Ni(II) and Cu(II) Hexaaza Macrobicyclic Complexes

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Synthesis and Characterization of New Nickel (II) and Copper (II) Complexes of the Hexaaza Macrobicyclic Ligand 8-Methyl-1,3,6,8,10,13-hexaazabicyclo[11,2,1]hexadecane

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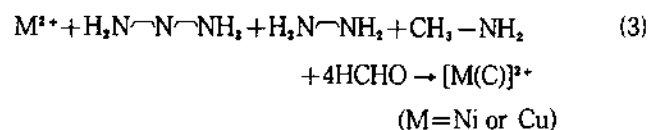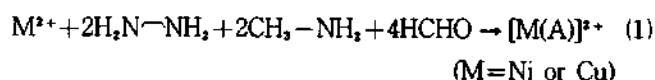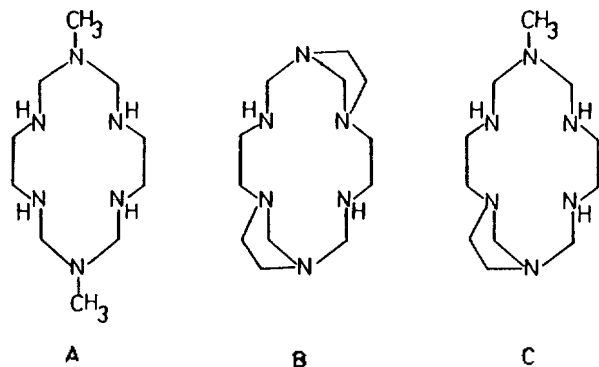*Department of Chemistry, Taegu University, Kyungsan 713-714. Received May 29, 1990*

Template condensation reaction of diethylenetriamine, ethylenediamine, methylamine, and formaldehyde in the presence of Ni(II) or Cu(II) ion yields new saturated hexaaza macrobicyclic complexes $[Ni(C)]^{2+}$ and $[Cu(C)]^{2+}$, where C is 8-methyl-1,3,6,8,10,13-hexaazabicyclo[11,2,1]hexadecane. The macrobicyclic complexes contain one 1,3-diazacyclopentane ring and one methyl pendant arm in the ligand C and have square planar geometry with 5-6-5-6 chelate ring sequence. Synthesis, characterization, and the properties of the macrobicyclic complexes are described.

Introduction

Metal template condensation reactions involving amines and formaldehyde have been utilized for the preparation of fully saturated polyaza macrocyclic and macropolycyclic complexes, since formaldehyde is an effective reagent to link two amine moieties and form $N-CH_2-N$ linkages.[1-9] For examples, Ni(II) and Cu(II) complexes of A and B were synthesized from the reactions of appropriate amines with formaldehyde in the presence of the metal ion as shown in Eq. 1[1] and 2[2], respectively.

Although numbers of macrocyclic complexes were prepared by the template reactions, most of them described in the literature were obtained by the reactions involving one or two kinds of amine species. However, the reactions of formaldehyde with amines of more than two kinds have not been reported yet.

In this work, we have designed and prepared new Ni(II) and Cu(II) complexes of a saturated hexaaza macrobicyclic ligand, 8-methyl-1,3,6,8,10,13-hexaazabicyclo[11,2,1]hexadecane(C), by the simple template condensation of formaldehyde with three amines such as diethylenetriamine, ethylenediamine, and methylamine. The structure of the new macrobicyclic ligand C, which contains both a methyl pendant arm at the uncoordinated nitrogen atom and one 1,3-diazacyclopentane ring, is intermediate between those of the macrocyclic ligand A and the macrotricyclic ligand B. This paper reports the synthesis and properties of the new Ni(II) and Cu(II) complexes of C. Comparisons of the properties of the macrobicyclic complexes with those of the macrocyclic and macrotricyclic complexes are also described.

$$M^{2+}+2H_2N\frown NH_2+2CH_3-NH_2+4HCHO \rightarrow [M(A)]^{2+} \quad (1)$$
$$(M=Ni \text{ or } Cu)$$

$$M^{2+}+2H_2N\frown\underset{H}{N}\frown NH_2+4HCHO \rightarrow [M(B)]^{2+} \quad (2)$$
$$(M=Ni)$$

$$M^{2+}+H_2N\frown N\frown NH_2+H_2N\frown NH_2+CH_3-NH_2 \quad (3)$$
$$+4HCHO \rightarrow [M(C)]^{2+}$$
$$(M=Ni \text{ or } Cu)$$

Experimental

Materials and Methods. All chemicals used in synthesis were of reagent grade and were used without further purification. Organic solvents for the spectroscopic measurement were of spectroscopic grade.

Infrared spectra were recorded on a Shimadzu IR-440 spectrophotometer. Conductance measurements were performed by using a Metrohm Herisau Conductometer E518. Electronic absorption spectra were obtained with a Perkin Elmer Lambda 5 UV/vis spectrophotometer. In kinetic and equilibrium studies, temperature was controlled using a circulating water bath. Elemental analyses were performed at the Kolon R & D Center. ^{1}H and ^{13}C-NMR spectra were recorded using a Bruker WP 80 FT NMR spectrometer. Electrochemical measurements were made by using a Yanaco Voltammetric Analyzer P-1000 equied with a FG-121B function generator and a Watanabe X-Y recorder. The electrochemical data were obtained in acetonitrile solutions containing 0.1 M (n-Bu)$_4$NClO$_4$ as supporting electrolyte. The working electrode was a platinum disk with platinum wire as the counter electrode. The reference electrode was a saturated calomel electrode (sce).

Synthesis. [Ni(C)](ClO$_4$)$_2$. To a solution of NiCl$_2$·6H$_2$O (6g) in methanol (50 ml) were slowly added diethylenetriamine (2.6 ml), 99% ethylenediamine (1.7 ml), 40% methylamine (2.2 ml), and paraformaldehyde (4g). The mixture was heated at reflux for 20 h, and then allowed to cool at room temperature. Excess perchloric acid was added dropwise to the resultant dark orange solution with stirring, and the solution was kept in a refrigerator until orange-yellow crystals formed. The crystals collected by filteration con-


A   B   C

tain the product and small amount (<10%) of yellow [Ni(B)₂
(ClO₄)₂ and/or [Ni(B)](ClO₄)₂ as by-products. The crude pro-
duct was dissolved in minimum volume of water and then
cooled to room temperature. The first crop of crystals con-
tained mainly [Ni(C)](ClO₄)₂. The pure crystals of the pro-
duct were separated by fractional recrystallizations of the
crude products from hot water. Yield: ~10%. *Anal.* Calcd
for $C_{11}H_{26}N_6NiCl_2O_8$: C, 26.4; H, 5.24; N, 16.8%. Found: C,
26.3; H, 5.47; N, 16.8%.

[Ni(C)](PF₆)₂. To a warm acetonitrile (15 ml) suspension
of [Ni(C)](ClO₄)₂(0.5g) was added excess NH₄PF₆. Then the
complex was dissolved and NH₄ClO₄ was precipitated. The
precipitates were removed by filteration, and water (20 ml)
was added to the filtrate. The resulting solution was concen-
trated to *ca.* 20 ml on a warm water bath and then cooled.
The yellow precipitates formed were filtered, washed with
methanol, and air dried.

[Cu(C)](ClO₄)₂. To a methanol solution (50 ml) of CuCl₂·
2H₂O (4.3g) were slowly added, with stirring, diethylenetri-
amine (2.6 ml), 99% ethylenediamine (1.8 ml), 40% methyl-
amine (2.2 ml), and paraformaldehyde (5 ml). The resulting
blue solution was heated under reflux for 24 h and then
allowed to cool at room temperature. Excess perchloric acid
was added dropwise to the solution with stirring and the solu-
tion was kept in a refrigerator until red precipitates formed.
The red precipitates were filtered, washed with methanol,
and air dried. The products were recrystallized from hot
water. Yield. ~10%. *Anal.* Calcd for $C_{11}H_{26}N_6CuCl_2O_8$: C,
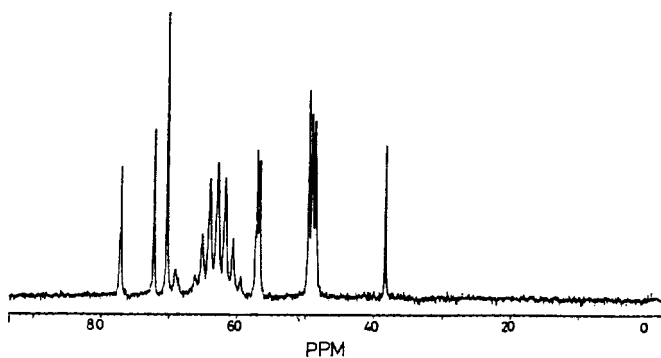26.2; H, 5.19; N, 16.6%. Found: C, 25.9; H, 5.23; N, 16.5%.

Results and Discussion

Synthesis. The reaction of excess formaldehyde with an
equimolar mixture of NiCl₂·6H₂O, diethylenetriamine, ethyl-
enediamine, and methylamine in methanol soluion, followed
by addition of excess perchloric acid or lithium perchlorate,
is expected to give a mixture of three hexaaza complexes,
[Ni(A)]²⁺, [Ni(B)]²⁺, and [Ni(C)]²⁺ as their diperchlorate
salts. However, the major product is orange crystals of the
macrobicyclic complex [Ni(C)](ClO₄)₂ which can be readly
isolated from the crude product by fractional recrystalliza-
tions from hot water. The isolation of the other complexes
which formed in the present work was not attempted. The
red macrobicyclic complex [Cu(C)](ClO₄)₂ was also obtained
from the similar method. The proposed synthetic route for
the hexaaza macrobicyclic complexes is shown in Scheme 1,
which is consistant with that reported for the formation of *A*[1]
or *B*[2] by the reaction of amines with formaldehyde in the
presence of the metal ion. All attempts to obtain the Ni(II)
complexes of hexaaza macrobicyclic ligands containing more
bulky pendant arms such as CH₂CH₃, CH₂CH₂CH₃, and
CH₂CH₂CH₂CH₃ by a method similar to that for [Ni(C)]
(ClO₄)₂ were unsuccessful, unexpectedly. When diethylene-
triamine, ethylenediamine, formaldehyde, and appropriate
primary alkylamine (ethylamine, *n*-propylamine, or *n*-butyl-
amine) were reacted in the presence of Ni(II) ion, the solution
turned dark orange and the macrotricyclic complex [Ni(C)]
(ClO₄)₂ was isolated as a main product. However, the macro-
bicyclic complexes with such bulky pendant arms were not
isolated. The failure to obtain such macrobicyclic complexes
in the present experimental condition is not clear.
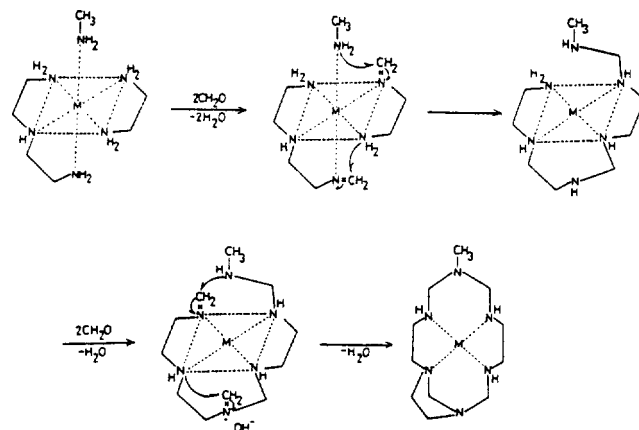
Scheme 1.

Characterizations. The macrobicyclic complexes [Ni
(C)](ClO₄)₂ and [Cu(C)](ClO₄)₂ are soluble in polar solvents
such as H₂O, MeCN, MeNO₂, DMF, and DMSO, but in-
soluble in MeOH. Although quantitative measurements were
not made, the solubility in water appeared to be higher than
that of the complexes of A but lower than that of the com-
plexes of B. The macrobicyclic complexes are extremely
stable in crystalline states and are decomposed very slowly
even in highly acidic solutions. Visible spectra of the com-
plexes $(2.0 \times 10^{-3}M)$ in 0.3 M HNO₃ solutions showed that
only about 17% of [Ni(C)]²⁺ and 10% of [Cu(C)]²⁺ were
decomposed in 10 h at 20 °C. The slow decomposition even in
low pH has been widely observed for various square planar
Ni(II) and Cu(II) complexes of A, B, and other macrocyclic
ligands with 5-6-5-6 chelate ring sequence and attributed to
the strong interactions between the metal ion and the donor
atom of the ligand.[1,2,9-13]

The molar conductance and spectral data are listed in
Table 1. The infrared spectra of [Ni(C)](ClO₄)₂ and [Cu(C)]
(ClO₄)₂ show single strong absorption bands at 3181 cm⁻¹ and
3235 cm⁻¹, respectively, which are assigned to the N–H stret-
ching vibrations of coordinated secondary amines. There are
no bands corresponding to unreacted primary amines. The
values of molar conductance for the Ni(II) and Cu(II) com-
plexes in acetonitrile and aqueous solutions indicate that the
complexes are 1:2 electrolytes. The electronic absorption
spectrum of [Ni(C)](ClO₄)₂ in nitromethane shows a broad
d-d transition band at 448 nm ($\epsilon = 77$ M⁻¹cm⁻¹), typical of a
square planar Ni-N₄ chromophore.[1,9,14,16] It has been re-
ported that the stepwise methylation on the coordinated
secondary nitrogen atoms of [Ni(cyclam)]²⁺ decreases the
ligand field strength.[17] However, the spectra of [Ni(C)]²⁺ are
quite similar to those of [Ni(A)]²⁺ and [Ni(B)]²⁺, indicating
that the ligand field strengths of the hexaaza complexes are
not affected significantly by the coordinated tertiary nitrogen
atom at the 1,3-diazacyclopentane ring fused to the ligand.
The spectra of [Cu(C)](ClO₄)₂ in the solutions show the bands
at 190-506 nm ($\epsilon = 102-113$ M⁻¹cm⁻¹) and are also com-
parable to those reported for other square planar Cu(II) com-
plexes of macrocyclic ligands with 5-6-5-6 chelate ring se-
quence.[1,2,9,18,19] ¹³C-NMR spectrum (Figure 1) of
[Ni(C)](PF₆)₂ measured in CD₃NO₂ is consistent with the
ligand structure. The carbon peaks of N-C-C-N linkages are
observed at 48.5, 49.0, 49.1, 49.4, 56.6, and 57.1 ppm and

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Figure 1. ^{13}C-NMR Spectrum of [Ni(C)](PF$_6$)$_2$ in CD$_3$NO$_2$. The Ex tra Peaks at 59-70 ppm Due to the Solvent.

those of N-C-N linkages at 70.3, 72.2, and 77.1 ppm. The peak at 38.3 ppm is assigned to the carbon of the pendant methyl group.

Cyclic voltammetry data for the Ni(II) and Cu(II) macrobicyclic complexes in acetonitrile solutions are given in Table 2. The complexes exhibit two one-electron waves corresponding to M(II)/M(III) and M(II)/M(I) processes. The oxidation potentials for [Ni(C)]$^{2+}$ and [Cu(C)]$^{2+}$ are +1.07 and +1.38 V vs. SCE, respectively, and fall between those for the corresponding metal complexes of A and B. The similar trend is also observed for the reduction potentials of the Ni(II) and Cu(II) complexes. This indicates that the electron density on the metal atom of the complexes is decreased with ligand structure in the order of A > C > B. This result is quite similar to the observation that the stepwise methylations on the coordinated nitrogen atoms of [Ni(cyclam)]$^{2+}$ make the oxidation more unfavorable process and the reduction more favorable process.[20]

Results of the above spectroscopic and chemical properties together with elemental analyses suggest that the new Ni(II) and Cu(II) complexes contain the macrobicyclic ligand C, which is coordinated to the metal ion in a square planar geometry. On our knowledge, this is the first report which describes the synthesis of macrocyclic complexes by the simple one-pot template condensation reaction of formaldehyde

with amines of three kinds.

Equilibrium between [Ni(C)]$^{2+}$ and [Ni(C)(S)$_2$]$^{2+}$ (S = solvent molecule). The visible spectra (Table 1) of [Ni(C)] (ClO$_4$)$_2$ also show that the molar extinction coefficients are some lower in coordinating solvents such as acetonitrile, water, DMF, and DMSO than in nitromethane. This indicates that the complex dissolves in the coordinating solvents to give an equilibrium mixture of the square planar [Ni(C)]$^{2+}$ and octahedral [Ni(C)(S)$_2$]$^{2+}$ (S = solvent molecule) species as shown in Eq. 4.[21-28] The equilibrium constants, K = [octahedral]/[square planar], and thermodynamic parameters for

$$[Ni(C)]^{2+} + 2S \xrightarrow{K} [Ni(C)(S)_x]^{2+} \qquad (4)$$
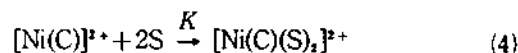
[Ni(C)]$^{2+}$ were determined in various solutions by the known methods[21-24] and are listed in Table 3 along with those for the complexes of A[1,29] and cyclam.[27] The conversion of the square planar into the octahedral species is an exothermic reaction and the values of $\Delta H°$ are in good agreement with those previously obtained for Ni(II) complexes of other macrocyclic ligands.[1,21,25-27] The negative value of $\Delta S°$ observed for the conversion of Ni(II) complexes has been ascribed to the decrease in translational entropy due to the coordination of two solvent molecules at the octahedral species.[1,27,28] Table 3 also shows that the values of K for the Ni(II) complexes are affected by the ligand structure. That is, in a given solvent system, the degree of formation of the octahedral species of [Ni(C)]$^{2+}$ is much smaller than that for [Ni(A)]$^{2+}$ or [Ni(cyclam)]$^{2+}$. It is interesting to find that the relative ligation ability of the solvent molecules also varies with the ligand structure. The value of K for [Ni(C)]$^{2+}$ varies with solvent in the order of MeCN > H$_2$O ≈ DMF > DMSO, which is differ from that for [Ni(cyclam)]$^{2+}$ (DMF > MeCN > DMSO > H$_2$O) and [Ni(A)]$^{2+}$ (MeCN > DMF > H$_2$O > DMSO). As one proceeds from cyclam, through A to C, the relative ligation ability of water molecule is increased but that of DMF is decreased. In the case of C, the ability of water is quite similar to that of DMF in spite of its relatively strong interactions with coordinated amines and self-interactions through hydrogen bonding.[24] It is also found that the value of K is less affected by the ligand structure in water

Table 1. Molar Conductance and Spectral Data of Hexaaza Macrobicyclic Nickel(II) and Copper(II) Complexes

Complex	IR spectra νN-H, cm^{-1}	Electronic spectra[a] λ_{max}, nm(ϵ, M^{-1}cm^{-1})	Molar conductance[a] Λ_M, ohm^{-1}mol^{-1}cm^2
[Ni(A)](ClO$_4$)$_2$[f]		449(56)	
[Ni(B)](ClO$_4$)$_2$[f]		447(80)	
[Ni(C)](ClO$_4$)$_2$	3181	448(77), 446(69)[b] 454(64)[c], 448(69)[d] 449(74)[e]	145, 210[b], 285[c]
[Ni(cyclam)]$^{2+}$[h,i]		460(68)[b]	
[Ni(Me$_2$cyclam)]$^{2+}$[j,k]		441(62)[b]	
[Cu(A)](ClO$_4$)$_2$[f]		486(73), 500(70)[b]	
[Cu(C)](ClO$_4$)$_2$	3235	490(102), 506(109)[b] 502(113)[c]	160, 201[b], 290[c]
[Cu(cyclam)]$^{2+}$[l]		508(92)	

[a] In nitromethane solutions at 25 °C otherwise unspecifed. [b] In aqueous solutions. [c] In acetonitrile solutions. [d] In DMF solutions. [e] In DMSO solutions. [f] Ref. 1. [g] Ref. 2. [h] Ref. 14. [i] cyclam = 1,4,8,11-tetraazacyclotetradecane. [j] Ref. 15. [k] Me$_2$cyclam = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane. [l] Ref. 19.

Table 2. Cyclic Voltammetric Data for the Nickel(II) and Copper (II) Complexes[a].

Complex	$[M(L)]^{2+} \to [M(L)]^{3+}$ V vs. SCE	$[M(L)]^{2+} \to [M(L)]^{+}$ V vs. SCE
Ni(A)[c]	+0.93	−1.55
Ni(B)	+1.43(i)[b]	−1.26
Ni(C)	+1.07(i)[b]	−1.40
Ni(cyclam)[d]	+0.91	−1.46
Ni(N-Me-cyclam)[d,e]	+1.00	−1.43
Ni(N-Me₂-cyclam)[d,f]	+1.16	−1.26
Cu(A)[c]	+1.32	−1.14(i)[b]
Cu(B)	+1.49(i)[b]	−0.70
Cu(C)	+1.38(i)[b]	−0.88

[a] Measured in 0.1 M (n-Bu)₄ acetonitrile solutions. [b] i = irreversible. [c] Ref. 1. [d] Ref. 20. [e] N-Me-cyclam = 1-methyl-1,4,8,11-tetraazacyclotetradecane. [f] N-Me₂-cyclam = 1,4-dimethyl-1,4,8,11-tetraazacyclotetradecane.

Table 3. Equilibrium Constants and Thermodynamic Parameters for $[Ni(L)]^{2+} + 2S \rightleftharpoons [Ni(L)(S)_2]^{2+}$ System at 25 °C

L	S	K	$-\Delta H°$, kcal·mol⁻¹	$-\Delta S°$, cal·K⁻¹mol⁻¹
cyclam[a]	MeCN	8.85	6.9	18.9
	DMF	27.15	8.5	21.8
	H₂O	0.43	3.3	12.8
	DMSO	2.13	4.2	12.6
A[b]	MeCN	1.01	8.8	29.4
	DMF	0.87	9.5	32.3
	H₂O	0.44	4.3	15.2
	DMSO	0.56	5.5	19.7
C	MeCN	0.20	1.8	9.1
	DMF	0.12	3.6	16.4
	H₂O	0.12	2.7	12.5
	DMSO	0.05	2.6	15.2

[a] Ref. 27. [b] Ref. 1 and 29.

than in more bulky solvent such as MeCN, DMF, or DMSO. This result strongly indicates that the degree of the formation of the octahedral species is largely affected by the steric factors of the macrocyclic ligands and the solvent molecules,[24,27] and that the steric repulsion at the axial coordinating sites of $[Ni(C)]^{2+}$. is more severe than that of [Ni(cyclam)]²⁺ and [Ni(A)]²⁺. It can be suggested that the macrobicyclic ligand C, which contain both one methyl pendant arm and one 1,3-diazacyclopentane ring, may exert severe steric repulsion of the Ni (II) complex with solvent molecules and makes the square planar-to-octahedral conversion more unfavorable process.

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