# Carbon Monoxide Binding to Nickel(I) Macrocyclic Complexes Generated by Electrochemical Method

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Nature uses characteristic properties of metal ions to perform specific biological functions.[1] Enzymes such as urease, carbon monoxide dehydrogenase (CODH), hydrogenase (H₂-ase), and methyl coenzyme M reductase contain Ni(II) ions.[2]

F430, a Ni(II) hydrocorphinoid complex, is a prosthetic group of *S*-methyl coenzyme M reductase which catalyzes the reductive cleavage of *S*-methyl coenzyme M to coenzyme M and methane in the final stage of carbon dioxide reduction in the methanogenic bacteria.[3] Although the function of F430 is not fully understood yet, an EPR signal detected in whole cells of *Methanobacterium thermoautotrophicum* has been attributed to a Ni(I) form of F430.[4] Isolated F430 (pentamethyl ester of F430) can be reduced to the Ni(I) species in THF, which was characterized by UV/vis and ESR spectroscopy.[5]
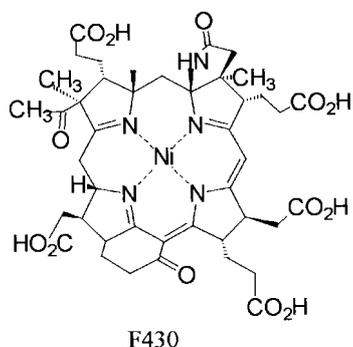


F430

Although X-ray structures of Ni(I) species of isobacteriochlorin, F430, and F430M have not been reported yet, analysis of EXAFS data suggests that their macrocyclic cores are expanded and distorted compared with the structures of the Ni(II) species.[6,7] For example, in the case of low spin Ni(II) F430M, the Ni-N bond distance is 1.90(2) Å, but the reduced Ni(I) F430M shows two sets of Ni-N bond distances of 1.88(3) Å and 2.03(3) Å.[6b] Recently, X-ray structures of some Ni(I) macrocyclic complexes in square-planar[8-11] and square-pyramidal[12] coordination geometry have been also reported. The results show two sets of Ni-N bond distances rather than a simple expansion of macrocyclic core compared with the parent Ni(II) species. Therefore, all Ni(I) macrocyclic complexes known so far show two different sets of Ni-N bond distances although proper explanation for

these observations has not been made yet.

Some Ni(I) macrocyclic complexes have been known to react with CO and the CO adducts have been characterized by the UV/vis, ESR, and IR spectra.[13-15] However, there have been no reports for the X-ray structure of Ni(I)-CO adducts yet. Only the EXAFS data for [Ni(**L₁**)CO]⁺ and [Ni(**L₂**)CO]⁺ showed that they had five-coordinate geometry with Ni-C bond distances of 1.80 and 1.78 Å respectively.[8]



**L₁**                **L₂**
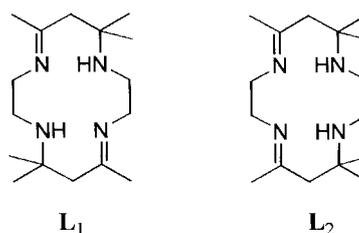
To obtain Ni(I)-CO adducts and to understand the property of Ni(I) complexes better, we measured the CO binding constants for various Ni(I) macrocyclic complexes (**cyclam** and **1**-**5**) by using electrochemical method and tried to find the factors which affect CO binding.



**cyclam**           **1**           **2**
                                          **(*R,R,S,S*)**

**3**              **4**             **5**
**(*R,R,S,S*)**       **(*R,R,S,S*)**       **(*R,S,R,S*)**
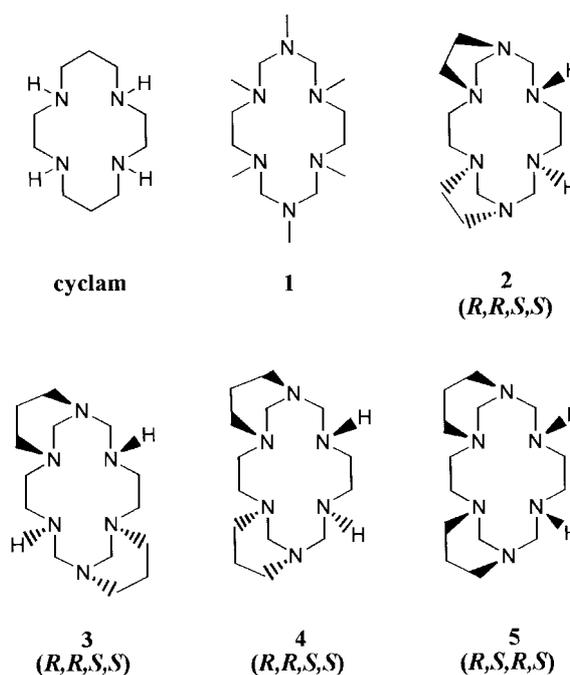
## Experimental Section

**Reagents**. All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. For the spectroscopic and physical measurements, organic solvents were dried and purified according to the literature methods.[16] ($n$-Bu)$_4$NPF$_6$ was recrystallized three times in ethanol and dried overnight at 100 °C under vacuum. Nitrogen and CO gases were purified by passing them through the columns filled with BTS catalyst and CaCl$_2$.

**Synthesis**. Various Ni(II) macrocyclic complexes [Ni(**L**)] (ClO$_4$)$_2$ (**L=1-5**) were synthesized by the one-pot template condensation reactions according to the literatures previously reported.[17-18]

**Electrochemistry**. Cyclic voltammetry was carried out with a BAS 100B/W electrochemical workstation using a conventional cell. The electrochemical data were measured in MeCN solution of 0.1 M ($n$-Bu)$_4$NPF$_6$. 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). To carry out the cyclic voltammetry under CO atmosphere, MeCN solution was degassed and then saturated with 1 atm CO. Solubility of CO in MeCN at 25 °C was assumed to be 0.0083 M/atm according to the literature.[19]

## Results and Discussion

The CO binding constants ($K_{CO}$) for Ni(I) complexes of **1-5** were determined by using cyclic voltammetry as previously reported.[20,21] The CO binding constant ($K_{CO}$) for electrochemically generated Ni(I) complex is defined by eq. 1 and 2.

$$Ni^{II}(L) + e^- \rightleftharpoons Ni^I(L) \qquad (1)$$

$$Ni^I(L) + CO \underset{}{\overset{K_{CO}}{\rightleftharpoons}} Ni^I(L)(CO) \qquad (2)$$
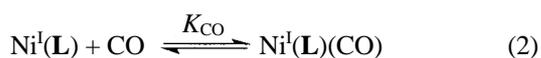
Application of Nernst equation yields the relationship between $K_{CO}$ and the reduction potential of Ni(II)/Ni(I) as described in eq. 3.

$$E_{1/2}(CO) = E_{1/2} + \frac{RT}{F}\ln(1 + K_{CO}[CO])$$

$$K_{CO} = \frac{1}{[CO]} \cdot \exp(\Delta E_{1/2} \cdot \frac{F}{RT} - 1) \qquad (3)$$

Here $E_{1/2}(CO)$ is the half-wave potential, $(E_{pc}(CO) + E_{pa}(CO))/2$, measured under CO, $E_{1/2}$ is the half-wave potential, $(E_{pc} + E_{pa})/2$, measured under nitrogen atmosphere for the Ni(II)/ Ni(I) reduction, and $\Delta E_{1/2}$ is $E_{1/2}(CO) - E_{1/2}$.[21-24]

To obtain $K_{CO}$ values, half-wave reduction potentials of Ni(II) complexes were measured under N$_2$ and CO atmosphere, respectively, and the data were fitted to eq. 3. In particular, the measurement of $\Delta E_{1/2}$ under 1 atm CO pressure allows the estimation of $K_{CO}$ value when the solubility of CO in MeCN at 25 °C is assumed to be 0.0083 M/atm according to the literature.[19] In the calculations, ±5 mV was assumed to be the maximum experimental error.
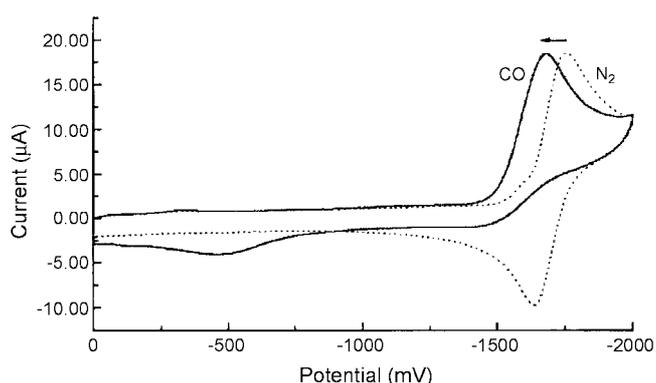


**Figure 1**. Cyclic voltammograms of [Ni(**1**)](ClO$_4$)$_2$. Ni concentration, 1.0 mM in MeCN with 0.1 M ($n$-Bu)$_4$NPF$_6$. Scan rate = 100 mV/s. Dotted line ( ··· ): measured under N$_2$ atmosphere. Solid line ( — ): measured under CO atmosphere (1 atm).
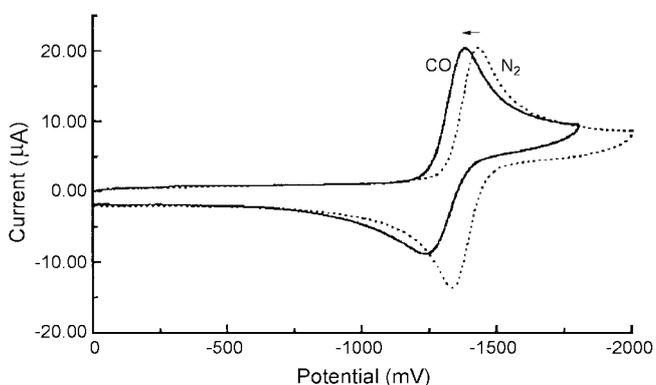


**Figure 2**. Cyclic voltammograms of [Ni(**3**)](ClO$_4$)$_2$. Ni concentration, 1.0 mM in MeCN with 0.1 M ($n$-Bu)$_4$NPF$_6$. Scan rate = 100 mV/s. Dotted line ( ··· ): measured under N$_2$ atmosphere. Solid line ( — ): measured under CO atmosphere (1 atm).

Typical cyclic voltammograms of [Ni(**1**)](ClO$_4$)$_2$ and [Ni(**3**)](ClO$_4$)$_2$ that are measured under N$_2$ and CO atmosphere are shown in Figures 1 and 2, respectively. When CO was bound to Ni(I), anodic shift occurred for the Ni(II)/Ni(I) reduction peak. Cyclic voltammograms of Ni(II) complexes of macrocycle **2-4** which were measured under CO atmosphere are reversible but those of **1** and **5** show only cathodic peaks indicating that CO binding to the complexes of **1** and **5** is irreversible. This may be attributed to the very slow dissociation of CO in the complexes of **1** and **5**. Probably the equilibrium between [Ni(**L**)(CO)]$^+$ and [Ni(**L**)]$^+$ (**L = 1** and **5**) cannot be attained within anodic scan time.[25]

The $K_{CO}$ values for various Ni(I) macrocyclic complexes are summarized in Table 1 together with Ni(II)/Ni(I) reduction potentials ($E_{1/2}$) of the complexes. Large $K_{CO}$ values ($10^3 \sim 10^4$) obtained in this study indicate the stabilization of Ni(I)-CO adducts. The CO binding constants of square planar Ni(I) complexes may be affected by the bond strength of Ni(I)-CO and the alterations of solvation and geometric structure around metal complex upon CO binding. They would reflect i) the electron density at the Ni(I) metal center, ii) susceptibility of formation of five-coordinate species with square pyramidal geometry, and iii) the solvation effect.[21]

**Table 1**. Reduction potentials of Ni(II)/Ni(I) and CO binding constants for Ni(I) complexes of various macrocyclic ligands[a]

| ligand | $E^b$ | | | $E(CO)^c$ | | | $\Delta E_{1/2}{}^g$ | $K_{CO}{}^h$ |
|---|---|---|---|---|---|---|---|---|
| | $E_{pc}{}^d$ | $E_{pa}{}^e$ | $E_{1/2}{}^f$ | $E_{pc}(CO)$ | $E_{pa}(CO)$ | $E_{1/2}(CO)$ | | |
| **cyclam**[i] | | | -1.75 | | | | | $2.8\times10^5$ |
| 1 | -1.75 | -1.64 | -1.70 | -1.68 | – | | | |
| 2 | -1.55 | -1.47 | -1.52 | -1.45 | -1.34 | -1.40 | 0.13 | $1.6\times10^4$ |
| 3 | -1.43 | -1.34 | -1.38 | -1.38 | -1.24 | -1.31 | 0.07 | $1.9\times10^3$ |
| 4 | -1.46 | -1.36 | -1.41 | -1.41 | -1.26 | -1.34 | 0.07 | $1.9\times10^3$ |
| 5 | -1.33 | -1.23 | -1.28 | -1.28 | – | | | |

[a]Measured in MeCN with 0.1 M ($n$-Bu)$_4$NPF$_6$ at 25 °C, volt *vs.* Ag/Ag$^+$ (0.01 M). [b]Measured under N$_2$ atmosphere. [c]Measured under CO atmosphere (1 atm). [d]Cathodic peak potential. [e]Anodic peak potential. [f]$E_{1/2} = (E_{pc} + E_{pa})/2$. [g]$\Delta E_{1/2} = E_{1/2}(CO) - E_{1/2}$. [h]Estimated from eq. 2. [i]Reference 8.

Since the metal atom locates above the plane made by four nitrogen donors when CO coordinates to the metal, the binding constants should be affected by the flexibility of macrocyclic ligand also. The crystal structure of Cu(I)-CO complex previously reported shows that the metal locates 0.096 Å above the ligand plane.[26]

The value of $K_{CO}$ is $(2.8 \pm 0.6) \times 10^5$ for **L** = **cyclam**[8] and the $K_{CO}$ values of **L** = **2-4** are in the order of $10^3\sim10^4$. They decrease in the order of **cyclam** > **2** > **3**~**4**. As shown in Table 1, the reduction potential of Ni(II)/Ni(I) increases in the order of **cyclam** > **1** > **2** > **3** > **4** > **5**. This indicates that the reduction of Ni(II) to Ni(I) is most difficult with cyclam and easiest with the ligand **5**. That is, the electron donating ability of the ligand to the metal is in the order of **cyclam** > **1** > **2** > **3** > **4** > **5**. If the macrocyclic ligand donates more electron density to the metal ion, the Ni(I) ion will bind CO better because stronger $\pi$-back bonding will form between metal and CO.

The smaller binding constants for **L** = **2**, **3**, and **4** than the simple macrocycle **cyclam** may also be explained by their larger steric hindrance against CO binding at the axial site due to the subring moieties. For **L** = **1** and **5**, the CO binding constant could not be estimated because the reactions were irreversible. However, since *R,S,R,S*-[Ni(**5**)](ClO$_4$)$_2$ has better geometric structure than *R,R,S,S*-[Ni(**4**)](ClO$_4$)$_2$ for the out of plane distortion of metal ion,[27] which is necessary for the CO binding, we may expect that [Ni(**5**)](ClO$_4$)$_2$ would have larger $K_{CO}$ value than [Ni(**4**)](ClO$_4$)$_2$. In addition, macrocyclic ligand **3** or **4** has larger ligand core than ligand **2**.[17a,17b] This makes the metal with **L** = **3** or **4** be reduced more easily than that with **L** = **2**, which is reflected by less negative $E_{1/2}$ value. This in turn gives smaller $K_{CO}$ value for **3** and **4** than for **2**. We would expect similar steric effect for **L** = **3** and **4**, because their macrocyclic ligands have similar core size and subring moieties. They actually showed very similar $K_{CO}$ values.

## Conclusion

Electrochemically generated Ni(I) macrocyclic complexes bind CO in MeCN and the binding constants were measured by the cyclic voltammetric method. The binding constants depend on the macrocyclic ligands. It is larger for monocyclic ligand (**L** = **cyclam**), whose complex is more difficult to be reduced from Ni(II) to Ni(I), than for macropolycyclic ligands (**L** = **2-5**). The larger core size of the macrocycle in **L** = **3** and **4**, which stabilizes Ni(I) complexes better, causes smaller $K_{CO}$ value than those with smaller core size (**L** = **2**). The bulky subring moieties of the macrocycle in **L** = **2-5** prevent CO access to the Ni(I) ion, which leads to the smaller $K_{CO}$ value.

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