FULL PAPER

Synthesis, Properties, and Reactions of Trinuclear Macrocyclic Nickel(II) and Nickel(I) Complexes: Electrocatalytic Reduction of CO2 by Nickel(II) Complex

Eun Young Lee,[a] Daewon Hong,[a] Han Woong Park,[a] and Myunghyun Paik Suh*[a]

The trinuclear Ni^{II} complex of trismacrocyclic ligand **1**, $[Ni_3(\mathbf{1})](ClO_4)_6$, where **1** is 8,8′,8″-(2,2′,2″-nitrilotriethyl)-tris(1,3,6,8,10,13,15-heptaazatricyclo[11.3.1.1³,¹⁵]octadecane), has been synthesized by template condensation reactions and shown to have poor axial binding ability. Cyclic voltammetry of the complex shows a three-electron reversible reduction at −1.59 V and an irreversible oxidation at +1.25 V vs. Ag/Ag⁺ (0.01 M). Differential pulse voltammetry and Osteryoung square-wave voltammetry indicate that the three Ni^{II} ions are electrochemically independent. A single crystal was obtained as $[Ni_3(\mathbf{1})](ClO_4)_3 \cdot Cl_3 \cdot 10H_2O$ and its X-ray structure was determined. When $[Ni_3(\mathbf{1})](ClO_4)_6$ was re-

duced to a Ni^I species by reaction with Na(Hg) in MeCN, $[Ni_3(\mathbf{1})](ClO_4)_3$ was isolated. $[Ni_3(\mathbf{1})](ClO_4)_6$ shows catalytic activity for the electrochemical reduction of CO_2 to CO in $MeCN/H_2O$ (9:1, v/v), as revealed by cyclic voltammetry and controlled-potential coulometry. The catalytic efficiency of $[Ni_3(\mathbf{1})]^{6+}$ is lower than that of $[Ni(cyclam)]^{2+}$. It gives a greater $i_p(CO_2)/i_p(N_2)$ value but produces less CO per nickel center (**3**: 8-methyl-1,3,6,8,10,13,15-heptaaza-tricyclo-[11.3.1.1³,¹⁵]octadecane) compared with monometallic $[Ni(\mathbf{3})]^{2+}$.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Multinuclear macrocyclic complexes can be interesting multi-electron redox catalysts and may act as models for polynuclear metalloenzymes. The synthesis and design of electrocatalyses to reduce abundant and inexpensive CO_2 may be important in lessening the greenhouse effect and in developing new sources of fuels.[1−3] CO_2 reduction may provide various products: carbon monoxide or formic acid, formaldehyde, methanol, and methane, by two-, four-, six-, and eight-electron reduction reactions, respectively. The high activation energy of CO_2 reduction at a platinum electrode, requiring a more negative potential than −2.24 V vs. SCE, is due to the high energy intermediate CO_2^- [4] but can be lowered by using catalysts. Some transition metal complexes with macrocyclic ligands − both mononuclear[5−19] and dinuclear[20−21] complexes − exhibit catalytic effects on the electrochemical reduction of CO_2 to CO or formate, shifting the CO_2 reduction potential by ca. +0.5 V. To obtain reduction products involving more than two electrons, multimetallic catalysts should be employed.

Here we report the synthesis of trinuclear Ni^{II} and Ni^I complexes of the trismacrocyclic ligand 8,8′,8″-(2,2′,2″-nitrilotriethyl)-tris(1,3,6,8,10,13,15-heptaaza-tricyclo-

[11.3.1.1³,¹⁵]octadecane) (**1**). We also report their electrocatalytic activity for CO_2 reduction compared with the mononuclear $[Ni(\mathbf{3})]^{2+}$ complex.

$[Ni_3(\mathbf{1})]^{6+}$ $[Ni(\mathbf{2})]^{2+}$ $[Ni(\mathbf{3})]^{2+}$
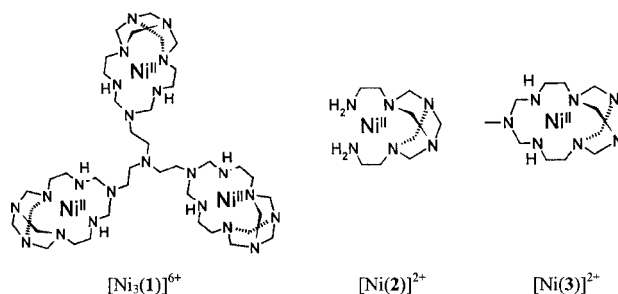
Results and Discussion

Synthesis and Properties of $[Ni_3(\mathbf{1})](ClO_4)_6$

The trinuclear trismacrocyclic complex $[Ni_3(\mathbf{1})](ClO_4)_6$ was synthesized by the template condensation of $[Ni(\mathbf{2})]^{2+}$ with tris(2-aminoethyl)amine and formaldehyde as described in Equation (1). Template condensation reactions involving amines and formaldehyde have provided various types of macrocyclic complexes that cannot be obtained in the absence of metal ions.[22−29] However, multinuclear macrocyclic complexes containing more than three metal ions are still very rare.[30]

$$3\,[Ni(\mathbf{2})]^{2+} + 6\,CH_2O + (H_2NCH_2CH_2)_3N \rightarrow [Ni_3(\mathbf{1})]^{6+} \qquad (1)$$

[a] School of Chemistry and Molecular Engineering, Center for Molecular Catalysis, Seoul National University,
Seoul 151−747, Republic of Korea,
Fax: (internat.) +82-2/886-8516
E-mail: mpsuh@snu.ac.kr
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

Although the reaction of Equation (1) seems to be entropically unfavorable, it provides the trismacrocyclic complex in ca. 50% yield. The amount of water present significantly affects the yield of $[Ni_3(1)](ClO_4)_6$, and the complex $[Ni_3(1)](ClO_4)_6$ was synthesized in $MeOH/H_2O$ (2:1, v/v). When water was absent, the starting complex did not dissolve into the solution and provided a poor yield.

$[Ni_3(1)](ClO_4)_6$ is soluble in MeCN, $MeNO_2$, DMSO, and hot water, but insoluble in MeOH and diethyl ether. The ^{13}C NMR spectrum (Figure 1) is consistent with the structure of trismacrocyclic ligand **1**. The molar conductance for $[Ni_3(1)](ClO_4)_6$, measured in $MeNO_2$ at 25 °C, depends on the concentration of the complex; 214 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for a 1.13×10^{-3} M solution and 393 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for a 5.16×10^{-5} M solution. In MeCN, the molar conductances are 439 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ at 2.77×10^{-4} M and 684 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ at 1.66×10^{-5} M. A plot of molar conductance in $MeNO_2$ at various concentrations is given in Figure S1 in the Supporting Information. Extrapolation of this plot to 0 M gives $434-491$ $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for a highly diluted $MeNO_2$ solution. The highly charged (+6) cation seems to form ion-pairs even in 10^{-5} M solutions. The electronic spectrum of $[Ni_3(1)](ClO_4)_6$ shows a maximum absorption at 439 nm with an extinction coefficient of 273 $cm^{-1}\cdot M^{-1}$ in $MeNO_2$. The λ_{max} value of $[Ni_3(1)](ClO_4)_6$ is similar to that of monometallic $[Ni(3)](ClO_4)_2$ (438 nm)[23] but its molar absorptivity is almost three times greater than that (83 $cm^{-1}\cdot M^{-1}$) due to the existence of three Ni^{II} chromophores. The spectrum depends slightly on the solvent used. The complex does not coordinate ligands such as NCS^-, Cl^-, pyridine, NH_3, and NO_3^- at the axial site in the noncoordinating solvent $MeNO_2$, as evidenced by the UV/Vis spectra. Upon addition of CN^-, however, the solution changed from yellow to pink and then the demetallation of Ni^{II} ions took place within a few minutes.
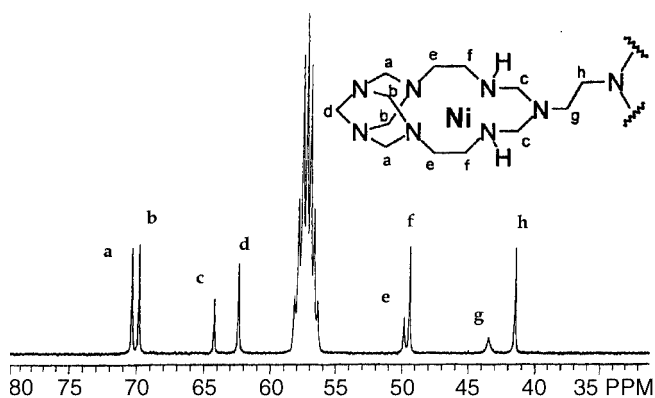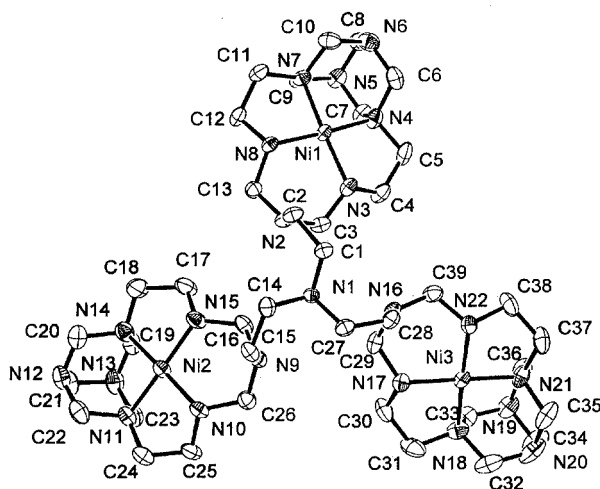

Figure 1. ^{13}C NMR spectrum of $[Ni_3(1)](ClO_4)_6$ in $[D_3]$nitromethane

Crystal Structure of $[Ni_3(1)](ClO_4)_3\cdot Cl_3\cdot 10H_2O$

We could not obtain single crystals of $[Ni_3(1)](ClO_4)_6$ by recrystallization from any solvent system. However, we acquired single crystals of $[Ni_3(1)](ClO_4)_3\cdot Cl_3\cdot 10H_2O$ by mixing $[Ni_3(1)](ClO_4)_6$ and NaCl in a hot solvent mixture of
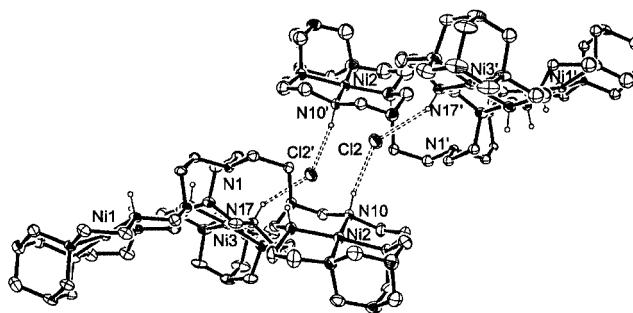
Figure 2. ORTEP views of the cation of $[Ni_3(1)]$-$(ClO_4)_3\cdot(Cl)_3\cdot 10H_2O$ with atomic numbering scheme: top view (a) and side view showing hydrogen bonded dimer (b); the atoms in (a) and (b) are represented by 20% probable thermal ellipsoids. Atoms marked $'$ are generated by symmetry operations: $1-x$, $-1-y$, $-z$. Hydrogen bonds are indicated as dashed lines.

MeCN, MeOH, and H_2O. An ORTEP view of the cation in $[Ni_3(1)](ClO_4)_3\cdot Cl_3\cdot 10H_2O$ is presented in Figure 2a. The three Ni^{II} macrocycles are linked by a tren group to form a bowl-shaped molecule. Three Ni^{II} ions in the molecule are almost at the corners of a triangle. The Ni1···Ni2, Ni2···Ni3, and Ni3···Ni1 distances are 9.062(3), 9.420(2), and 8.983(2) Å, respectively. The Ni1···Ni2···Ni3, Ni2···Ni3···Ni1, and Ni3···Ni1···Ni2 angles are 58.12(2), 58.94(2), and 62.94(1)°, respectively. The central tertiary nitrogen (N1) of the tren unit is 2.624(5) Å above the triangular plane made by the Ni1, Ni2, and Ni3 atoms. The dihedral angles between the square-coordination planes involving Ni1 and Ni2, Ni2 and Ni3, and Ni3 and Ni1 are 51.15(16), 49.53(22), and 46.42(18)°, respectively. There are three ClO_4^- and three Cl^- anions per trismacrocyclic complex. The ClO_4^- anions are found at the open hollow part of the bowl, and Cl^- anions and water molecules are out of the bowls. A Cl^- anion (Cl2) connects two molecules through hydrogen bonds with the secondary amines of the

macrocycle, involving N10 and N17 [Cl2···N10 3.204 Å, Cl2···H−N10 169.7°, Cl2···N17(1−x, −1−y, −z) 3.248 Å, Cl2···H−N17(1 − x, −1 − y, −z) 147.4°], as shown in Figure 2b.

In each macrocycle, the Ni^{II} ion exhibits square-planar coordination geometry, being coordinated with two secondary and two tertiary nitrogen atoms of the ligand. The Ni^{II} ions are displaced from their square-coordination planes by 0.057(3), 0.032(3), and 0.049(3) Å, respectively, showing a slight square-pyramidal distortion. The average Ni−N bond length is 1.927(2) Å, which falls in the range (1.86−1.94 Å) normally observed for square-planar Ni^{II} complexes.[23] In general, N-methylation of the secondary nitrogen donors of the macrocyclic complex decreases the ligand-field strength and increases the Ni−N distances.[23,31] However, the present complex shows no significant differences in the Ni−N distances for the secondary and tertiary amines. The local environment of every Ni^{II} ion possesses a pseudo-mirror plane that is perpendicular to the square coordination plane. The average N−C distances and average C−N−C angles involving coordinated tertiary nitrogens (N4, N7, N11, N14, N18, N21) are 1.504(3) Å and 109.2(1)°. The average N−C distances and average C−N−C angles involving uncoordinated tertiary nitrogens (N5, N6, N12, N13, N19, N20) are 1.451(3) Å and 110.4(1)°, indicating the contribution of sp^2 hybridization.[22−27]

Electrochemical Behavior of [Ni$_3$(1)](ClO$_4$)$_6$

The cyclic voltammogram of an MeCN solution of [Ni$_3$(1)](ClO$_4$)$_6$ shows a reversible reduction peak at −1.59 V and an irreversible oxidation peak at +1.25 V vs. Ag/Ag$^+$(0.01 M) (Table 1), which are very similar to those (−1.61 V and +1.10 V, respectively) for the monocyclic [Ni(3)]$^{2+}$ complex.[22,23] Bulk electrolysis at −1.8 V vs. Ag/Ag$^+$ (0.01 M) indicated n = 3.16 for the Ni^{II}/Ni^I reduction. The differential pulse and Osteryoung square-wave voltammograms show only one peak at −1.59 V vs. Ag/Ag$^+$ (0.01 M), indicating that the three Ni^{II} ions in the complex are electrochemically independent and that reduction of the three Ni^{II} centers takes place simultaneously.

Synthesis of Ni^I Complex

Numerous Ni^I azamacrocyclic complexes have been reported[32−50] but few have been isolated from solution. The trinuclear Ni^I complex [Ni$_3$(1)](ClO$_4$)$_3$ was prepared by reducing the Ni^{II} complex with Na(Hg) in MeCN under an N$_2$ atmosphere. The Ni^I complex was isolated together with the impurity NaClO$_4$, which was hardly removed by recrystallization, and so the analysis data for the Ni^I complex are relatively poor. The electronic absorption spectrum of the Ni^I complex (Table 1) shows maximum absorptions at 524 nm and 319 nm. These λ_{max} are similar to those of [Ni(3)]$^+$, whose X-ray structure displays the square-planar geometry around the Ni^I ion.[41] For Ni^I complexes λ_{max} is often shifted ca. 100 nm to longer wavelengths, with extinction coefficients increasing by ca. 5−10 times, compared with those of the corresponding Ni^{II} complexes.[26,41,43] The complex [Ni$^I_3$(1)](ClO$_4$)$_3$ (powder sample) shows an anisotropic axial EPR spectrum with g values of $g_\perp$ = 2.069 and g_{II} = 2.247 (Figure 3), indicating that the Ni^I ions have a square-planar coordination geometry with an unpaired electron in the d $d_{x^2-y^2}$ orbital.[23] The g values are similar to those of the Ni^I complex of 3.[23,41]
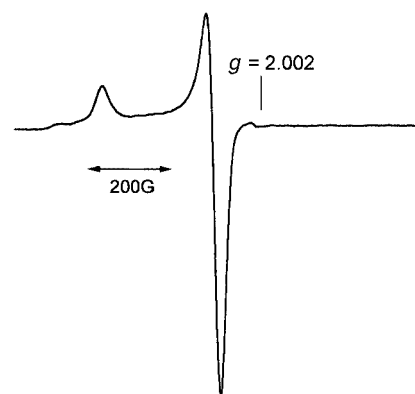

Figure 3. EPR powder spectrum of [Ni$^I_3$(1)](ClO$_4$)$_3$ at room temperature.

The Ni^I complex [Ni$_3$(1)](ClO$_4$)$_3$ is very sensitive to air and moisture. For example, a red-purple MeCN solution of the Ni^I complex exposed to air turned yellow, the color of

Table 1. Properties of Ni^{II} and Ni^I complexes

Compd.	λ_{max} nm (ε, M^{-1}·cm^{-1})	Ni$^{II} \to$ Ni$^{I[a]}$			Ni$^{II} \to$ Ni$^{III[a]}$			EPR[b]	ref.
		$E_{cathodic}$	E_{anodic}	$E_{1/2}$	$E_{cathodic}$	E_{anodic}	$E_{1/2}$		
[Ni$_3$(1)]$^{6+}$	439(265),[c] 439(283)[d]	−1.63	−1.55	−1.59(r)	+1.22	+1.37	+1.25(i)		this work
[Ni(3)]$^{2+}$	442(80),[c] 438(83)[d]	−1.64	−1.57	−1.61(r)			+1.10(qr)		[41]
[Ni$_3$(1)]$^{3+}$	524(1080), 319(4010)[c]							g = 2.202, $g_\perp$ = 2.058	this work
[Ni(3)]$^+$	538(600), 330(2020)[c]							g = 2.240, $g_\perp$ = 2.062	[41]

[a] Measured in MeCN with 0.1 M (nBu)$_4$NPF$_6$; volts vs. Ag/Ag$^+$ (0.01 M); working electrode, glassy carbon; scan rate, 50 mV s^{-1}; 20 °C; r: reversible; qr: quasi-reversible; i: irreversible. [b] Powder samples at room temperature. [c] Measured in MeCN. [d] Measured in MeNO$_2$.

Ni^{II} complex, in less than 15 min. When CO$_2$ gas was bubbled through an MeCN solution, the change to yellow was abrupt, [Ni$_3$(**1**)](ClO$_4$)$_6$ was isolated from solution, and CO gas was detected in the head space of the reaction vessel.

Electrochemical Reduction of CO$_2$ Catalyzed by [Ni$_3$(**1**)]$^{6+}$

Some Ni^{II} tetraaza macrocyclic complexes have shown catalytic activity in the electroreduction of CO$_2$.[5−21] In particular, [Ni(cyclam)]$^{2+}$ is an efficient and selective catalyst on a Hg electrode in water.[5] Ni^{II} systems that can be easily reduced to Ni^{I} species are efficient electrocatalysts for reducing CO$_2$.[14] Since the complex [Ni$_3$(**1**)]$^{6+}$ exhibits a much more anodic Ni^{II}/Ni^{I} reduction potential than [Ni(cyclam)]$^{2+}$, and its trinuclear Ni^{I} species is stable enough to be isolated, we expected that [Ni$_3$(**1**)]$^{6+}$ would catalyze the electroreduction of CO$_2$, which we then investigated by cyclic voltammetry and controlled potential coulometry. In a typical cyclic voltammetric experiment, a solution of trinuclear Ni^{II} complex (2.0 mM) was prepared in a MeCN/H$_2$O (9:1, v/v) solution containing 0.1 M NaClO$_4$. Under N$_2$ atmosphere, the cyclic voltammogram of [Ni$_3$(**1**)](ClO$_4$)$_6$ showed a reversible Ni^{II}/Ni^{I} reduction peak at $E_{1/2} = -1.39$ V ($E_{cathode} = -1.44$ V and $E_{anode} = -1.35$ V) vs. SCE. When the complex solution was saturated with CO$_2$, the current intensity at -1.44 V increased ca. three times compared with that measured under N$_2$, and the anodic peak
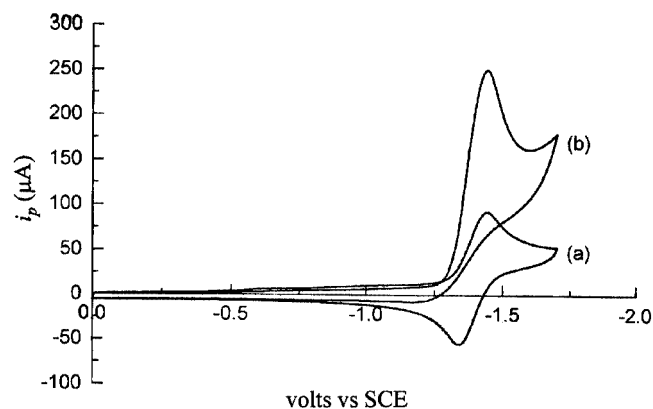
at -1.35 V disappeared (Figure 4). This indicates that the complex acts as a catalyst for the electrochemical reduction of CO$_2$.[51] The results of the same experiment with the mononuclear Ni^{II} complexes of cyclam and **3** are summarized in Table 2. In the cyclic voltammetry, the peak current (i_p) measured under N$_2$ can be described as $i_p = (2.69 \times 10^5)n^{3/2}AD_o^{1/2}v^{1/2}C_o^*$.[51] The diffusion coefficients (D_o) of [Ni$_3$(**1**)]$^{6+}$ and [Ni(**3**)]$^{2+}$, measured in MeCN/H$_2$O (9:1, v/v) by rotating disk electrode, are 1.8×10^{-5} and 8.8×10^{-5} cm^2 s^{-1}, respectively. Theoretically, when the concentrations of the complexes are the same, i_p(N$_2$) of [Ni$_3$(**1**)]$^{6+}$ should be 2.35 times greater than that of [Ni(**3**)]$^{2+}$. The ratio of i_p(N$_2$) of [Ni$_3$(**1**)]$^{6+}$ versus that of [Ni(**3**)]$^{2+}$ is 2.1−2.3 (Table 2). Although all catalysts showed peak potentials at -1.44 to -1.49 V vs. SCE in the presence of CO$_2$, the trinuclear Ni^{II} complex of **1** showed a much greater catalytic current than the monometallic complex of **3**. To exclude the effect of n and D$_o$ values on the catalytic efficiencies, the ratio of peak current measured under CO$_2$ vs. that measured under N$_2$, i_p(CO$_2$)/i_p(N$_2$), was compared (Table 2). The i_p(CO$_2$)/i_p(N$_2$) for [Ni$_3$(**1**)]$^{6+}$ is ca. 3 while those of [Ni(**3**)]$^{2+}$ and [Ni(cyclam)]$^{2+}$ are 2 and 5, respectively. This indicates that [Ni$_3$(**1**)]$^{6+}$ is a better catalyst than [Ni(**3**)]$^{2+}$ in terms of the catalytic current although it is not a better catalyst than [Ni(cyclam)]$^{2+}$.

The solvent system as well as the electrode material dramatically affects the catalytic peak current. For example, that of [Ni(cyclam)]$^{2+}$ (10^{-3} M) increased ca. 50 times under CO$_2$ with H$_2$O as solvent and a Hg dropping mercury electrode.[5] However, here it increased by only ca. 5 times in MeCN/H$_2$O (9:1, v/v) at a glassy carbon electrode. In the present study, experiments could not be performed in 100% water because of the low solubility of the Ni^{II} complexes of **1** and **3** in water. In MeCN without added water, a catalytic current was not observed under CO$_2$ both with [Ni$_3$(**1**)]$^{6+}$ and [Ni(**3**)]$^{2+}$ complexes, probably due to the lack of a proton source. Protons are needed in CO$_2$ reduction according to Equation (2).

$$2\,Ni^{I} + 2\,H^+ + CO_2 \rightarrow 2\,Ni^{II} + CO + H_2O \qquad (2)$$

The concentration of the catalyst also affects catalytic activity and turnover number. This was especially so for a Hg electrode, where the active catalyst is a species adsorbed on the electrode, and saturation of catalytic activity occurred

Figure 4. Cyclic voltammogram of [Ni$_3$(**1**)](ClO$_4$)$_6$ at a glassy carbon electrode in MeCN/H$_2$O (9:1, v/v) measured under N$_2$ (a) and under CO$_2$ (b). Volts vs. SCE; concentration of complex, 2.0 mM; electrolyte, 0.1 M NaClO$_4$; scan rate, 100 mV s^{-1}.

Table 2. Cyclic voltammetry data for the electrocatalytic reduction of CO$_2$ by Ni^{II} complexes

catalyst	Under N$_2$[a]		Under CO$_2$[a]		i_p(CO$_2$)/i_p(N$_2$)[b]
	$E_{cathode}$[c] (i_p)[d]	E_{anode}[c] (i_p)[d]	$E_{cathode}$[c] (i_p)[d]	E_{anode}[c] (i_p)[d]	
[Ni$_3$(**1**)]$^{6+}$	−1.44 (+78.5)	−1.35 (−67.8)	−1.44 (+239)	[e]	3.04
[Ni(**3**)]$^{2+}$	−1.41 (+38.0)	−1.34 (−30.1)	−1.49 (+79.4)	[e]	2.09
[Ni(cyclam)]$^{2+}$	−1.56 (+31.8)	−1.47 (−27.3)	−1.47 (+154)	[e]	4.84

[a] In MeCN/H$_2$O (9:1, v/v) with 0.1 M NaClO$_4$; conc. of catalyst, 2.0 mM; working electrode, glassy carbon; scan rate, 100 mV s^{-1}. [b] Cathodic peak current ratio. [c] Volts vs. SCE. [d] μ ampere. [e] No peak was observed.

Table 3. Effect of catalyst concentration on the electroreduction of CO_2 catalyzed by $[Ni_3(1)](ClO_4)_6$[a]

c (mM)	Under N₂		Under CO₂		$ip(CO_2)/ ip(N_2)$[d]
	$E_{cathode}$[b] (i_p)[c]	E_{anode}[b](ip)[c]	$E_{cathode}$[b](ip)[c]	E_{anode}[b](ip)[c]	
0.1	−1.705(0.46)	−1.621(−0.27)	−1.669(1.29)	−	2.80
0.5	−1.683(1.95)	−1.621(−1.44)	−1.677(5.40)	−	2.77
2.0	−1.685(10.1)	−1.620(−6.90)	−1.663(21.44)	−	2.12

[a] In MeCN/H₂O (9:1, v/v) with 0.1 M TBAP; working electrode, controlled growth Hg. Electrochemical measurements were made after the solution was purged with N₂ for 30 min and then with CO₂ for 30 min. [b] Volts vs. Ag/Ag⁺(0.01 M). [c] μA. [d] Cathodic peak current ratio.

at $5 \times 10^{-6}-2 \times 10^{-3}$ M of catalyst.[12,52] To see if catalytic saturation took place under the present experimental conditions, $i_p(CO_2)$ was measured at various concentrations of $[Ni_3(1)]^{6+}$ ($1.0 \times 10^{-4}-2.0 \times 10^{-3}$ M). The results obtained for a Hg electrode are summarized in Table 3, and those for a glassy carbon electrode are presented in Figure 5. For both electrode materials, saturation of catalytic activity was not observed in the concentration range employed.
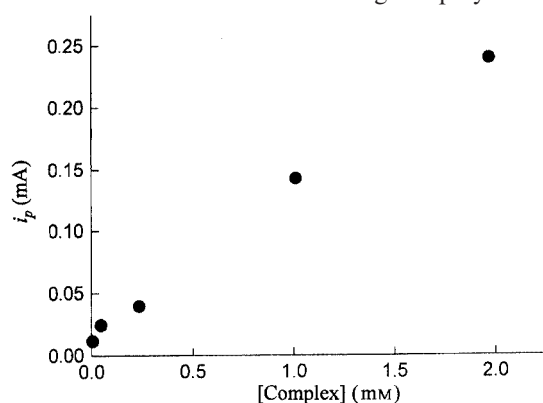

Figure 5. Effect of $[Ni_3(1)](ClO_4)_6$ concentration on the intensity of the catalytic wave for CO_2 electroreduction. Measured in MeCN/H₂O (9:1, v/v) with 0.1 M NaClO₄; glassy carbon electrode; scan rate, 100 mV s⁻¹.

It has been reported that the electrode material affects the electrocatalytic reduction of CO_2. For example, $[Ni^I(cyclam)]^+$ adsorbed on Hg is a better catalyst than that on a glassy carbon electrode.[52] For $[Ni_3(1)]^{6+}$ complex (2.0 mM), however, $i_p(CO_2)/i_p(N_2)$ measured on a glassy carbon electrode is 3.04 (Table 2) and that measured on the controlled growth mercury electrode is 2.12 (Table 3). This indicates that electrode-adsorption is less important for the present trinuclear catalyst.

Controlled potential coulometric experiments were carried out with CO_2-saturated MeCN/H₂O (9:1, v/v) solutions in the presence of $[Ni_3(1)]^{6+}$ and $[Ni(3)]^{2+}$ using a mercury pool electrode. The CO_2 reduction products were analyzed by GC both for gas and solution samples. Interestingly, CO was the only product, and other reduction products, including formate and H₂, were not detected. The amount of CO evolved depends on the applied voltage (Figure 6), with higher voltages producing more CO. In addition, CO production started to saturate within 0.5 h (Figure 7) and, therefore, the CO evolved after 30 min at the applied potential of −1.6 V vs. SCE was measured for various Ni^II catalysts (Table 4). The relative electrocatalytic efficiencies of

the complexes, in terms of CO production per mol of catalyst, almost parallel the order of $i_p(CO_2)/i_p(N_2)$; $[Ni(cyclam)]^{2+} > [Ni_3(1)]^{6+} > [Ni(3)]^{2+}$ (Table 2). However, when the number of nickel centers is considered, $[Ni_3(1)]^{6+}$ is not as good as the monometallic complexes, $[Ni(cyclam)]^{2+}$ and $[Ni(3)]^{2+}$. $[Ni_2(biscyclam)]^{4+}$ produced only ca. half of the amount of CO gas or HCOO⁻ per nickel center in DMF compared with that produced by the monometallic catalyst $[Ni(cyclam)]^{2+}$.[20] This is because an electrode(Hg)-adsorbed species was important in this electrocatalytic reaction, and only one metal center of $[Ni_2(biscyclam)]^{4+}$ was directly involved in each reaction cycle. The larger surface area of $[Ni_2(biscyclam)]^{4+}$ led to a smaller superficial surface density than that of $[Ni(cyclam)]^{2+}$, resulting in a poorer catalytic efficiency. For the present study, the TON value of $[Ni_3(1)]^{6+}$ (2.6) is slightly less than that of $[Ni(3)]^{2+}$ (3.9) (Table 4).
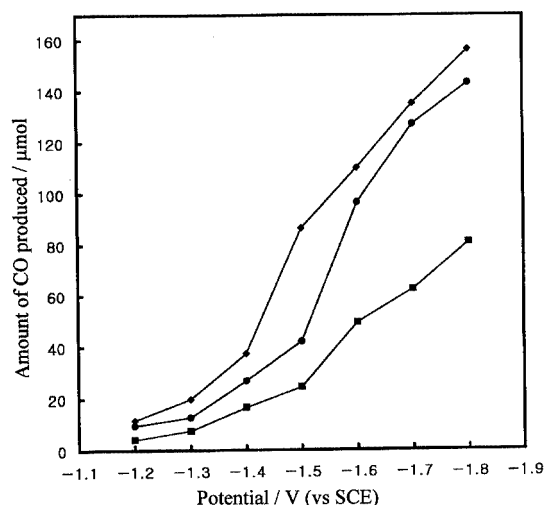

Figure 6. Effect of applied potential on CO production in the electrocatalytic reduction of CO_2. $[Ni_3(1)](ClO_4)_6$ (●); $[Ni(3)](ClO_4)_2$ (■); $[Ni(cyclam)](ClO_4)_2$ (◆). Volts vs. SCE; measured in 0.1 M NaClO₄ in MeCN/H₂O (9:1, v/v); electrolysis time, 30 min; 20 °C; CO₂ pressure, 1 atm; working electrode, Hg pool; concentration of catalyst, 1.0 mM.

The catalytic activity of the Ni^II complexes of 1 and 3 might be attributed to their ready reduction to Ni^I species. In CO_2 reduction catalyzed by cobalt macrocyclic complexes, the CO_2 adduct of the reduced complex was proposed as an intermediate, and a five-coordinate cobalt(I)−CO₂ was isolated from the reaction.[53−54] Hydrogen bonding between the coordinated CO_2 and the N−H of the macrocycle was important in stabilizing this ad-

Table 4. CO production from the electrochemical reduction of CO_2 catalyzed by Ni^{II} complexes[a][b]

catalyst	applied potential volts vs. SCE	conc. of catalyst	CO produced in 0.5 h (µmol)	Turnovers[c] per 0.5 h at 20 °C	current efficiency (%)
$[Ni_3(\mathbf{1})]^{6+}$	−1.6	1.0 mM	96.5	2.6	96.2
$[Ni(\mathbf{3})]^{2+}$	−1.6	1.0 mM	49.2	3.9	95.3
$[Ni(cyclam)]^{2+}$	−1.6	1.0 mM	110	8.4	98.7

[a] Measured in MeCN/H_2O (9:1, v/v) with 0.1 M $NaClO_4$; 25 mL of solution with 25 µmol of complex; concentration of complex, 1.0×10^{-3} M; electrolysis time, 0.5 h. [b] Measured at 20 °C and 1 atm; working electrode, Hg pool. [c] Number corresponds to twice the number of mol of CO produced in 0.5 h per mol of nickel center.
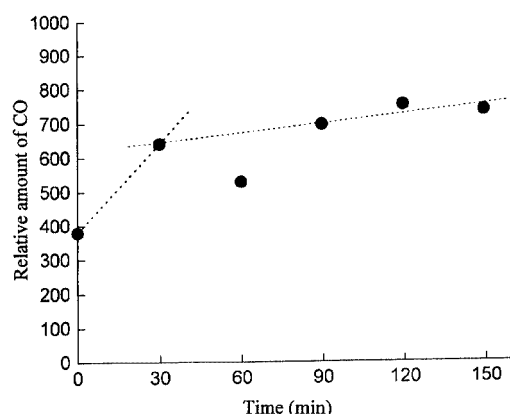

Figure 7. Relative amount of CO vs. MeCN detected by GC during the electroreduction of CO_2 catalyzed by $[Ni_3(\mathbf{1})](ClO_4)_6$; t, electrolysis time; applied potential, −1.6 V vs. SCE; glassy carbon electrode; data at $t = 0$ min is CO contained in the background CO_2 gas that is saturated with MeCN vapor

duct.[20] In the present study, it may be assumed that the Ni^{I} species binds CO_2 in the transition state, even though Ni^{II} species have poor coordinating ability. The secondary amines in the macrocycle **1** might promote the formation of the CO_2 adducts. It has been reported that the Ni^{II} complex of bismacrocyclic ligand **4** is highly active and selective catalyst for the photochemical reduction of CO_2[55] although the Ni^{II} species has poor binding ability for the solvent water molecule, similarly to $[Ni_3(\mathbf{1})]^{6+}$.

4
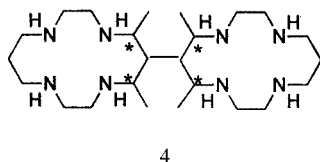
Conclusion

The trinuclear Ni^{II} complex $[Ni_3(\mathbf{1})]^{6+}$, in which three macrocyclic complexes are linked by a flexible tren bridge, was prepared and its X-ray structure was determined. The three Ni^{II} centers in $[Ni_3(\mathbf{1})]^{6+}$ are electrochemically independent and are easily reduced to Ni^{I} by reaction with Na(Hg) in MeCN. The complex $[Ni_3(\mathbf{1})](ClO_4)_6$ shows catalytic activity for the electrochemical reduction of CO_2 to CO in MeCN/H_2O (9:1, v/v), exhibiting a greater catalytic current than monometallic $[Ni(\mathbf{3})]^{2+}$ but producing less CO

gas per nickel center. The catalytic efficiencies of $[Ni_3(\mathbf{1})]^{6+}$ and $[Ni(\mathbf{3})]^{2+}$, in terms of $i_p(CO_2)/i_p(N_2)$ and turnover number, are lower than that of $[Ni(cyclam)]^{2+}$.

Experimental Section

Reagents: All chemicals and solvents used in the syntheses were reagent grade and used without further purification. For the synthesis of Ni^{I} complex and the physicochemical measurements, reagents and solvents were purified according to the literature procedure[56] and deaerated prior to use. $[Ni(\mathbf{2})](ClO_4)_2$ and $[Ni(\mathbf{3})](ClO_4)_2$ were prepared and recrystallized according to the methods previously reported.[22] N_2 and CO_2 gases were deaerated and dried by passing through a BASF column and then a $CaCl_2$ column.

Measurements: IR spectra were recorded with a Bruker IFS48 FT IR spectrophotometer. Conductance was measured by a SUNTEX SC-170 conductivity meter. Electronic absorption spectra were obtained on a Beckman DU68 UV/Vis spectrophotometer equipped with an electronic temperature controller. ^{13}C NMR spectra were recorded on a Gemini-300 FT NMR spectrometer. EPR spectra were obtained on a Bruker ER 200E spectrometer. Elemental analyses (EA) were performed by the analytical laboratory of Seoul National University and by The Korea Basic Science Center, Seoul. Electrochemical experiments were performed on a BAS 100B/W electrochemical analyzer. Cyclic voltammetry, differential pulse voltammetry, and Osteryoung square-wave voltammetry were carried out in MeCN containing 0.1 M $(nBu)_4NPF_6$. The working electrode was a glassy carbon, the auxiliary electrode was a coiled platinum wire, and the reference electrode was Ag/Ag^+ (0.01 M in MeCN). The electrochemical reduction of the Ni^{II} complex to Ni^{I} was performed by controlled potential coulometry, carried out at −1.8 V vs. Ag/Ag^+ (0.01 M) in an MeCN solution of 0.1 M $(nBu)_4NPF_6$ under a N_2 atmosphere until the end current became 1% of the initial value.

Synthesis

Caution! *Perchlorate salts of metal complexes are potentially explosive and should be handled with care.*

$[Ni_3(\mathbf{1})](ClO_4)_6$: Tris(2-aminoethyl)amine (96%, 0.34 g, 2.2 mmol) and triethylamine (4.0 mL, 29 mmol) were added to a solution of $[Ni(\mathbf{2})](ClO_4)_2$ (3.05 g, 6.5 mmol) dissolved in hot MeOH/H_2O (2:1, v/v, 120 mL). The mixture was then heated at reflux. Excess 37% formaldehyde (3.76 mL, 50 mmol) mixed with MeOH (5 mL) was introduced dropwise over 1 hour and the solution was heated at reflux for an additional 2 h, during which time a yellow precipitate formed. The precipitate was filtered off from the hot solution and was washed with MeOH and dried in vacuo. It was then purified

by recrystallization from $H_2O/MeOH$ (1:1, v/v). The compound was not obtained as single crystals in any solvent. Yield: ca. 50% (5.31 g). $C_{39}H_{84}Cl_6N_{22}Ni_3O_{24}$ (1634.1): calcd. C 28.67, H 5.18, N 18.86; found C 29.29, H 5.30, N 18.87. UV/Vis: λ_{max} (ε) = 439 nm (251 cm^{-1} M^{-1}) in MeCN; 439 nm (273 cm^{-1} M^{-1}) in $MeNO_2$. IR (Nujol mull): $\tilde{\nu}$ = 3207 cm^{-1} (ν_{N-H}), 1100 cm^{-1} (br., ν_{Cl-O}). ^{13}C NMR ([D_3]nitromethane): δ = 41.5, 43.4, 49.4, 49.8, 62.4, 64.2, 69.8, 70.3 ppm.

Preparation of Single Crystals of [Ni_3(1)](ClO_4)_3·Cl_3·10H_2O: [$Ni_3(1)$](ClO_4)$_6$ (0.143 g) and NaCl (0.2 g) was added to a mixture of MeCN (6 mL), MeOH (6 mL), and H_2O (0.5 mL). The solution was then heated until the complex went into the solution. The resultant yellow solution was filtered while hot, and the filtrate was allowed to stand at room temperature until orange crystals formed, which were then filtered off, washed with mother liquor, and dried in air. $C_{39}H_{104}Cl_6N_{22}Ni_3O_{22}$ (1622.2): calcd. C 28.88, H 6.46, N 19.00; found C 28.17, H 6.29, N 18.69.

[Ni^I_3(1)](ClO_4)_3: The synthesis, experiments with, and manipulation of the Ni^I compound should be conducted under strict exclusion of air by using Schlenk lines since the compound is air-sensitive. **Method 1.** [$Ni_3(1)$](ClO_4)$_6$ (1.0 g, 0.6 mmol) was stirred with 5% Na(Hg) (3 g, 6.5 mmol) in MeCN (50 mL) for 20 min as the yellow complex slowly went into a red-purple solution. The solution was filtered, concentrated to one-third of the initial volume, and then allowed to stand in a refrigerator under strict exclusion of air until a red precipitate formed. The precipitate was then filtered off, washed with MeCN, and dried in vacuo. Yield: 70% (0.56 g). $C_{39}H_{84}Cl_3N_{22}Ni_3O_{12}$ (1335.7): calcd. C 35.07, H 6.34, N 23.07; found C 32.01, H 5.42, N 20.85. **Method 2.** [$Ni_3(1)$](ClO_4)$_3$ can be prepared in solution by bulk electrolysis of [$Ni_3(1)$](ClO_4)$_6$. A solution of [$Ni_3(1)$](ClO_4)$_6$ (1.0 × 10^{-3} M) was prepared in MeCN containing 0.1 M (nBu)$_4$NPF$_6$. A current was passed through the solution at −1.8 V vs. Ag/Ag$^+$ (0.01 M) for ca. 3 h until the intensity of end current became 1% of the initial value. The solution, which became reddish purple, was then frozen and its EPR spectrum was measured.

Electrochemical Reduction of CO_2: The electrochemical reduction of CO_2 was measured by cyclic voltammetry and controlled-potential coulometry. Cyclic voltammetry was performed on MeCN/H_2O (9:1, v/v) solutions of Ni^{II} complex (2.0 mM) containing 0.1 M (nBu)$_4$NPF$_6$ by using a glassy carbon or a controlled growth mercury electrode. Measurements were made with the solutions saturated with N_2 and then with CO_2. Controlled-potential coulometric experiments were performed at 20 °C by using a Hg pool as working electrode and a platinum plate as auxiliary electrode with a solution (25 mL) containing 1.0 mM of the Ni^{II} complex in a gas-tight electrolysis cell (internal gas volume; 32 mL). After CO_2 gas was bubbled through the solution for 30 min, a fixed potential (voltage range: −1.2 to −1.6 V vs. SCE) was applied for 30 min. The gas products were analyzed with a Hewlett−Packard 5890 Gas Chromatograph with a thermal conductivity detector. A Porapak Q column (8′ × 1/8′′, 80−100 mesh) and He carrier gas were used for CO analysis. Molecular sieves, 13X column (7′ × 1/8′′, 60−80 mesh), and N_2 gas were used for H_2 analysis. The CO (or H_2) peak was identified by comparing its retention time with that of standard CO (or H_2) gas. The CO was quantified by using a prepared standardization curve; the average of the three repeated experiments was obtained. Turnover frequencies were calculated as twice the number of mol of CO produced in 30 min per mol of electrocatalyst.

X-ray Crystallographic Study for [Ni_3C_{39}H_{84}N_{22}]-(ClO_4)_3·Cl_3·10H_2O: $C_{39}H_{104}Cl_6N_{22}Ni_3O_{22}$, M_r = 1622.27 g/mol^{-1},

a = 15.969(5) Å, b = 16.148(5) Å, c = 16.722(5) Å, α = 105.051(5)°, β = 114.812(5)°, γ = 94.227(5)°, V = 3697(2) Å^3, Z = 2, $d_{calcd.}$ = 1.457 g/cm^{-3}, triclinic, space group $P\bar{1}$ (No.2), μ = 1.052 mm^{-1}, $F(000)$ = 1708, T = 298 K. An orange rod-shaped single crystal (0.20 × 0.25 × 0.50 mm) was mounted on an Enraf Nonius Kappa CCD diffractometer. Data were collected with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) through use of the ω-2θ scan technique. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using *DENZO*.[57] The scaling and global refinement of crystal parameters were performed by *SCALEPACK*.[57] No absorption correction was made. Of 16696 reflections measured in the range 2.68 < 2θ < 55.22, 9361 were assumed to be observed [$I > 2\sigma(I)$]. The crystal structures were solved by direct methods[58] and refined by full-matrix least-squares refinement using the *SHELXL-97* computer program.[59] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors, except for oxygen atoms with severe thermal disorder: three from ClO_4^- anions (O4, O9, O10) and eight from water (OW2, OW3, OW5, OW6, OW7, OW8, OW9, OW10). All hydrogen atoms were allowed to ride on their bonded atoms with values of 1.2× those of the bonded atoms. Convergence of the 783 variable parameters by full-matrix, least-squares refinement on F^2 reaches R_1 = 0.0918 [$I > 2\sigma(I)$] and wR_2= 0.2554 with a goodness-of-fit of 1.061. ORTEP drawings were made with ORTEP-3 for windows.[60] Crystallographic data are summarized in Table S1, and selected bond lengths and angles are provided in Table S2, of the Supporting Information.

CCDC-194395 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

[1] M. M. Halmann and M. Steinberg, *Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology*, Lewis Publishers, Boca Raton, London, New York, Washington D. C. **1999**, Chapter 12.

[2] [2a] *Catalytic Activation of Carbon Dioxide* (Ed.: W. M. Ayers), ACS Symposium Series No 363, American Chemical Society, Washington D. C., **1988**. [2b] A. Behr, *Carbon Dioxide Activation by Metal*, VCH, New York, **1988**.

[3] H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.* **2001**, *101*, 953−996.

[4] I. Taniguchi, in J. O′. M. Bockris (Ed.), *Modern Aspects of Electrochemistry, No. 20: Electrochemical and Photoelectrochemical Reduction of Carbon Dioxide*, Plenum Press, New York, **1989**, 327.

[5] M. Beley, J.-P. Collin, R. Ruppert, J.-P. Sauvage, *J. Am. Chem. Soc.* **1986**, *108*, 7461.

[6] E. Kimura, M. Haruta, T. Koike, M. Shionoya, K. Takenouchi, Y. Iitaka, *Inorg. Chem.* **1993**, *32*, 2779.

[7] S. Meshitsuka, M. Ichikawa, K. Tamaru, *J. Chem. Soc., Chem. Commun.* **1974**, 158.

[8] B. Fischer, R. Eisenberg, *J. Am. Chem. Soc.* **1980**, *102*, 7361.

[9] E. Fujita, J. Haff, R. Sanzenbacher, H. Elias, *Inorg. Chem.* **1994**, *33*, 4627.

[10] S. C. Rasmussen, M. M. Richter, E. Yi, H. Place, K. J. Brewer, *Inorg. Chem.* **1990**, *29*, 3926.

[11] C. M. Bolinger, N. Story, B. P. Sullivan, T. J. Meyer, *Inorg. Chem.* **1988**, *27*, 4582.

[12] F. Abba, G. D. Santis, L. Fabbrizzi, M. Licchelli, A. M. M. Lanfredi, P. Pallavincini, A. Poggi, F. Ugozzoli, *Inorg. Chem.* **1994**, *33*, 1366.

[13] C. Arana, M. Keshavarz, K. T. Potts, H. D. Abruna, *Inorg. Chim. Acta* **1994**, *225*, 285.

[14] M. Shionoya, E. Kimura, Y. Iitaka, *J. Am. Chem. Soc.* **1990**, *112*, 9237.

[15] D. Behar, T. Dhanasekaran, T. Neta, C. M. Hosten, D. Ejeh, P. Hambright, E. Fujita, *J. Phys. Chem. A* **1998**, *102*, 2870.

[16] R. W. Hay, J. A. Crayston, T. J. Cromie, P. Lightfoot, D. C. L. de Alwis, *Polyhedron* **1997**, *16*, 3557.

[17] K. Bujno, R. Bilewicz, L. Siegfried, T. Kaden, *Electrochimica Acta* **1997**, *42*, 1201.

[18] K. Bujno, R. Bilewicz, L. Siegfried, T. Kaden, *J. Electrochim. Chem.* **1996**, *407*, 131.

[19] K. Bujino, R. Bilewicz, L. Siegfried, T. A. Kaden, *J. Electroanal. Chem.* **1998**, *445*, 47.

[20] J.-P. Collin, A. Jouaiti, J.-P. Sauvage, *Inorg. Chem.* **1988**, *27*, 1986.

[21] C. de Alwis, J. A. Crayston, T. Cromie, T. Eisenblätter, R. W. Hay, Y. D. Lampeka, L. V. Tsymbal, *Electrochimica Acta* **2000**, *45*, 2061.

[22] M. P. Suh, W. Shin, H. Kim, C. H. Koo, *Inorg. Chem.* **1987**, *26*, 1846.

[23] M. P. Suh, *Adv. Inorg. Chem.* **1997**, *44*, 93.

[24] M. P. Suh, B. Y. Shim, T.-S. Yoon, *Inorg. Chem.* **1994**, *33*, 5509.

[25] M. P. Suh, W. Shin, S.-G. Kang, M. S. Lah, T.-M. Chung, *Inorg. Chem.* **1989**, *28*, 1602.

[26] M. P. Suh, S. K. Kim, *Inorg. Chem.* **1993**, *32*, 3562.

[27] M. P. Suh, S.-G. Kang, V. L. Goedken, S. H. Park, *Inorg. Chem.* **1991**, *30*, 365.

[28] R. J. Geue, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson, M. R. Snow, *J. Am. Chem. Soc.* **1984**, *106*, 5478.

[29] G. A. Bottomley, I. J. Clark, I. I. Creasen, L. M. Engelhart, R. J. Geue, K. S. Hagen, J. M. Harrowfield, G. A. Lawrance, P. A. Lay, A. M. Sargeson, A. J. See, B. W. Skelton, A. H. White, F. R. Wilner, *Aust. J. Chem.* **1994**, *47*, 143.

[30] P. V. Bernhardt, E. J. Hayes, *J. Chem. Soc., Dalton Trans.* **1998**, 3539.

[31] M. Cheon, M. P. Suh, W. Shin, *Bull. Kor. Chem. Soc.* **1992**, *13*, 363.

[32] L. R. Furenlid, M. W. Renner, D. J. Szalda, E. Fujita, *J. Am. Chem. Soc.* **1991**, *113*, 883.

[33] F. V. Lovecchio, E. S. Gore, D. H. Busch, *J. Am. Chem. Soc.* **1974**, *96*, 3109.

[34] R. R. Gagne, D. M. Ingle, *Inorg. Chem.* **1981**, *20*, 420.

[35] N. Jurban, G. Ginzburg, H. Cohen, D. Meyerstein, *J. Chem. Soc., Chem. Commun.* **1982**, 517.

[36] N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh, D. Meyerstein, *Inorg. Chem.* **1985**, *24*, 251.

[37] A. James, H. Espenson, *J. Am. Chem. Soc.* **1986**, *108*, 713.

[38] J. Lewis, M. Schroder, *J. Chem. Soc., Dalton Trans.* **1982**, 1085.

[39] P. Chmielewski, M. Grzeszczuk, L. Latos-Grazynski, J. Lisowski, *Inorg. Chem.* **1989**, *28*, 3546.

[40] A. M. Stolzenberg, M. T. Stershic, *Inorg. Chem.* **1987**, *26*, 3082.

[41] M. P. Suh, H. K. Kim, M. J. Kim, K. Y. Oh, *Inorg. Chem.* **1992**, *31*, 3620.

[42] D. J. Szalda, E. Fujita, R. Sanzenbacher, H. Paulus, H. Elias, *Inorg. Chem.* **1994**, *33*, 5855.

[43] M. P. Suh, Y. J. Lee, J. W. Jeong, *J. Chem. Soc., Dalton Trans.* **1995**, 1577.

[44] M. P. Suh, K. Y. Oh, J. W. Lee, Y. Y. Bae, *J. Am. Chem. Soc.* **1996**, *118*, 777.

[45] M. S. Ram, C. G. Riordan, R. Ostrander, A. L. Rheingold, *Inorg. Chem.* **1995**, *34*, 5884.

[46] J. S. Kim, J. H. Reibenspies, M. Y. Darensbourg, *J. Am. Chem. Soc.* **1996**, *118*, 4115.

[47] A. L. Rheingold, *Inorg. Chem.* **1996**, *35*, 5408.

[48] W. Grabarse, F. Mahlert, E. Duin, *J. Mol. Biol.* **2001**, *309*, 315.

[49] E. Pereira, L. Gomes, B. de Castro, *J. Chem. Soc., Dalton Trans.* **1998**, 629.

[50] T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* **2000**, *122*, 6375.

[51] A. J. Bard, L. R. Faulkner, *Electrochemical Methods, Fundamentals and Application*; John Wiley & Sons, Inc. New York, **1980**, Chapters 6 and 11.

[52] M. Fujihira, Y. Hirata, K. Suga, *J. Electroanal. Chem.* **1990**, *292*, 199.

[53] E. Fujita, D. J. Szalda, D. Creutz, N. Sutin, *J. Am. Chem. Soc.* **1988**, *110*, 4870.

[54] E. Fujita, C. Creutz, N. Sutin, D. Szalda, *J. Am. Chem. Soc.* **1991**, *113*, 343.

[55] K. Mochizuki, S. Manaka, I. Takeda, T. Kondo, *Inorg. Chem.* **1996**, *35*, 5132.

[56] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, **1988**.

[57] Z. Otwinowsky, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology* (Eds.: C. W. Carter, Jr. R. M. Sweet), Academic Press, **1996**, vol. *276* pp 307−326.

[58] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[59] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, **1997**.

[60] L. J. Farrugia, *ORTEP-3* for Windows, Version 1.07, Univerity of Glasgow, Scotland, **2001**.