Notes

Synthesis of Dinickel(I) and Dinickel(II) Complexes of Bismacrocyclic Ligands

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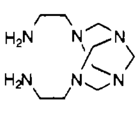
Bismacrocyclic complexes incorporating two metal ions are of interest because they can act as multielectron redox agents or catalysts and can be regarded as models for polynuclear metalloenzymes. Furthermore, they can exhibit interesting physical properties due to the metal–metal interactions.

We have demonstrated that the simple template condensation reaction of amines and formaldehyde produced various macrocyclic complexes.[1-5] For example, the Ni(II) complexes of **1–3** have been prepared by the template condensation reactions of amines and formaldehyde in the presence of a metal ion as described in eqs 1–3.[1,2] A few bismacrocyclic Ni(II) complexes have been synthesized by utilizing these synthetic methods.[6,7] Recently, we have demonstrated that some macrocyclic ligands including **2** stabilize the Ni(I) state.[8] The Ni(I) complexes react with alkyl halides, water, and carbon dioxide.[9] In order to synthesize the bismacrocyclic complexes containing two Ni(I) centers that can interact with such substrates, we now have prepared the bismacrocyclic Ni(II) and Ni(I) complexes of **4–6**. The Ni(I) complexes of **5** and **6** are the first examples of Ni(I) complexes with bismacrocyclic ligands.



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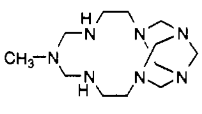

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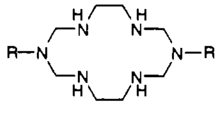

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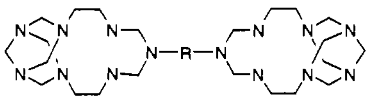
$$\mathrm{Ni^{2+} + en + CH_2O + NH_3 \rightarrow [Ni(\mathbf{1})]^{2+}} \qquad (1)$$

$$\mathrm{[Ni(\mathbf{1})]^{2+} + CH_2O + CH_3NH_2 \rightarrow [Ni(\mathbf{2})]^{2+}} \qquad (2)$$

$$\mathrm{Ni^{2+} + en + CH_2O + RNH_2 \rightarrow [Ni(\mathbf{3})]^{2+}} \qquad (3)$$



4; R = $-(CH_2)_2-$
5; R = $-(CH_2)_4-$
6; R = $-CH_2-p-C_6H_4-CH_2-$

Experimental Section

Materials. All chemicals and solvents used in the syntheses of Ni(II) complexes were of reagent grade and were used without purification. However, they were purified according to the literature[10] and were deaerated thoroughly prior to use for the physicochemical measurements and for the syntheses of Ni(I) complexes. $[Ni(\mathbf{1})](ClO_4)_2$ was synthesized by the method previously described in the literature.[1]

Measurements. Infrared spectra were recorded with a JASCO IR-810 spectrophotometer. Conductance measurements were performed by using a TOA CM-30ET conductometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 80 FT NMR spectrometer. Electronic absorption spectra were obtained on a Shimadzu 260 UV/vis spectrophotometer. EPR spectra were recorded on a Bruker ER 200E-SRC spectrometer. Cyclic voltammetry was carried out with a BAS 100A electrochemical analyzer and Ametek DMP-40 series digital plotter. The electrochemical data were obtained in MeCN with 0.1 M $(n-Bu)_4NPF_6$. The working electrode was a platinum disk, the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl. Elemental analyses were performed by Korea Basic Science Center, Seoul.

Synthesis. Synthesis and manipulation of Ni(I) complexes were performed under a nitrogen atmosphere with the use of standard Schlenk techniques.

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

$[Ni^{II}_2(\mathbf{4})](ClO_4)_4$. $[Ni(\mathbf{1})](ClO_4)_2$ (1.6 g) was stirred in hot methanol (40 mL), and water was added until a clear solution was obtained. To this solution was slowly added 36% aqueous formaldehyde (5.0 mL), ethylenediamine (1.0 mL), and triethylamine (4.0 mL). The mixture was heated at reflux for 48 h until a yellow solution resulted. The solution was filtered hot to remove insoluble material and then allowed to stand at room temperature until a yellow precipitate formed. The precipitate was filtered out, washed with methanol, and dried in *vacuo*. The precipitate was recrystallized from hot water. Yield: ~2%. Anal. Calcd for $Ni_2C_{24}H_{52}N_{14}Cl_4O_{16}$: C, 27.40; H, 4.98; N, 18.64. Found: C, 27.27; H, 4.89; N, 18.27.

$[Ni^{II}_2(\mathbf{5})](ClO_4)_4 \cdot H_2O$. $[Ni(\mathbf{1})](ClO_4)_2$ (1.6 g) was stirred in hot methanol (40 mL), and water was added until a clear solution was obtained. To this solution was slowly added 36% aqueous formaldehyde (6.0 mL) and 1,4-diaminobutane (3.0 mL). The mixture was heated at reflux for 8 h until a yellow precipitate formed. The precipitate was filtered out while the mixture was hot, washed with methanol, and dried in *vacuo*. Yield: ~30%. Anal. Calcd for $Ni_2C_{26}H_{58}N_{14}Cl_4O_{17}$: C, 28.44; H, 5.32; N, 17.85. Found: C, 28.14; H, 5.13; N, 17.69.

$[Ni^{II}_2(\mathbf{6})](PF_6)_4$. $[Ni(\mathbf{1})](ClO_4)_2$ (1.5 g) was stirred in a hot mixture of MeCN (40 mL) and methanol (10 mL), and water was added until a clear solution was obtained. Into this solution was added paraformaldehyde (1.1 g) and a solution of *p*-xylenediamine (0.8 g) in MeCN (15 mL). The mixture was heated at reflux for 6 days, during which time all starting materials went into the solution and then a yellow precipitate of $[Ni^{II}_2(\mathbf{6})](ClO_4)_4$ formed. The precipitate was filtered out, washed with methanol, and dried in *vacuo*. Yield: ~30%. The perchlorate salt $[Ni^{II}_2(\mathbf{6})](ClO_4)_4$ was suspended in MeCN, and excess NH_4PF_6 was added. The perchlorate complexes went into the solution, and the white precipitate of NH_4ClO_4 formed. NH_4ClO_4 was filtered off, and water was added dropwise to the solution until yellow crystals formed, which were filtered out, washed with methanol, and dried in *vacuo*. Anal. Calcd for $Ni_2C_{30}H_{56}N_{14}P_4F_{24}$: C, 27.50; H, 4.30; N, 14.97. Found: C, 28.24; H, 4.21; N, 14.99.

$[Ni^{II}_2(L)](PF_6)_4$ (L = 4, 5). The complexes were prepared from $[Ni_2(L)](ClO_4)_4$ (L = **4**, **5**) by a method similar to that for $[Ni_2(\mathbf{6})](PF_6)_4$.

$[Ni^{I}_2(\mathbf{5})](ClO_4)_2$. Ni(II) complex $[Ni_2(\mathbf{5})](ClO_4)_4$ (0.8 g) and Na(Hg) (25 g) were suspended in dry and degassed MeCN (100 mL), and the suspension was stirred for 1 h under nitrogen. The complex went into the solution as the reduction proceeded, and the color of the solution

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Table I. Properties of Ni(II) Complexes

compd	IR:[a] ν_{NH} (cm^{-1})	UV/vis:[b,c] λ_{max}, nm (ϵ)	Λ_M:[b,c] Ω^{-1} cm^{-2} M^{-1}	^{13}C NMR:[d] δ, ppm	ref
$[Ni_2(4)](PF_6)_4$	3230	440 (152)[c]	317[c]	46.6, 47.9, 54.4, 67.0, 68.9, 74.6, 75.4	this work
$[Ni_2(5)](PF_6)_4$	3250	440 (152),[b] 434 (171)[c]	479[b]	25.1, 46.6, 49.1, 54.4, 66.8, 69.0, 74.7, 75.4	this work
$[Ni_2(6)](PF_6)_4$	3239	442 (161)[b]	526[b]	46.7, 53.7, 54.4, 66.7, 67.0, 74.7, 75.4, 129.4, 137.6	this work
$[Ni(2)](ClO_4)_2$[e]	3213	442 (80),[b] 438 (83)[c]		37.7, 46.6, 54.4, 68.5, 69.0, 74.6, 75.3	1

[a] Measured with Nujol mull. [b] Measured in MeCN. [c] Measured in $MeNO_2$. [d] Measured in MeCN-d_3. [e] Reference 1.

Table II. Cyclic Voltammetry Data of Nickel(II) Complexes[a,b]

	Ni(II) → Ni(III)				Ni(II) → Ni(I)			
compd	E_{anodic}	$E_{cathodic}$	$E_{1/2}$	*n* value[c]	E_{anodic}	$E_{cathodic}$	$E_{1/2}$	*n* value[c]
$[Ni_2(4)](PF_6)_4$	+1.43	+1.30	+1.37 (qr)	2.0	−1.33	−1.38	−1.36 (r)	1.9
$[Ni_2(5)](PF_6)_4$	+1.49 (i)		+1.49 (i)	1.9	−1.27	−1.35	−1.31 (qr)	1.7
$[Ni_2(6)](PF_6)_4$			>+2.0		−1.24	−1.31	−1.27 (r)	1.7
$[Ni(2)](ClO_4)_2$[d]			+1.38 (qr)				−1.33 (r)	

[a] Measured in MeCN with 0.1 M $(n\text{-}Bu)_4NPF_6$, V vs Ag/AgCl reference electrode. [b] i = irreversible; qr = quasi-reversible; r = reversible. [c] Estimated from the peak currents. [d] Reference 1.

Table III. Properties of Nickel(I) Complexes

compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[a]	EPR data[b]
$[Ni_2(5)](ClO_4)_2$	535 (690), 328 (2400)	$g_\parallel = 2.239$, $g_\perp = 2.061$
$[Ni_2(6)](PF_6)_2\cdot 2CH_3CN$	536 (1300), 332 (4600)	$g_\parallel = 2.238$, $g_\perp = 2.059$
$[Ni(2)]ClO_4$[c]	538 (600), 330 (2020)	$g_\parallel = 2.240$, $g_\perp = 2.062$

[a] Measured in MeCN. [b] The spectra were measured with powder samples at room temperature. [c] Reference 8.

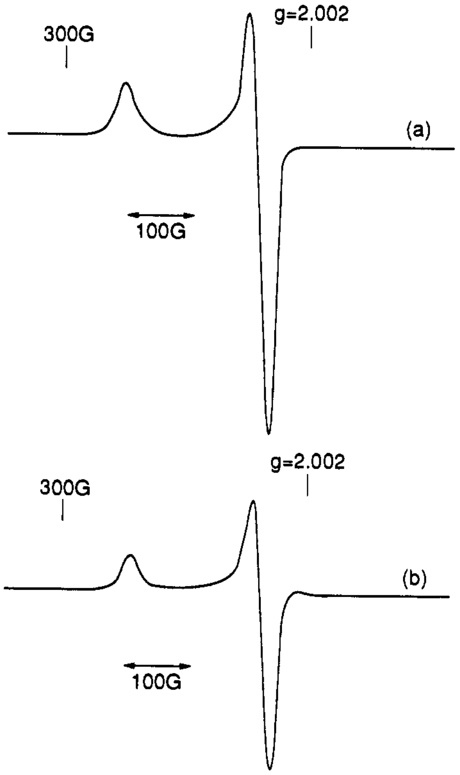

Figure 1. EPR powder spectra of (a) $[Ni^{I}_2(5)](ClO_4)_2$ and (b) $[Ni^{I}_2(6)](PF_6)_2\cdot 2CH_3CN$ measured at room temperature.

turned to deep violet. The solution was filtered and concentrated to one-third of the initial volume under nitrogen. The solution was allowed to stand in a refrigerator for ~2 days until red crystals formed, which were filtered out, washed with MeCN, and dried in *vacuo*. Yield: ~80%. Anal. Calcd for $Ni_2C_{26}H_{56}N_{14}Cl_2O_8$: C, 35.44; H, 6.40; N, 22.25. Found: C, 34.25; H, 5.95; N, 22.46.

$[Ni^{I}_2(6)](PF_6)_2\cdot 2CH_3CN$. $[Ni_2(6)](PF_6)_4$ was reduced with Na(Hg) in MeCN by a method similar to that for the synthesis of $[Ni^{I}(5)](ClO_4)_2$. Red crystals were obtained. Yield: ~80%. Anal. Calcd for $Ni_2C_{34}H_{62}N_{16}P_2F_{12}$: C, 37.05; H, 5.67; N, 20.33. Found: C, 37.72; H, 5.67; N, 20.10.

Results and Discussion

The dinickel(II) complexes of the bismacrocyclic ligands **4**–**6** were synthesized by the template condensation reactions of **1** with formaldehyde and various primary diamines as described in eq 4.

$$1 + CH_2O + NH_2\text{-}R\text{-}NH_2 \rightarrow [Ni_2(L)]^{4+} \qquad (4)$$

$$L = 4,\ R = \text{-}(CH_2)_2\text{-};\ L = 5,\ R = \text{-}(CH_2)_4\text{-};\ L = 6,\ R = \text{-}CH_2\text{-}p\text{-}C_6H_4CH_2\text{-}$$

The properties of Ni(II) complexes of bismacrocyclic ligands are summarized in Table I. The values of molar conductance for the complexes indicate that the complexes are 1:4 electrolytes.[11] The infrared spectra of the Ni(II) complexes of **4**–**6** show a single absorption band near 3200 cm^{-1}, which is attributed to the NH stretch of the coordinated secondary amines in the macrocycle. The broad band at ca. 1100 cm^{-1} for ClO_4^- salts or that at ca. 840 cm^{-1} for PF_6^- salts shows no significant splitting, indicating the absence of interactions between the anions and the complex cations. Electronic absorption spectra of the dinickel(II) complexes of **4**–**6** show a d–d transition band at 435–440 nm (ϵ = ~150), which is similar to that of the square-planar Ni(II) complex of the monocyclic ligand **2**. However, the extinction coefficients are almost doubled due to the two chromophores in the molecule. The spectra indicate that the ligand field strength of the bismacrocyclic complexes is not significantly affected by the type or the length of bridging chain between the two macrocycles. ^{13}C DEPT-NMR spectra (Table I) of PF_6^- salts of the Ni(II) complexes show seven, eight, and nine unique peaks for **4**, **5**, and **6**, respectively, which is consistent with the ligand structures. Cyclic voltammetry data (Table II) indicate two-electron oxidation and two-electron reduction peaks for both **4** and **5** that are attributed to Ni(II)–Ni(III) and Ni(II)–Ni(I) couples and a single two-electron reduction wave for **6**. It has been reported that the consecutive oxidation of two equivalent and independent metal centers involves potential separation of 36 mV on the statistical base.[12,13] However, it is difficult to observe such a small difference. If the two metal ions interact with each other, two peaks are separated noticeably. The Ni(II) bismacrocyclic complexes in this study show that the complexes

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(14) The synthesis of the Ni(I) complex of **4** was not attempted because the starting Ni(II) complex was synthesized in low yield.

release or accept two electrons nearly at the same potential, indicating the absence of metal–metal interactions. The reduction potentials of Ni(II)/Ni(I) are similar for the ligands **2** and **4**–**6** whereas the oxidation potentials of Ni(II)/Ni(III) for **5** and **6** differ substantially from those of **2** and **4**. This probably reflects the difficulty of formation of a six-coordinate Ni(III) species in the case of **5** and **6** because of the steric hindrance between the axial acetonitrile ligands of the two different nickel centers. This is caused by the free rotation of the long flexible bridging chain. In general, Ni(III) species prefer six-coordination while Ni(I) species prefer four-coordination.[8,16,17]

The Ni(I) complexes of **5** and **6** were prepared by the reduction of Ni(II) complexes with Na(Hg) in MeCN.[14] The complexes were extremely sensitive to oxygen and moisture. The spectroscopic properties of Ni(I) complexes are summarized in Table III, and the EPR spectra are presented in Figure 1. The isolation of Ni(I) macrocyclic complexes is still very rare, and only a few Ni(I) complexes of monomacrocyclic ligands have been reported.[8,15] It is clearly shown here that the bismacrocyclic ligands **5** and **6** in this study stabilize two Ni(I) ions. The electronic absorption spectra of the Ni(I) complexes of **5** and **6** are similar to that of the Ni(I) complex of **2** in square-planar geometry.[8] The anisotropic axial EPR spectra with $g_{\parallel}$ values being greater than the $g_{\perp}$ values indicate that the nickel ions are in a d^9 electronic state.[8,16–18] The characteristic UV/vis and EPR spectra show that the two Ni(I) ions of the bismacrocyclic complexes are in the square-planar geometry.[8] The reactions of the bismacrocyclic Ni(I) complexes with various substrates are now under investigation.

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