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A New Cyclam with an NH_2-Pendant Donor, 6-Amino-1,4,8,11-tetraazacyclotetradecane, and Its Nickel(II) Complexes

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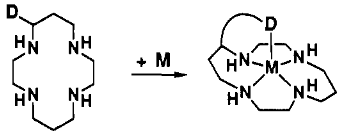
A new cyclam with a pendant primary amino donor, 6-amino-1,4,8,11-tetraazacyclotetradecane, **3**, has been synthesized from diethyl aminomalonate and 1,9-diamino-3,7-diazanonane in refluxing MeOH, followed by BH_3·THF reduction. Reaction of **3** with $Ni(ClO_4)_2·6H_2O$ in a pH 8.5 aqueous solution yielded a Ni^{II} complex **14**, whose X-ray crystal structure has shown that the pendant NH_2 axially coordinates to Ni^{II} and the cyclam moiety takes a *trans* I configuration. X-ray crystal data of **14**: $C_{10}H_{25}N_5Ni(ClO_4)_2·2H_2O$, monoclinic, space group $P2_1$ with $a = 8.943(5)$ Å, $b = 13.552(7)$ Å, $c = 8.729(5)$ Å, $\beta = 98.96(5)°$, $\rho_c = 1.617$ g cm^{-3} for $Z = 2$, $V = 1045(2)$ Å^3, $R_w = 0.075$, and $R = 0.075$. The axial NH_2 donor in an acidic solution dissociates with a protonation constant (log *K*) of 3.8 at 25 °C, $I = 0.10$ ($NaClO_4$), as measured by the spectroscopic titration, yielding a transient NH_3^+-pendant N_4-coordinate complex **15** with the same *trans* I configuration. **15** slowly isomerizes with a first-order rate constant of 0.40 h^{-1} at 60 °C and pH 3.0 to an N_4-coordinate **16** with a more stable *trans* III configuration, as determined by X-ray crystal analysis. X-ray crystal data of **16**: $C_{10}H_{26}N_5Ni(ClO_4)_3·1.5H_2O$, monoclinic, space group $P2_1/a$, with $a = 15.288(9)$ Å, $b = 17.217(10)$ Å, $c = 8.451(8)$ Å, $\beta = 93.77(5)°$, $\rho_c = 1.797$ g cm^{-3} for $Z = 4$, $V = 2219(5)$ Å^3, $R_w = 0.088$, and $R = 0.062$. The NH_3^+ pendant in **16** reversibly deprotonates to **17** with log *K* of 6.0 at 25 °C and $I = 0.10$ ($NaClO_4$). At pH 7.6 and 25 °C, the orange solution of **17** is converted back to the purple solution of **14** with a first-order rate constant of 2.3×10^{-2} h^{-1}. The NH_3^+-pendant, N_4-coordinate, *trans* III cyclam complex **16** is more efficient than any other isomer mentioned above or cyclam complex **8** in catalyzing electrochemical reduction of CO_2 to CO.

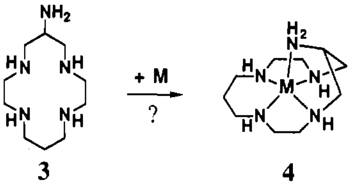
Introduction

Cyclam (1,4,8,11-tetraazacyclotetradecane) is one of the most versatile tetraamine ligands.[1] Lately, various donor pendants have been attached for further functionalization.[2] For instance, phenol-,[1k,3,4] catechol-,[5] pyridyl-,[1k,6,7] and imidazole-attached cyclams[8,9] (their general structures represented by **1**) were designed, where these intramolecular donors (D) easily coordinate to the metal ions from an axial direction in **2** and dramatically alter the properties of the cyclam metal complexes.



1 **2**

We now have synthesized a new cyclam appended with an amine ("amino-pendant cyclam") **3** by using our original synthetic route (see Scheme I). From **3**, another type of a pendant



3 **4**

"amino-pendant cyclam"

coordinating complex **4** may be prepared with metal ions.[10] Earlier,[11] a diamino-pendant cyclam **5** was synthesized as complexes by metal template reactions from Cu^{II}(ethylenedi-

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(10) After this work was finished metal-template syntheses of monoamino-substituted cyclam (6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine) and its N_5-coordinate Cr^{III} complex with *trans* III configuration were reported: see ref 17b. However, thermodynamic or kinetic study in an acid solution was not performed.

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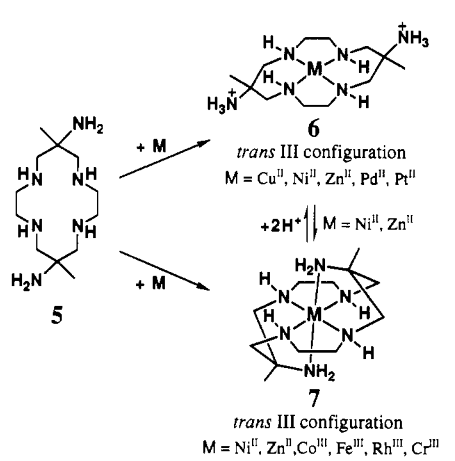
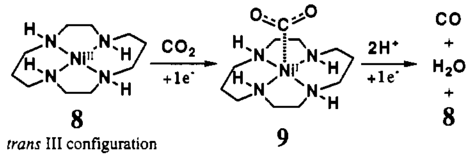


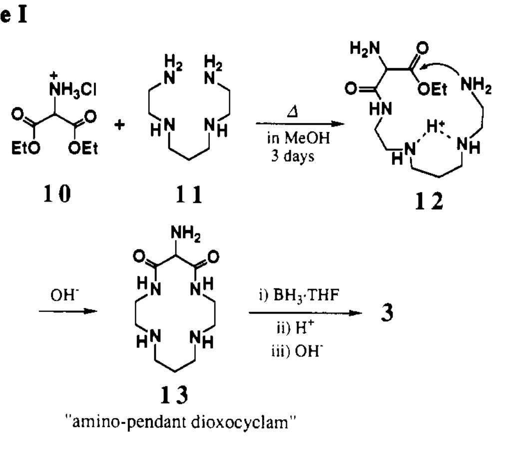
amine)$_2$ and formaldehyde and nitroethane, followed by $NaBH_4$ reduction. A similar template reaction was extended to other metal ions, Co^{III},[12] Ni^{II},[12a] Fe^{III},[13] Pd^{II},[14] Pt^{II},[14] oxovanadium(IV),[15] Rh^{III},[16] Cr^{III},[17] Zn^{II},[18] Cd^{II},[19] and Pt^{IV}.[20] Depending on the preferred coordination geometry of the metal ion, the diamine-attached cyclam ligand **5** may form four- (**6**) or six-coordinate (**7**) complexes, all characterized by X-ray crystal structures. Co^{III}, Fe^{III}, Rh^{III}, and Cr^{III} complexes are octahedral with the two amines coordinating from both axial sites (structure **7**). Ni^{II} and Zn^{II} complexes are similarly octahedral at pH > 7, while, at lower pH, the coordinating pendant amines become protonated to yield square-planar complexes **6**. **5** may rather act as an exclusive quadridentate ligand for Cu^{II}, low-spin Ni^{II}, Pd^{II}, and Pt^{II} that prefer square-planar coordination geometries. In all of these diamine-pendant cyclam complexes, the macrocyclic N_4 retains the *trans* III configuration.[21] All these structural elucidations were based on static states. However, the dynamic behaviors in solution have not been well investigated.

Another interesting aspect with our complex **4** and its possible isomers is that the 6th coordination site remains open and offers a potential site for catalysis (oxygenation, etc.). We have conducted a preliminary test of its catalytic efficiency of the electrochemical reduction of CO_2 to CO to compare it with Ni^{II}–cyclam **8**, where the reactive species is proposed to be Ni^{I}–cyclam

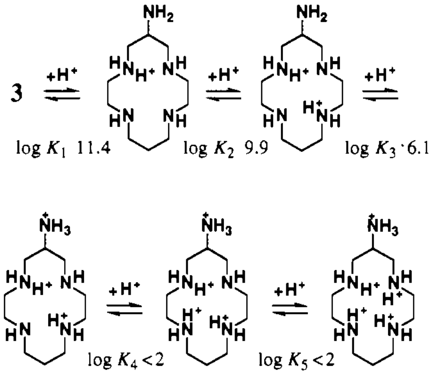


9.[1b,22] With the previous Ni^{II} complex **6**, such a catalytic function has not been reported. In this paper, we present a new (nonmetal template) synthetic method for **3** and its Ni^{II} complexes, and discuss the catalytic function in electroreduction of CO_2 to CO.

Scheme I



Scheme II



Results and Discussion

New Ligand 3 (Scheme I) and Protonation Constants. An anhydrous MeOH solution of diethyl aminomalonate hydrochloride, **10**, containing 1 equiv of 1,9-diamino-3,7-diazanonane, **11**, was refluxed for 3 days. The presence of 1 equiv of HCl in **10** is essential for the satisfactory cyclization yield.[23] The proton migrates from the less basic amino group in **10** to the more basic central part of the amines of **11**, whereupon a template effect by this proton facilitates the cyclization, as depicted by **12**. The cyclized product ("amino-pendant dioxocyclam") **13** was purified by silica gel column chromatography, which was isolated as a trihydrochloride salt by recrystallization from 6 M HCl/MeOH. **13**·3HCl was passed through anion-exchange resin to get an acid-free form **13**, which was recrystallized from CH_3CN. **13** by itself is a good ligand for Cu^{II}, Ni^{II}, and Pt^{II} (like the previous unsubstituted "dioxocyclam"[24]), which will be reported elsewhere.

Reduction of **13** with BH_3·THF complex in THF at 65 °C for 1 day gave 6-amino-1,4,8,11-tetraazacyclotetradecane, **3**, which was purified as a pentahydrobromide salt. The hydrobromide salt was freed of 5 HBr by passing it through anion-exchange resin. The final ligand **3** was thus obtained as an acid-free form.

The protonation constants (K_n) of **3** were determined by potentiometric pH titrations at $I = 0.10$ ($NaClO_4$) and 25 °C.

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(23) This cyclization method was applied to the synthesis of an amino-pendant 12-membered macrocyclic triamine, 3-amino-1,5,9-triazacyclododecane, being a nonplanar N_4 ligand, which along with its metal complexes will be reported elsewhere.

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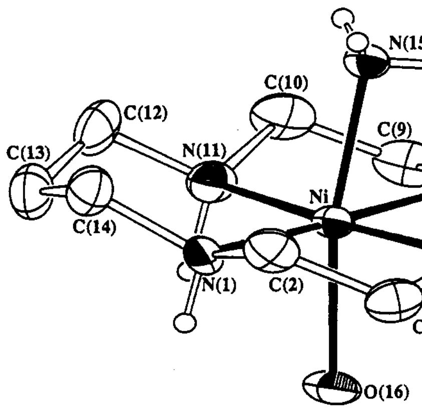
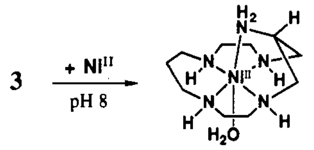


Figure 1. ORTEP drawing (50% probability) of **14**. The C-binding hydrogens, perchlorates, and crystal water are omitted for clarity.

The five protonation constants (log K_1–log K_5) are assigned as in Scheme II. This assignment came from the following facts: (i) Pendantless cyclam (1,4,8,11-tetraazacyclotetradecane) has two large protonation constants log K_1 of 11.8 and log K_2 of 10.6, while the remaining two are below 2.[1j] (ii) ^{1}H NMR–pD titration of **3** (in D_2O at 25 °C) disclosed that the third protonation constant of log K_3 = 6.6 ± 0.2 is assigned to the pendant primary amine (see Experimental Section).

Isolation of Octahedral Ni^{II} Complex 14 and the X-ray Crystal Structure. Treatment of **3** with $Ni(ClO_4)_2$ in H_2O at 60 °C at pH 8 (with 1 M NaOH) precipitated **14**$(ClO_4)_2$·H_2O as violet prisms.[25]



14
trans I configuration

The X-ray crystal study of **14** has disclosed a six-coordinate structure with the four NH's of cyclam at equatorial and the pendant NH_2 and a H_2O at axial positions; see Figure 1. Tables II and III show the selected fractional coordinates, bond lengths, and bond angles for **14**. The average bond distance between Ni^{II} and the secondary nitrogens (N(1), N(4), N(8), N(11)) is ca. 2.07 Å, which is equivalent to 2.067 Å for a (high-spin) Ni^{II}-cyclam complex, **8**·Cl_2.[26] The axial Ni^{II}–N(15) bond distance of 2.141 Å is considerably longer. Ni^{II} ion is not placed in the center of the N_4 cavity but nearer to N(1) and N(11) (average Ni–N distance = 2.055 Å) than to N(4) and N(8) (2.086 Å) to assist the axial binding. The N(15)–Ni–O(16) bond angle is 170.1°, indicating considerable steric strain in the axial NH_2 coordination.

Most interesting with the structure of **14** is its cyclam structure being in the *trans* I configuration; i.e. all the four NH hydrogens orient to the other direction of the NH_2-coordinating site. The pedantless cyclam with most of metal ions tends to take on the *trans* III configuration (see **8**), which is thermodynamically the most stable form.[21] Exceptionally, Hg^{II}–cyclam[27] and Ni^{II}–tetramethyl cyclam complexes[28] take on the *trans* I configurations. In the present Ni^{II} complex, however, the *trans* III cyclam configuration does not seem as stable as the *trans* I isomer, as described below.

Table I. Summary of Crystal Data for **14** and **16**

	14	**16**
formula	$C_{10}H_{25}N_5Ni(ClO_4)_2$·2$H_2O$	$C_{10}H_{26}N_5Ni(ClO_4)_3$·1.5$H_2O$
fw	509.0	600.4
cryst system	monoclinic	monoclinic
space group	$P2_1$	$P2_1/a$
cryst color	violet	orange
cell dimens		
a, Å	8.943(5)	15.288(9)
b, Å	13.552(7)	17.217(10)
c, Å	8.729(5)	8.451(8)
β, deg	98.96(5)	93.77(5)
V, Å^3	1045(2)	2219(5)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.617	1.797
temp, K	298	298
radiation	Cu Kα (λ = 1.54178 Å)	
μ, cm^{-1}	42.6	53.5
2θ range, deg	6–156	
R^a	0.075	0.062
$R_w{}^b$	0.075	0.088

[a] $R = \sum(\|F_o| - |F_c\|)/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2}$; $w = 1/\sigma^2(F_o)$.

Table II. Selected Fractional Coordinates (×10^4) and Isotropic Temperature Factors for **14**

atom	x	y	z	B_{eq}, Å^2
Ni	2830.5(1.6)	−34.6(0)	2445.0(1.6)	2.77(2)
N(1)	5110(8)	186(6)	3104(8)	3.3(1)
C(2)	5870(13)	−700(10)	2508(13)	4.3(2)
C(3)	5028(14)	−1609(9)	2746(14)	4.4(2)
N(4)	3342(10)	−1512(6)	2098(10)	3.6(1)
C(5)	2906(15)	−1691(8)	401(13)	4.6(2)
C(6)	1956(13)	−828(10)	−420(11)	4.4(2)
C(7)	439(12)	−683(10)	25(12)	4.6(2)
N(8)	550(9)	−327(7)	1665(9)	3.9(1)
C(9)	−281(13)	600(11)	1904(14)	5.4(2)
C(10)	640(14)	1499(10)	1702(15)	5.1(2)
N(11)	2159(11)	1403(7)	2673(10)	4.0(1)
C(12)	3229(16)	2167(8)	2285(16)	5.6(2)
C(13)	4791(16)	2016(10)	3200(16)	5.5(2)
C(14)	5733(14)	1139(10)	2670(15)	5.0(2)
N(15)	2848(8)	56(7)	−1(8)	3.2(1)
O(16)	2605(8)	−363(6)	4828(7)	4.4(1)

Table III. Selected Bond Distances and Bond Angles of **14**

Bond Distances, Å			
Ni–N(1)	2.052(7)	Ni–N(4)	2.086(9)
Ni–N(8)	2.085(8)	Ni–N(1)	2.058(9)
Ni–N(15)	2.141(7)	Ni–O(16)	2.167(7)
Bond Angles, deg			
N(1)–Ni–N(4)	87.1(3)	N(1)–Ni–N(8)	176.1(3)
N(1)–Ni–N(11)	97.3(3)	N(1)–Ni–N(15)	96.3(3)
N(1)–Ni–O(16)	89.9(3)	N(4)–Ni–N(8)	89.8(3)
N(4)–Ni–N(11)	175.3(4)	N(4)–Ni–N(15)	82.8(3)
N(4)–Ni–O(16)	89.9(3)	N(8)–Ni–N(11)	85.7(3)
N(8)–Ni–N(15)	81.0(3)	N(8)–Ni–O(16)	92.4(3)
N(11)–Ni–N(15)	95.1(3)	N(11)–Ni–O(16)	91.7(3)
N(15)–Ni–O(16)	170.1(3)		

pH-Dependent Isomerization of 14 to 16 (Scheme III). The apparent steric strain by the axially coordinating pendant NH_2 has led us to examine its dissociation in acidic solution.[29] This was easily followed by observing the UV absorption change from purple (λ_{max} 494 (ϵ 7) and 325 nm (ϵ 11) at pH 7.6) **14** to a yellow (λ_{max} 448 nm (ϵ 55) at pH 2.7) intermediate complex. The intermediate structure was assigned to **15**, where the pendant NH_2 group dissociates with protonation, while the cyclam remains

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(25) Recently, we succeeded in synthesizing a square-planar gold(III)–3 complex with the uncoordinating amino pendant: Kimura, E.; Kurogi, Y.; Koike, T.; Shionoya, M.; Iitaka, Y. *J. Coord. Chem.* **1993**, *28*, 33.
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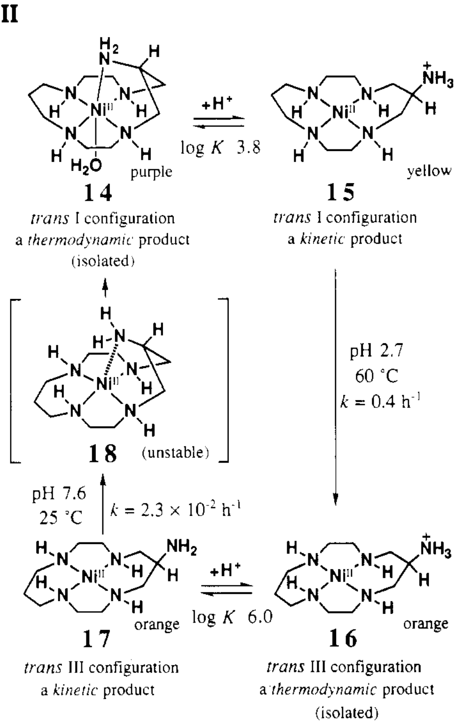
(29) In the following discussion, our premise is that the crystal structure **16** (*trans* I cyclam) remains the same in aqueous solutions, too.

Scheme III



in the same *trans* I configuration. The protonation constant (log *K*) for the pendant NH_2 group of **14** to form **15** is estimated to be 3.8 ± 0.1 by spectroscopic measurement at various pH's (2.7, 3.1, 3.6, 3.8, 4.1, 6.5, 7.6), 25 °C, and $I = 0.10$ ($NaClO_4$); see Figure 2a–c.

However, the immediate product **15** with *trans* I cyclam configuration gradually changed at elevated temperature in an acidic solution to a stationary-state **16** (*trans* III configuration) with λ_{max} 457 (ϵ 28) and 333 nm (ϵ 11) at pH 2.7; see Figure 2c–e. The first-order rate law was established at pH 2.7 and 60 °C with a rate constant *k* of 0.40 ± 0.08 h^{-1}. We obtained orange crystals of **16**$(ClO_4)_3 \cdot 1.5H_2O$ after gradual evaporation of the aqueous solution at room temperature.

X-ray Crystal Structure of the Square-Planar Ni^{II} Complex 16. The X-ray crystal structure for **16** is shown in Figure 3. Tables IV and V show the selected fractional coordinates, bond lengths, and bond angles for **16**. An N_4-coordinate, square-planar geometry for low-spin Ni^{II} is evident. The average bond distance between Ni^{II} and the secondary nitrogens (N(1), N(4), N(8), N(11)) is shortened to 1.94 Å (see Table V), which is close to that of 1.92 Å for a low-spin Ni^{II}–cyclam complex.[30] The atoms N(1), N(4), N(8), and N(11) in the cyclam skeleton are coplanar, and the Ni^{II} ion is in this plane. Now, the cyclam configuration is *trans* III; i.e., the two NH hydrogens orient to a side opposite that of the other two. Namely, the protonation on the axial NH_2 group removes the steric strain produced by the NH_2 coordination, and the cyclam configuration turns from a *trans* I configuration to the most stable *trans* III configuration.

Conversion of 16 Back to 14. The pH–titration of **16** (isolated crystals) in aqueous solution with 0.10 M NaOH solution has shown a pK_a value of 6.00 ± 0.05 (25 °C, $I = 0.10$ ($NaClO_4$)) for the pendant NH_3^+ group, which is almost the same as that for free ligand $\mathbf{3}\cdot 3H^+ \rightleftharpoons \mathbf{3}\cdot 2H^+$ (log $K_3 = 6.1$). The *trans* III configuration remained intact during this titration, as concluded from following facts: (i) The back-titration of **17** (within 1 h at 25 °C) with 0.1 M $HClO_4$ yielded the starting NH_3^+-pendant species **16**. (ii) The UV absorption maxima of **17** (λ_{max} 458 nm (ϵ 10), 332 nm (11)) are almost the same as those for **16**. However, the NH_2 pendant in **17** slowly comes to bind to Ni^{II} from an axial site, which is accompanied by reversion of the cyclam *trans* III to *trans* I configuration, i.e., to the starting N_5-coordinate complex **14**. At pH 7.6, 25 °C, and $I = 0.10$, a first-order rate constant of (2.3 ± 0.5) × 10^{-2} h^{-1} for this process is estimated by following the decrease in the visible absorption at 458 nm. Figure 4a–c shows the UV spectral changes of **17** to **14**. The reason why the

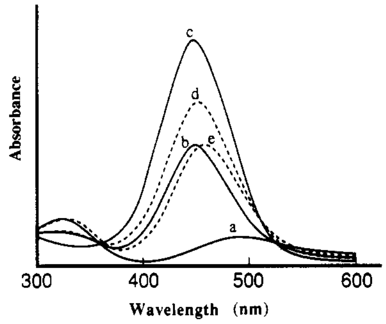


Figure 2. UV absorption spectrum change for **14** (10 mM) to **15** at 25 °C and $I = 0.10$ ($NaClO_4$) [(a) pH 7.6, (b) pH 3.8, (c) pH 2.7] and for **15** (10 mM) to **16** at 60 °C, $I = 0.10$ ($NaClO_4$), and pH 2.7 [(d) after 2 h, (e) after 24 h]. All spectra are measured at 25 °C.

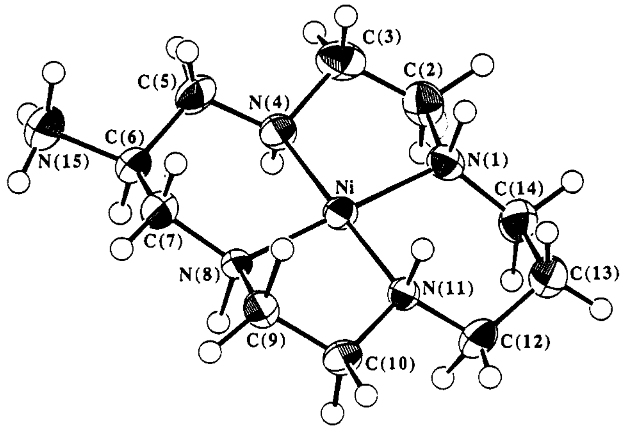


Figure 3. ORTEP drawing (50% probability) of **16**. The perchlorates and crystal waters are omitted for clarity.

Table IV. Selected Fractional Coordinates (×10^4) and Isotropic Temperature Factors for **16**

atom	*x*	*y*	*z*	B_{eq}, $Å^2$
Ni	1288.3(6)	7537.3(5)	1036(1)	2.23(5)
N(1)	1873(3)	7138(3)	−770(5)	2.7(2)
C(2)	2261(4)	7803(4)	−1634(7)	3.6(3)
C(3)	2598(5)	8362(4)	−384(7)	3.8(3)
N(4)	1837(3)	8528(3)	613(5)	2.8(2)
C(5)	2128(4)	9056(4)	1941(7)	3.7(3)
C(6)	1376(4)	9214(3)	2947(7)	3.1(3)
C(7)	1145(4)	8509(4)	3911(6)	3.1(3)
N(8)	708(3)	7914(2)	2864(5)	2.3(2)
C(9)	473(4)	7217(3)	3829(6)	2.8(3)
C(10)	85(4)	6640(3)	2636(6)	3.0(3)
N(11)	746(3)	6542(2)	1436(5)	2.3(2)
C(12)	348(4)	6116(4)	32(7)	3.4(3)
C(13)	1014(4)	5910(4)	−1123(7)	3.7(3)
C(14)	1368(4)	6620(4)	−1924(6)	3.6(3)
N(15)	1614(4)	9870(3)	4081(6)	4.1(3)

Table V. Selected Bond Distances and Bond Angles of **16**

Bond Distances, Å			
Ni–N(1)	1.945(5)	Ni–N(4)	1.944(5)
Ni–N(8)	1.943(4)	Ni–N(11)	1.942(4)
Bond Angles, deg			
N(1)–Ni–N(4)	86.6(2)	N(1)–Ni–N(8)	178.7(2)
N(1)–Ni–N(11)	92.7(2)	N(4)–Ni–N(8)	94.5(2)
N(4)–Ni–N(11)	179.3(2)	N(8)–Ni–N(11)	86.2(2)

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[30] Barefield, E. K.; Bianchi, A. B.; Billo, E. J.; Connolly, P. J.; Paoletti, P.; Summers, J. S.; Van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 4197.

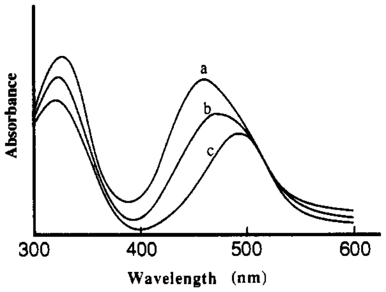


Figure 4. UV absorption spectral changes for **17** (10 mM) to **14** at 25 °C and $I = 0.10$ (pH 7.6 HEPES buffer): (a) 0 h; (b) after 24 h; (c) after 1 week.

Table VI. Redox Properties of the Ni^{II} Complexes **8** and **14–16** and Their Catalytic Efficiency and Selectivity in Electrochemical CO_2 Reduction[a]

electrocatal (cyclam config)	$E_{1/2}$ (V vs SCE)		generated CO (mL)	turnover freq for CO production, h^{-1}	CO/H_2
	$Ni^{III/II}$ [b]	$Ni^{II/I}$ [c]			
8 (*trans* III)	+0.65	−1.56[d]	10.4	128	2500
14 (*trans* I)	+0.56[d]	*e*	*f*	*f*	*f*
15 (*trans* I)[g]	+0.63	−1.55[h]	3.0	37	50
16 (*trans* III)	+0.72	−1.50[h]	14.8	182	1200

[a] For experimental conditions, see Experimental Section; [Ni^{II} complex] $= 1.7 \times 10^{-4}$ M in 0.1 M KNO_3 (pH 3.0). Electrolysis, 25 °C, 1 h. Errors for CO_2 reduction experiments are within ±15%. [b] 0.1 M $NaClO_4$, 25 °C, pH = 3.0. A glassy-carbon rod was employed as the working electrode. [c] 0.1 M $NaClO_4$, 25 °C, pH = 3.0. A hanging mercury electrode was employed as the working electrode. [d] At pH 7.0. [e] No reduction wave at pH 7.0. [f] At pH > 7, unidentified salts were precipitated from the CO_2-saturated solution. [g] A solution of **15** was prepared in situ by adjusting pH (=3.0) of the solution of **14** and immediately measured. The conversion from **15** to **16** is very slow under these conditions. [h] Irreversible.

possible intermediate, N_5-coordinate, *trans* III complex **18** is less stable than the *trans* I isomer **14** is not clear at this moment.

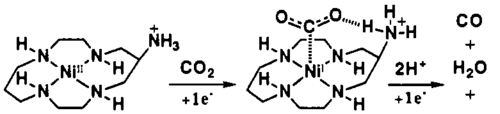
Redox Properties of Ni^{II} Complexes 8 and 14–16 and a Preliminary Study of Their Catalytic Reduction of CO_2 to CO. Due to the proton affinity of the pendant amino group in **14–16**, it is reasonable to expect that their redox behaviors are significantly affected by the solution pH. So far, few results have been reported on the electrochemical behavior of amino-pendant cyclam complexes in aqueous solution at various pH.[31]

Redox potentials for Ni^{II} complexes **8** and **14–16** were measured by cyclic voltammetry in aqueous solution. The results are summarized in Table VI. The N_5-coordinate complex **14** showed a quasi-reversible wave for Ni^{III}/Ni^{II} at +0.56 V (vs SCE) at pH 7, indicating more stabilized Ni^{III} compared with cyclam complex **8** ($E_{1/2}$ = +0.65 V). The N_4-coordinate **16** (*trans* III) with an NH_3^+ pendant destabilizes Ni^{III}, and hence the $E_{1/2}$ value is +0.72 V, 70 mV more positive than that for the pendantless cyclam complex **8**. The transient N_4-coordinate **15** showed an intermediate $E_{1/2}$ of +0.63 V. Unlike cyclam complex **8**, the N_5-coordinate **14** did not show the reduction ($Ni^{II} \rightarrow Ni^{I}$) wave at all. The reduction ($Ni^{II} \rightarrow Ni^{I}$) process for **16** occurred at −1.50 V in the first sweep, which implies a little more stabilized Ni^{I} than the one from **8** ($E_{1/2}$ −1.56 V), apparently due to the electron-withdrawing NH_3^+-pendant effect. However, in the second scan, the first reduction wave almost disappeared, suggesting that certain reductive reactions of the Ni^{II} species (such as Ni-H complex formation, conformational change, etc.) may occur with the NH_3^+ pendant. With the N_4-coordinate **15** in *trans* I configuration, a similar trend was observed.

We observed the irreversible $Ni^{II} \rightarrow Ni^{I}$ reduction current for **16** growing into a much larger wave under CO_2 atmosphere, in a fashion similar to that for cyclam complex **8**. This is a clear indication of the catalytic reduction of CO_2.[1b]

Ni^{II}–cyclam complex **8** is now known as an extremely selective electrocatalyst through Ni^{I} species for CO_2 reduction to CO in water.[1b,32] We thus measured the catalytic efficiencies in the controlled potential (−1.30 V vs SCE) electrolysis at the Hg electrode of CO_2-saturated aqueous solution (pH 3.0) under common conditions (Table VI). The NH_3^+-pendant Ni^{II} complex **16** with *trans* III configuration has given better results in terms of the CO yield and its rate than **8**. However, the ratio for production of H_2 with respect to CO with **16** is ca. twice as much as with **8**, due to a possible interaction of Ni^{I} with the NH_3^+ pendant before the CO_2 attack.

We previously reported that the yield in CO production decreases as an electron-withdrawing group (e.g., fluorine atom) is attached to the cyclam.[1j] However, in the present case, the introduction of an electron-withdrawing NH_3^+ group in cyclam **16** resulted in an increase of CO production, suggesting an effective interaction between the substrate CO_2 and the $^+NH_3$ group of **16**. A η^1-C coordinated Ni^{I}–CO_2 complex **9**, where CO_2 is staggered to the Ni–N bonds, is postulated as a key intermediate in the CO_2 reduction as calculated by Sakaki.[22] If this were valid, a proposed intermediate may be viewed as **19**, which involves a favorable electrostatic attraction between $O^{\delta-}$ of CO_2 and $H^{\delta+}$ of the NH_3^+ group.



16 **19** **16**

In conclusion, the amino-pendant cyclam **3** has proven to be a potentially interesting and versatile functional ligand as metal complexes for catalyses (and oxygenation) at the 6th coordination site. The reactivity at this position can be controlled by the media pH.

Experimental Section

General Methods. All the starting materials for synthesis were obtained commercially and used without further purification unless otherwise stated. Gases of analytical grade were employed. ^1H NMR spectra were recorded on a JEOL GX-400 spectrometer (400 MHz) at 25 °C. 3-(Trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (Merck) in D_2O and tetramethylsilane in $CDCl_3$ were used as internal references. IR and UV spectra were taken on a Shimadzu FTIR-4200 and a Hitachi U-3200 double beam spectrophotometer, respectively. For TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254}) were used. All reagents used in CO_2 reduction experiments and other analyses were analytical grade.

Synthesis of 6-Amino-5,7-dioxo-1,4,8,11-tetraazacyclotetradecane, 13. Refluxing diethyl aminomalonate hydrochloride, **10** (10.6 g, 50 mmol), and 1,9-diamino-3,7-diazanonane, **11** (8.0 g, 50 mmol), in 1.00 L of dry MeOH for 3 days afforded dioxocyclam derivative **13** as its trihydrochloride salt (9.6 g, 27 mmol) after purification by silica gel column chromatography (eluent $CH_2Cl_2/MeOH/28\%$ aqueous NH_3 = 100:10:1) and recrystallization from 6 M HCl/EtOH. After neutralization of the acid salt via anion-exchange column chromatography (Amberlite IRA 400), recrystallization of the residue from CH_3CN yielded **13** as colorless needles in 45% yield: mp 182–183 °C; IR (KBr pellet) ν_{CO} = 1701 cm^{-1}; ^1H NMR (in $CDCl_3$) δ 1.63–1.70 (2 H, m, CCH_2C), 1.7–2.3 (4 H, br, NH), 2.46–2.54 (2 H, m, NCH), 2.61–2.68 (2 H, m, NCH), 2.71–2.79 (2 H, m, NCH), 2.80–2.87 (2 H, m, NCH), 3.32–3.41 (2 H, m, CONCH), 3.46–3.57 (2 H, m, CONCH), 4.11 (1 H, s, COCHCO), 7.7–8.0 (2 H, br, CONH); ^{13}C NMR (in $CDCl_3$) δ 28.7, 39.0, 49.4, 50.4, 57.6, 170.3. Anal. Calcd for $C_{10}H_{21}N_5O_2$: C, 49.4; H, 8.7; N, 28.8. Found: C, 49.1; H, 8.6; N, 28.5. Protonation constants (log *K*) are 9.73 ± 0.02, 6.07 ± 0.02, and 4.15 ± 0.02 at 25 °C and $I = 0.10$ ($NaClO_4$).

Synthesis of 6-Amino-1,4,8,11-tetraazacyclotetradecane, 3. The obtained dioxomacrocycle **13** (2.4 g, 10 mmol) was added to a solution of freshly distilled BH_3·THF (200 mmol) in 200 mL of dry THF at 0 °C. The solution was stirred at room temperature for 1 h and then heated

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(31) *N*-(aminoethyl)cyclam–Ni^{II} complex: Pallavicini, P. S.; Perotti, A.; Poggi, A.; Seghi, B.; Fabbrizzi, L. *J. Am. Chem. Soc.* **1987**, *109*, 5139.

(32) Collin, J.-P.; Sauvage, J.-P. *Coord. Chem. Rev.* **1989**, *93*, 245.

at reflux for 1 day. After decomposition of the excess amount of BH_3 with 6 M aqueous HCl at 0 °C, the solvent was evaporated. Crystallization of the residue from 47% aqueous HBr afforded pentahydrobromide salt 3·5HBr as colorless crystals (4.5 g, 7.5 mmol). The acid-free ligand **3** was obtained by anion-exchange chromatography, followed with crystallization from CH_3CN in 62% yield: mp 154 °C; ^1H NMR (in $CDCl_3$) δ 0.8–1.5 (2 H, br, NH_2), 1.65–1.75 (2 H, m, CCH_2C), 1.7–2.3 (4 H, br, NH), 2.58–2.86 (16 H, m, NCH), 3.05–3.13 (1 H, m, NCH=); ^{13}C NMR (in $CDCl_3$) δ 29.4, 49.1, 49.2, 50.4, 50.5, 57.0. Anal. Calcd for $C_{10}H_{25}N_5$: C, 55.8; H, 11.7; N, 32.5. Found: C, 56.0; H, 11.6; N, 32.3. Protonation constants (log *K*) at 25 °C and $I = 0.10$ ($NaClO_4$) are 11.41 ± 0.03, 9.94 ± 0.03, 6.08 ± 0.02, <2, and <2.

Synthesis of NH_2-Pendant Cyclam–Ni^{II} Complex 14. **3** (0.43 g, 2.0 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.77 g, 2.1 mmol) were dissolved in 20 mL of distilled water and stirred at 60 °C for 2 h. The reaction mixture was concentrated to 5 mL and adjusted to pH 8 with 0.1 M NaOH. After addition of 5 mL of 2-propanol, the resulting solution was allowed to stand at room temperature to obtain violet prisms of $\mathbf{14}(ClO_4)_2 \cdot H_2O$ in 46% yield. Anal. Calcd for $C_{10}H_{25}N_5Ni(ClO_4)_2 \cdot 2H_2O$: C, 23.6; H, 5.7; N, 13.8. Found: C, 23.9; H, 5.7; N, 13.8.

Synthesis of NH_3^+-Pendant Cyclam–Ni^{II} Complex 16. Ni^{II} complex **14** (50 mg, 98 μmol) was dissolved in 10 mL of 10 mM $HClO_4$ and stirred at 80 °C for 12 h. After addition of 10 mL of 2-propanol, the resulting solution was allowed to stand for several days at room temperature to obtain orange crystals of $\mathbf{16}(ClO_4)_3 \cdot 1.5H_2O$ in 87% yield. The crystal H_2O molecules are easily removed at 50 °C and 1 mmHg pressure (as judged by gradual decomposition of the crystal form to fine powder). Anal. Calcd for $C_{10}H_{26}N_5Ni(ClO_4)_3$: C, 21.0; H, 4.6; N, 12.2. Found: C, 21.1; H, 4.9; N, 12.4.

Potentiometric pH Titrations. The preparation of the test solutions, the calibration of the electrode system (Orion Research 811 pH meter and Orion 91-02 electrode with 90-0019 reference electrode filling solution), and the calculation method for protonation constants (log K_n) were described earlier.[4] All samples were kept under argon (>99.999% purity) atmosphere, and the solution temperature was maintained at 25.0 ± 0.1 °C. For the determination of log K_n values, at least three independent titrations were always made. The K_n values are defined as $[H_nL]/[H_{n-1}L]a_{H^+}$.

NMR Measurements. Solutions of **3** (10 mM) for ^1H NMR–pD titrations were made up in D_2O (99.9 atom % D from Aldrich), and the pD (=3.4, 4.0, 5.0, 6.0, 6.4, 6.9, 7.1, 7.4, 9.4) was adjusted with DCl (Merck). The pD value was corrected for a deuterium isotope effect using pD = [pH meter reading] + 0.40.[33] The determination of the microscopic protonation constants of **3** is the same as described in Geraldes's procedure for macrocyclic polyamines.[34] The third protonation constant of **3** can be assigned for the pendant amino nitrogen by following the chemical shifts of the macrocyclic CH protons as a function of pD. Typical ^1H NMR signals (δ) of **3** at pD 9.4 (6.4) [3.4] are assigned as follows: C–CH_2–C, 1.89 (1.90) [2.00]; $NDCH_2$, 2.9–3.2 (3.0–3.4) [3.1–3.5]; D_2NCH, 3.27 (3.63) [3.80].

Isomerization Kinetics of Ni^{II} Complexes 15 to 16 and 17 to 14. The *trans* I Ni^{II} complex **15** isomerized with first-order dependence of [**15**] to produce to the *trans* III Ni^{II} complex **16** at 60 ± 1 °C, $I = 0.10$ ($NaClO_4$) and pH 2.7 (adjusted by 10 mM HCl). An isomerization rate of 0.40 ± 0.08 h^{-1} was measured by following the decrease in 448-nm absorption at 25 °C. Similarly an isomerization rate of $(2.3 \pm 0.5) \times 10^{-2}\ h^{-1}$ for the isomerization of **17** to **14** at 25.0 ± 0.5 °C and $I = 0.10$ (pH 7.6 HEPES buffer) was determined by following the decrease in 458-nm absorption.

Crystallographic Study. A pale violet crystal (0.15 × 0.15 × 0.30 mm) of **14** and a yellow crystal (0.35 × 0.20 × 0.12 mm) of **16** were used for data collection at 25 °C. The lattice parameters and intensity data were measured on a Philips PW1100 diffractometer with graphite-monochromated Cu Kα radiation. Crystallographic data for **14** and **16** are displayed in Table I. All calculations were performed using the Philips PW1100 crystallographic software package. The structures were solved by the heavy-atom method and refined anisotropically by using 2074 and 2553 independent observed reflections, respectively. For **14**, 27 H atoms were found on the difference electron-density map, and two H atoms of Ni^{II}-binding water molecule were not found. For **16**, 26 H atoms were found, and 1.5 water H atoms were not found. One water molecule (O2(W)) of **16** takes a half-occupancy factor and is located near the center of symmetry and seems to be distributed in the two sites across the center of symmetry. The ORTEP drawings of **14** and **16** are shown in Figures 1 and 2, respectively. Selected fractional coordinates and equivalent isotropic temperature factors are given in Tables II and III. Selected bond distances and bond angles are shown in Tables IV and V. The full crystal data and data collection parameters, atomic positional parameters, bond distances, and bond angles are given as supplementary material.

Electrochemical Measurements. Cyclic voltammetric measurements were performed with a Yanako P-1100 polarographic analyzer at 25.0 ± 0.1 °C in H_2O with 0.10 M $NaClO_4$ as supporting electrolyte, and the solution was bubbled with pure Ar gas. A three-electrode system was employed: a glassy carbon rod or a hanging mercury electrode as the working electrode, a Pt wire as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. The cyclic voltammograms with scan rate of 100–200 mV s^{-1} were evaluated graphically. All the solutions were kept at 1.0 mM. Experimental errors are within ±5 mV.

Analytical Methods for CO_2 Reduction. Controlled-potential electrolysis experiments were performed in a gastight electrolysis cell with a Yanako VE-8 controlled-potential electrolyzer. The gastight cell was a 50-mL three-necked round-bottomed flask equipped with three side arms. Mercury was used as the working electrode (14 mL; purity >99.9%). The counter electrode (Pt) and the reference electrode (SCE) were separated from the working electrode compartment. The cell volume was 142 mL, of which 108 mL was occupied by gases. The aqueous solution (20 mL) was degassed before electrolysis by bubbling CO_2 through it for 30 min, followed by pH adjusting at pH 3.0 with aqueous $HClO_4$ solution. The internal pressure within the electrolysis cell was kept equal to 1 atm by using syringe techniques. Turnover frequencies were calculated as moles of CO produced per mole of an electrocatalyst in 1 h.

Gas samples (0.5 mL), taken at various intervals with a gastight syringe through a septum and a valve, were analyzed for H_2 on a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector by using a 3 m × 2.6 mm o.d. column packed with 13X-S molecular sieves at 50 °C using N_2 as carrier gas, or a Shimadzu GC-4CMPF FID gas chromatograph, and for CO with a Shimadzu MTN-1 methanizer using N_2 as carrier gas. Experimental errors are within ±15%.

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Supplementary Material Available: Tables of full crystal data and data collection parameters, atomic coordinates, equivalent isotropic temperature factors, anisotropic temperature factors, bond lengths, and bond angles for **14** and **16** (12 pages). Ordering information is given on any current masthead page.

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