Template Synthesis and Crystal Structure of a Novel Mononuclear Nickel(II) Complex with a Face-to-Face Bis(macrocyclic) Ligand

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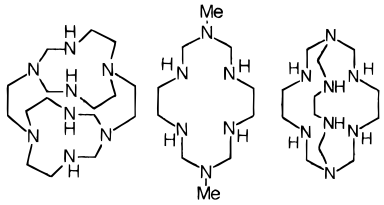
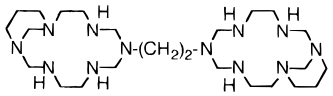
There has been considerable interest in the synthesis of polyaza bis(macrocyclic) ligands and their transition metal complexes.[1−8] Such compounds often generate interesting chemical properties which are not observed in monomeric macrocyclic compounds. Various types of side-by-side bis(macrocyclic) compounds, in which two macrocyclic units are linked together by one bridging group, have been prepared and investigated.[1−5] Several types of face-to-face bis(macrocyclic) complexes which contain two macrocyclic units linked together by two bridging groups, such as bis(porphyrin) and bis(cyclidene) compounds, also have been reported.[6−8] However, most of them reported to date have been prepared from multistep reactions of preformed monomeric macrocycles.[6−8] We have been interested in the synthesis of new types of face-to-face bis(macrocyclic) complexes by one-step metal template condensation reactions.

Metal-directed condensation reaction of coordinated polyamines with formaldehyde has been employed in the preparation of various saturated polyaza macrocyclic,[9,11] macropolycyclic,[10,12−14] and side-by-side bis(macrocyclic) complexes[3,4] containing $N-CH_2-N$ linkages. For example, the mononuclear nickel(II) complexes of **2** (ref 9) and **3** (ref 10) and the dinuclear nickel(II) complexes of **4** (ref 3) have been synthesized by the reactions of eqs 1−3, respectively. It has been revealed that



1 **2** **3**



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$$Ni^{2+} + 2en + MeNH_2 + 4HCHO \longrightarrow [Ni(\mathbf{2})]^{2+} \quad (1)$$

$$Ni^{2+} + 3en + 2NH_3 + 6HCHO \longrightarrow [Ni(\mathbf{3})]^{2+} \quad (2)$$

$$2Ni^{2+} + 2H_2N(CH_2)_3NH(CH_2)_2NH_2 + 3en + 8HCHO \longrightarrow [Ni_2(\mathbf{4})]^{4+} \quad (3)$$

$$Ni^{2+} + 2N(CH_2CH_2NH_2)_3 + 4HCHO \longrightarrow [Ni(\mathbf{1})]^{2+} \quad (4)$$

such reactions are simple, selective, and inexpensive synthetic routes toward various types of saturated polyaza macrocyclic compounds which could not be prepared by other methods. Utilizing the characteristics of the reactions, we have designed and prepared a new mononuclear nickel(II) complex [Ni(**1**)]$(ClO_4)_2$ by the one-pot reaction of tris(aminoethyl)amine (tren) and formaldehyde in the presence of the metal ion. Interestingly, the ligand **1** contains two fully saturated 10-membered tetraaza macrocyclic subunits (1,3,6,9-tetraazacyclodecane) that are linked together by two ethylene chains through nitrogen (N^1 and N^6) atoms in an antiparallel face-to-face arrangement and encapsulates only one metal ion. The synthesis and crystal structure of the nickel(II) complex are reported.

Experimental Section

Measurements. IR spectra were recorded of either Nujol mulls or KBr pellets on a Shimadzu IR-440 spectrophotometer, electronic spectra with a Shimadzu UV-160 spectrophotometer, and conductance measurements with a Metrohm Herisau E518 conductometer. Elemental analyses and FAB mass spectra were performed at the Korea Basic Science Institute, Seoul, Korea. Magnetic susceptibilities were measured with a Johnson Matthey MK-1 magnetic susceptibility balance.

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Table 1. Crystal and Refinement Data for $[Ni(\mathbf{1})](ClO_4)_2$

formula	$C_{16}H_{36}Cl_2N_8NiO_8$
fw	598.14
space group (No.)	$P2_1/n$ (14)
a (Å)	8.884(2)
b (Å)	15.453(2)
c (Å)	9.647(2)
β, deg	116.21(3)
V (Å^3)	1188.2(4)
Z	2
D_{calc} (g/cm^3)	1.672
μ (cm^{-1})	11.02
$F(000)$	628
T (°C)	20(2)
λ (Å)	0.710 73
rflns collected	1995
indep rflns	1886 [R(int) = 0.0191]
data/restraints/params	1882/0/160
goodness-of-fit on F^2	1.067
final R indices [$I > 2\sigma(I)$][a]	$R = 0.0339$, $R_w = 0.0831$
R indices (all data)[a]	$R = 0.0356$, $R_w = 0.0869$
largest diff peak and hole (e/Å^3)	0.725 and −0.330

[a] $R = \sum||F_o| - |F_c||/\sum|F_c|$. $R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.55P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

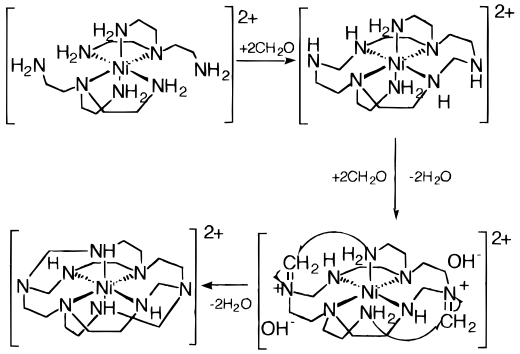
Molar susceptibilities were corrected for diamagnetism of the ligands and the anion by use of Pascal's constants.

Safety Note. Although we have experienced no problems with the compound reported in this work, perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great **CAUTION**.

Synthesis of $[Ni(1)](ClO_4)_2$. All chemicals used in the synthesis were of reagent grade. To a methanol solution (*ca.* 25 mL) of $Ni(OAc)_2 \cdot H_2O$ (3.0 g, 12.1 mmol) were added tris(2-aminoethyl)amine (3.6 mL, 24.2 mmol) and paraformaldehyde (2.2 g, 72.3 mmol). The mixture was heated to reflux for 24 h and then cooled to room temperature. After water (*ca.* 10 mL) had been added, concentrated $HClO_4$ (*ca.* 2.0 mL) and an excess amount of $NaClO_4$ were added to the resulting solution. The mixture was left at room temperature. The purple solids formed were filtered off and washed with methanol. The crude product often contains the perchlorate salt of the protonated tris(2-aminoethyl)amine. Pure crystals of the product were isolated by simple recrystallization of the crude product from a hot water−acetonitrile (3:1) mixture. Yield: ∼30%. Anal. Calcd (found) for $C_{16}H_{36}N_8NiCl_2O_8$ (fw = 598.14): C, 32.13 (32.04); H, 6.07 (6.14); N, 18.73 (18.58). FAB mass (*m/z*): 498 ($[M - ClO_4]^+$), 397 ($[M - 2ClO_4 - H]^+$).

Crystal Structure Analysis. Purple crystals of $[Ni(\mathbf{1})](ClO_4)_2$ suitable for X-ray study were grown from water−acetonitrile. A crystal (0.30 × 0.40 × 0.50 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10° < \theta < 13°$). Intensity data were collected with a θ range of 2.70−25.27° in the $\omega/2\theta$ scan mode for $-9 \le h \le 10$, $0 \le k \le 18$, $-11 \le l \le 0$. Three standard reflections were monitored every 1 h during data collection. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with ψ scans were applied to the data (the range of correction: 0.89−1.00). The structure was solved by using Patterson methods using SHELXS-86 and refined by full-matrix least-squares techniques on F^2 by using SHELXL-93 with 1882 reflections above the 2σ level and 160 parameters.[15] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were positioned geometrically and refined using a riding model. The final cycle of the refinement converged with $R = 0.034$. Crystal and refinement data are listed in Table 1.

Scheme 1



Results and Discussion

Synthesis and Properties. It has been reported that the nontemplate or metal ion template condensation reaction of tren and various dialdehydes in a 2:3 molar ratio yields various unsaturated hexaaza macrobicyclic compounds, *i.e.*, Schiff base cryptands.[16] In this work the one-pot reaction (eq 4) of excess formaldehyde with a 1:2 molar mixture of nickel(II) ion and tren, followed by the addition of an excess of $NaClO_4$, produced the mononuclear complex $[Ni(\mathbf{1})](ClO_4)_2$ in which two saturated 10-membered tetraaza macrocyclic units are linked together by two ethylene chains. The proposed routes to give the complex are shown in Scheme 1, which is similar to those reported for the complexes of **2**−**4**.[3,9,10] The complex $[Ni(tren)]^{2+}$ (refs 13 and 17) initially reacts with formaldehyde to form the macromonocyclic complex containing $N-CH_2-N$ linkages.

The uncoordinated secondary amino groups of $N-CH_2-N$ linkages may react with additional formaldehyde to produce the iminium ions and then result in the formation of the complex of **1**. Four secondary nitrogen atoms and two of the four tertiary nitrogen atoms of the ligand are coordinated to the metal ion in an octahedral geometry; the tertiary nitrogen atoms in the $N-CH_2-N$ linkages are not involved in coordination. The present synthetic method is quite interesting because the formation and linking of the two 10-membered tetraaza macrocycles are performed by the simple one-pot reaction.

The nickel(II) complex is soluble in polar solvents such as water, nitromethane, and acetonitrile. The infrared spectrum of the complex shows a single strong peak at 3290 cm^{-1}, which is attributed to N−H stretching vibrations of the coordinated secondary amino groups. No absorption near 1600 cm^{-1} assignable to primary amines was observed. The values of molar conductance measured in water (210 Ω^{-1} mol^{-1} cm^2), nitromethane (165 Ω^{-1} mol^{-1} cm^2), and acetonitrile (285 Ω^{-1} mol^{-1} cm^2) at 20 °C indicate that the complex is a 1:2 electrolyte. The magnetic moment of $[Ni(\mathbf{1})](ClO_4)_2$ in the solid state is 2.95 μ_B at room temperature, which is consistent with a d^8 electronic configuration in an octahedral geometry. The FAB mass spectrum of the complex shows two groups of peaks due to the fragments formed by stepwise liberation of the perchlorates at *m/z* 498 ($[M - ClO_4]^+$) and 397 ($[M - 2ClO_4 - H]^+$).

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(17) The visible spectrum of $[Ni(tren)_2]^{2+}$ [354 (ϵ = 8.5 M^{-1} cm^{-1}); 557 nm (ϵ = 7.2 M^{-1} cm^{-1})] in water is comparable to that of $[Ni(N\text{-}Me\text{-}dien)_2]^{2+}$ (N-Me-dien = 4-methyl-1,4,7-triazaheptane) [348 (ϵ = 7.5 M^{-1} cm^{-1}); 554 nm (ϵ = 6.1 M^{-1} cm^{-1})], indicating that the two complexes have a similar octahedral coordination geometry in solutions.

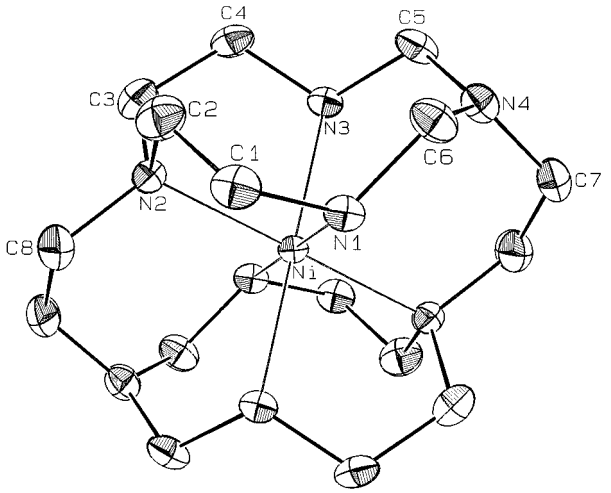

Figure 1. ORTEP drawing of $[Ni(\mathbf{1})]^{2+}$ in $[Ni(\mathbf{1})](ClO_4)_2$ with atomic labeling scheme.

The electronic absorption spectrum of $[Ni(\mathbf{1})]^{2+}$ measured in acetonitrile shows maximum absorptions at 820 ($\epsilon = 5.5$ M^{-1} cm^{-1}), 520 ($\epsilon = 5.3$ M^{-1} cm^{-1}), and 333 nm ($\epsilon = 7.0$ M^{-1} cm^{-1}). The spectrum is comparable with those of the cryptand complex $[Ni(\mathbf{3})]^{2+}$ [510 ($\epsilon = 8.0$ M^{-1} cm^{-1}) and 316 nm ($\epsilon = 11.2$ M^{-1} cm^{-1})][10] and $[Ni(en)_3]^{2+}$ [540 nm ($\epsilon = 6.9$ M^{-1} cm^{-1}) and 333 nm ($\epsilon = 9.0$ M^{-1} cm^{-1})], supporting the proposal that the metal ion is in an octahedral environment. However, the wavelengths of the bands for the present complex are somewhat longer than those of $[Ni(\mathbf{3})]^{2+}$,[10] indicating that the ligand field strength of the former is weaker than that of the latter. The above results together with elemental analysis of the compound prepared in this work correspond to the mononuclear nickel(II) complex of **1**. The structure of the complex was confirmed by X-ray crystallography (see below).

The nickel(II) complex of **1** is extremely stable in the solid state. It is also stable against ligand substitution with the strong field ligand CN^-; the complex did not react with the anion even in boiling water. The complex is relatively stable against decomposition even at low pH at room temperature; the visible spectra of the complex (5.0×10^{-3} M) in 0.5 M HCl solution indicated that less than 3% of the complex was decomposed in 10 h at 25 °C. This behavior is similar to the behaviors observed for various square-planar nickel(II) complexes of 14-membered polyaza macrocyclic ligands such as **2** and **4**.[3,9] However, the complex was slowly decomposed in concentrated strong acid at high temperature; in 6.0 M HCl solution, the dissociation reaction was found to proceed to completion within 10 min at *ca.* 70 °C. After the resulting acidic solution had been neutralized by addition of NaOH at room temperature, the addition of $NaClO_4$ produced only the complex $[Ni(tren)_2](ClO_4)_2$. All efforts to isolate the free ligand **1** were unsuccessful, indicating that the free ligand is unstable; diaminomethane groups ($R_2N-CH_2-NR_2$) in organic compounds are known to be unstable unless both of the nitrogen atoms are tertiary.[10,18] The preperation of **1** as its nickel(II) complex supports the proposal that the diaminomethane groups can be stabilized by the coordination of the nitrogen atoms.[3,9−14]

Crystal Structure. The ORTEP drawing (Figure 1) of the complex cation $[Ni(\mathbf{1})]^{2+}$ shows that the ligand consists of two 10-membered tetraaza macrocyclic subunits which are linked together by two ethylene chains through the nitrogen atoms with an antiparallel face-to-face arrangement. The ligand serves as a hexadentate ligand, and the complex has a tetragonally distorted octahedral coordination geometry with an inversion center at the metal ion; the Ni···N(4) distance [3.082(3) Å] indicates that the N(4) atom is not involved in coordination. The shortest Ni···O(ClO_4^-) is 4.062(3) Å, indicating uncoordination of the perchlorate anions. The ligand acts as a three-dimensional cage encapsulating only one metal ion; each macrocyclic subunit is too small to bind the metal ion at the center of the hole.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[Ni(\mathbf{1})](ClO_4)_2$[a]

Ni−N(1)	2.143(2)	Ni−N(2)	2.119(2)
Ni−N(3)	2.144(2)	N(1)−C(1)	1.480(4)
N(1)−C(6)	1.497(4)	N(2)−C(2)	1.500(4)
N(2)−C(3)	1.478(4)	N(2)−C(8)	1.475(4)
N(3)−C(4)	1.490(4)	N(3)−C(5)	1.513(4)
N(4)−C(5)	1.431(4)	N(4)−C(6)	1.419(4)
N(4)−C(7)	1.459(4)	C(3)−C(4)	1.506(5)
N(1)−Ni−N(1)′	180.0	N(2)−Ni−N(2)′	180.0
N(3)−Ni−N(3)′	180.0	N(1)−Ni−N(2)	83.07(9)
N(1)−Ni−N(2)′	96.93(9)	N(1)−Ni−N(3)	93.62(9)
N(1)−Ni−N(3)′	86.38(9)	N(2)−Ni−N(3)	82.13(9)
N(2)−Ni−N(3)′	97.87(9)	C(1)−N(1)−C(6)	113.5(2)
C(2)−N(2)−C(3)	108.8(2)	C(4)−N(3)−C(5)	113.5(2)
C(5)−N(4)−C(6)	116.5(3)	C(5)−N(4)−C(7)	118.8(3)
C(6)−N(4)−C(7)	118.8(3)	N(2)−C(3)−C(4)	112.9(2)
N(4)−C(5)−N(3)	115.0(2)	N(3)−C(4)−C(3)	113.0(2)
N(2)−C(8)−C(7)′	118.5(3)	N(4)−C(7)−C(8)′	119.5(3)

[a] Symmetry transformations used to generate equivalent atoms: prime, $-x + 2$, $-y + 2$, $-z$.

Selected bond distances and angles of the complex are listed in Table 2. The six Ni−N bond distances range from 2.119(2) to 2.144(2) Å. The bond distances are typical for high-spin octahedral nickel(II) complexes. However, the average Ni−N bond distance (2.135 Å) is *ca.* 0.03 Å longer than that of $[Ni(\mathbf{3})]^{2+}$ (2.10 Å).[10] This agrees with the electronic spectral data that indicate the ligand field to be weaker for the present complex than for the complex of **3**. Somewhat unexpectedly, the Ni−N(1) (secondary) and Ni−N(3) (secondary) distances are *ca.* 0.035 Å longer than the Ni−N(2) (tertiary) distance [2.119(2) Å]. This result is different from the generally observed trend that Ni−N(secondary) bond distances are shorter than Ni−N (tertiary) distances for most polyaza macrocyclic nickel(II) complexes.[13,14,19] It is clear that the coordination geometry around the nickel(II) ion is strongly affected by the steric factor of the $-CH_2CH_2-$ chains which link the two 10-membered macrocyclic subunits.

The N−Ni−N bond angles somewhat deviate from those of the ideal octahedral geometry. The N(1)−Ni−N(3) angle [93.62(9)°] involved in the six-membered chelate ring is much larger than the N(1)−Ni−N(2) [83.07(9)°] and N(2)−Ni−N(3) [82.13(9)°] angles in the five-membered chelate rings, as usual. One of the remarkable structural features of the complex is that the N(1)−Ni−N(3) angle is even larger than the N(1)−Ni−N(3)′ angle [86.38(9)°] involved in the two macrocyclic subunits. It is also interesting to observe that the angles about the uncoordinated N(4) atom significantly deviate from the ideal tetrahedral angles with a C(5)−N(4)−C(7) angle of 118.8(3)°. The average N(4)−C distance (1.436 Å) is also *ca.* 0.05 Å shorter than that of N(2)−C (1.484 Å). The N(4) atom lies 0.204(3) Å out of the C(5)−C(6)−C(7) plane; the distance is much shorter than that of the N(2) atom from the C(2)−C(3)−C(8) plane. These findings support the sp^2-like hybridization

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of the N(4) atom. Similar sp^2-like hybridization of the uncoordinated tertiary nitrogen atoms has also been reported for the nickel(II) complex of **3**.[10]

Concluding Remarks. The results show that the new compound prepared in this work is the mononuclear nickel(II) complex of the face-to-face bis(macrocyclic) ligand **1**, in which two saturated 10-membered tetraaza macrocyclic subunits are linked together by two ethylene chains. The present synthetic method is quite interesting because the formation and linking of the two 10-membered macrocycles are performed by a simple one-pot reaction. As far as we know, $[Ni(\mathbf{1})]^{2+}$ is the first mononuclear nickel(II) complex of a saturated face-to-face bis(macrocyclic) ligand prepared by a one-step reaction. The formation of the 10-membered tetraaza macrocyclic ring (1,3,6,9-tetraazacyclodecane) was not reported to date.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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