122)	
$[Cu(\mathit{ms}\text{-}5,12\text{-}Me_2[14]aneN_4)]^{2+}$[19]		508 (92)	

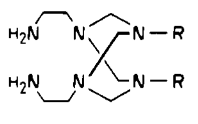
[a] In aqueous solutions at 25 °C unless otherwise specified. [b] In CH_3NO_2 solutions at 25 °C. [c] In Me_2SO solutions with excess NaSCN. [d] $[14]\text{-}macN_4L_c$ stands for 1,4,8,11-tetraazacyclotetradecane-2,3-dione.

purple-red crystals formed were filtered, washed with methanol, and recrystallized from hot water. Yield: ~40%. Anal. Calcd for $CuC_{10}H_{26}N_6Cl_2O_8$: C, 24.37; H, 5.32; N, 17.05. Found: C, 24.22; H, 5.30; N, 16.96.

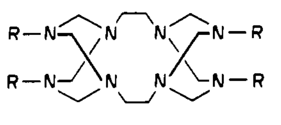
$[Cu(C)](ClO_4)_2$. This complex was prepared by a method similar to that for $[Cu(B)](ClO_4)_2$ except that 33% ethylamine (17 mL) was used instead of methylamine. Yield: ~30%. Anal. Calcd for $CuC_{12}H_{30}N_6Cl_2O_8$: C, 27.67; H, 5.81; N, 16.13. Found: C, 27.32; H, 5.86; N, 15.65.

Results and Discussion

Synthesis and Properties. New hexaaza macrocyclic complexes $[M(B)](ClO_4)_2$ and $[M(C)](ClO_4)_2$ (M = Ni, Cu) were prepared by the template condensation of ethylenediamine, formaldehyde, and alkylamine (methylamine for B and ethylamine for C, respectively) in the presence of the metal ion. Complexes of G and H were also expected to form, as the template condensation of ethylenediamine, formaldehyde, and ammonia produced the complexes of D and because molecular models do not show significant steric hindrance. However, they have never been isolated.



G

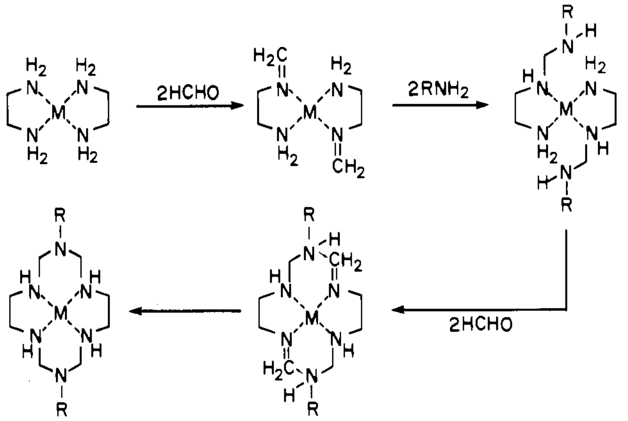


H

A possible route for the formation of the macrocyclic complexes is shown in Scheme I. According to this scheme, the reaction is initiated by the formation of an imine from the reaction of formaldehyde with ethylenediamine which is coordinated to a metal ion. Then the imine is attacked by alkylamine to yield a *gem*-diamine. The *gem*-diamine subsequently condenses with a neighboring imine group, producing a six-membered ring.

Complexes $[Ni(L)](ClO_4)_2$ and $[Cu(L)](ClO_4)_2$ (L = B, C) are soluble in polar solvents such as H_2O, CH_3CN, CH_3NO_2, Me_2SO, and DMF and insoluble in alcohols. The values of molar conductance (Table I) for $[Ni(L)](ClO_4)_2$ and $[Cu(L)](ClO_4)_2$ indicate that they are 1:2 electrolytes. $[Ni(L)](ClO_4)_2$ and $[Cu(L)](ClO_4)_2$ are extremely stable in the crystalline state and in solution and are relatively stable against ligand dissociation even in highly acidic solutions. Spectra of aqueous solutions of $[Ni(B)](ClO_4)_2$ (4.0×10^{-3} M) and those of $[Ni(C)](ClO_4)_2$ (4.0×10^{-3} M) indicate that 35% and 50%, respectively, of the complexes were decomposed in 10 h at 25 °C upon the addition of HNO_3 (0.3 M). Under the same conditions, only 6% of $[Cu(B)](ClO_4)_2$ and 8% of $[Cu(C)](ClO_4)_2$ were decomposed in 20 h.[6] The Ni(II) and Cu(II) complexes of the 14-membered tetraaza macrocyclic ligands with a 5-6-5-6 chelate ring have been reported to be stable against ligand dissociation, and their decomposition rates are very slow even at low pH.[7-9]

Scheme I



$[Ni(B)](ClO_4)_2$ and $[Ni(C)](ClO_4)_2$ react with excess KSCN in aqueous solutions to form tetragonal complexes $[Ni(B)(NCS)_2]$ and $[Ni(C)(NCS)_2]$, whose IR spectra (Table I) show that the nitrogen atoms of NCS^- ligands are coordinated to the Ni(II) ion.[10] Pink complexes of $[Ni(B)(NCS)_2]$ and $[Ni(C)(NCS)_2]$ are not soluble in most of the solvents such as CH_3CN, EtOH, DMF, and CH_3NO_2 and dissociate axial NCS^- ligands in water or Me_2SO to become yellow $[Ni(B)]^{2+}$ and $[Ni(C)]^{2+}$.

The infrared spectra (Table I) of the Ni(II) and Cu(II) complexes of B and C show a single absorption around 3200 cm^{-1}, which is attributed to ν_{N-H} of the coordinated secondary amines. The electronic spectra (Table I) of $[Ni(B)]^{2+}$ and $[Ni(C)]^{2+}$ are comparable to 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] Similarly, the spectra of $[Cu(B)]^{2+}$ and $[Cu(C)]^{2+}$ are also comparable to those of the other square-planar Cu(II) complexes with tetraaza macrocyclic ligands.[15-18,21] ^1H NMR spectra of the Ni(II) complexes of B

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(6) Because aqueous solutions of the Ni(II) or Cu(II) complexes (3.0×10^{-3} M) produce precipitates upon the addition of perchloric acid (0.3 M), the spectra were measured with HNO_3 (0.3 M).

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Table II. Cyclic Voltammetric Data for Ni(II) and Cu(II) Complexes with 14-Membered Macrocycles[a,b]

complex	oxidn pot., V $[M(L)]^{2+} \rightarrow [M(L)]^{3+}$	redn pot., V $[M(L)]^{2+} \rightarrow [M(L)]^{+}$	ref
Ni(B)	+0.93	−1.55	this work
Ni(C)	+0.90	−1.47	this work
Ni([14]aneN$_4$)	+0.91	−1.46	19
Ni(Me$_2$[14]aneN$_4$)	+0.92	−1.49	19
Cu(B)	+1.31	−1.14 (i)[c]	this work
Cu(C)	+1.32	−1.07 (i)[c]	this work
Cu([14]aneN$_4$)	+1.35	−1.10	20

[a] Measured in acetonitrile solutions; 0.1 M $(n\text{-Bu})_4NClO_4$; vs SCE. [b] Redox potentials of this work and ref 19 were measured against a Ag/Ag$^+$ (0.1 M) reference electrode and converted to the values measured against the SCE by adding +0.24 V. [c] i = irreversible.

Table III. Thermodynamic Data for the Equilibrium $[Ni(L)]^{2+} + 2H_2O \rightleftharpoons [Ni(L)(H_2O)_2]^{2+}$[a]

L	$K_{25^\circ C}$	$-\Delta H^\circ$, kJ mol^{-1}	$-\Delta S^\circ$, J K^{-1} mol^{-1}	ref
B	0.17	36	136	this work
	(0.44[b]	17[b]	64[b])	this work
C	0.23	19	75	this work
	(0.36[b]	10[b]	43[b])	this work
[13]aneN$_4$	0.15	31	126	32
[14]aneN$_4$	0.41	23	84	23
N$_4$7[c]	0.64	20	71	27
N$_4$8[c]	0.33	23	88	27
N$_4$9[c]	1.26	26	84	27

[a] I = 0.1 (NaClO$_4$) and T = 25 °C unless otherwise specified. [b] Measured in pure water. [c] Abbreviations: N$_4$7 = 1,4,7,10-tetraazacyclotetradecane, N$_4$8 = 1,4,7,10-tetraazacyclopentadecane, and N$_4$9 = 1,4,7,10-tetraazacyclohexadecane.

and C exhibit very broad peaks in D_2O, $CH_3CN\text{-}d_3$, and $Me_2SO\text{-}d_6$ but sharp resolvable peaks in $CH_3NO_2\text{-}d_3$. This indicates that a considerable amount of paramagnetic octahedral species of $[Ni(B)S_2]^{2+}$ and $[Ni(C)S_2]^{2+}$ exists in the donating solvents (S), whereas the Ni(II) complexes of B and C exist primarily as diamagnetic square-planar species in $CH_3NO_2\text{-}d_3$. ^{13}C NMR spectra of $[Ni(L)](PF_6)_2$ measured in $CH_3NO_2\text{-}d_3$, which are summarized in the Experimental Section, show three carbon peaks for $[Ni(B)]^{2+}$ and four carbon absorptions for $[Ni(C)]^{2+}$, as expected for the square-planar geometry of B and C. Cyclic voltammetry data are summarized in Table II. Table II shows that oxidation and reduction potentials of the Ni(II) and Cu(II) complexes of B and C do not differ significantly from those of [14]aneN$_4$ complexes. This suggests that macrocycles B and C have Lewis basicities and hole sizes similar to those of the [14]aneN$_4$ ligand in spite of the structural differences.

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 ligands B and C must be unstable because they contain methylenediamine moieties with secondary nitrogens.

Equilibrium between $[Ni(L)]^{2+}$ and $[Ni(L)(H_2O)_2]^{2+}$ in Water (L = B, C). Some tetraaza macrocyclic Ni(II) complexes exist in water as equilibrium mixtures of yellow diamagnetic square-planar $[Ni(L)]^{2+}$ and blue (or violet) paramagnetic octahedral $[Ni(L)(H_2O)_2]^{2+}$.[21-27]

$$[Ni(L)]^{2+} + 2H_2O \overset{K}{\rightleftharpoons} [Ni(L)(H_2O)_2]^{2+} \tag{3}$$

The equilibrium has been reported to be dependent on temperature, ionic strength, and the nature of the added electrolytes.[22] New hexaaza macrocyclic Ni(II) complexes examined in this study also manifest such an equilibrium process. Thermodynamic data for the equilibrium process are listed in Table III. The equilibrium constants were calculated from absorbance values at I = 0.1 (NaClO$_4$) by taking the molar extinction coefficient measured in nitromethane as that of pure square-planar species in the aqueous solutions.[28] The thermodynamic parameters obtained for the hexaaza macrocyclic Ni(II) complexes of the present study are comparable to those previously obtained for the complexes of tetraaza macrocyclic ligands such as [14]aneN$_4$. Although stronger Ni–N bonds are involved in the square-planar species (Ni–N = 1.88–1.91 Å) than in the octahedral species (Ni–N = 2.07–2.10 Å),[29,30] this endothermic effect is exceeded by the exothermic effect resulting from the formation of the two axial Ni–OH$_2$ bonds, making net ΔH° values negative. The values of ΔS° for various ligand systems, except for B and [13]aneN$_4$, 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}.[30] The values of ΔH° and ΔS° for the square-planar $\rightleftharpoons$ octahedral conversion of Ni(II) complexes are much more negative for B than for C. The reason for the steric effect is not clear. However, interactions of solvent molecules with the square-planar and the octahedral complexes (e.g. at the uncoordinated nitrogens) could be affected by the alkyl substituents. The large negative values of ΔH° and ΔS° for [13]aneN$_4$ have been explained by the formation of *cis*-$[Ni(L)(H_2O)_2]^{2+}$ with the folded macrocycle and the second-sphere hydrogen bonds of the third water molecules.[32] However, molecular models of folded *cis*-$[Ni(B)(H_2O)_2]^{2+}$ show severe nonbonded interactions between methyl substituents of the nitrogen atoms and the coordinated water molecules. Thus, the folded cis geometry is not probable for $[Ni(B)(H_2O)_2]^{2+}$.

Acknowledgment. We thank the Korea Science and Engineering Foundation for the financial support.

Registry No. $[Ni(B)](ClO_4)_2$, 114596-06-4; $[Ni(B)](PF_6)_2$, 114596-07-5; $[Ni(C)](ClO_4)_2$, 114596-09-7; $[Ni(C)](PF_6)_2$, 114613-98-8; $Ni(B)(NCS)_2$, 114596-10-0; $Ni(C)(NCS)_2$, 114596-11-1; $[Cu(B)](ClO_4)_2$, 114596-13-3; $[Cu(C)](ClO_4)_2$, 114596-15-5; $[Ni(B)]^{3+}$, 114596-16-6; $[Ni(C)]^{3+}$, 114596-17-7; $[Cu(B)]^{3+}$, 114596-18-8; $[Cu(C)]^{3+}$, 114596-19-9; $[Ni(B)]^{+}$, 114596-21-3; $[Ni(C)]^{+}$, 114596-20-2; $[Cu(B)]^{+}$, 114596-23-5; $[Cu(C)]^{+}$, 114596-22-4; ethylenediamine, 107-15-3; formaldehyde, 50-00-0; methylamine, 74-89-5; ethylamine, 75-04-7.

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(28) Correct molar extinction coefficients of the square-planar species may be measured by increasing the ionic strength (up to 7 M NaClO$_4$),[23,24] since the increase in the ionic strength lowers the K value. In the present study, however, this was not possible due to the very limited solubility of the complexes in water at $I > 0.1$ (NaClO$_4$).
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