High Electrocatalytic Activity of *RRSS*-[Ni^{II}HTIM](ClO$_4$)$_2$ and [Ni^{II}DMC](ClO$_4$)$_2$ for Carbon Dioxide Reduction (HTIM = 2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradecane, DMC = *C-meso*-5,12-Dimethyl-1,4,8,11-tetraazacyclotetradecane)

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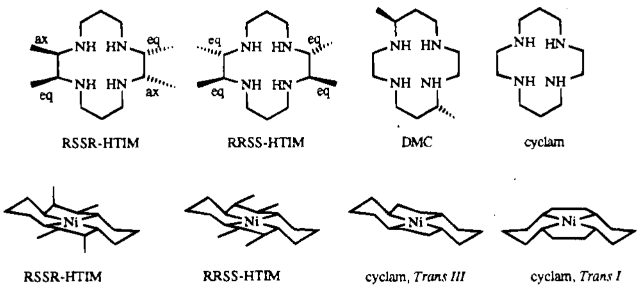
Ni(cyclam)$^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) is a very effective and selective catalyst for the electrochemical reduction of CO$_2$ to CO relative to the reduction of water to H$_2$ in aqueous solution.[2−8] However, photochemical reduction of CO$_2$ using a photosensitizer, a sacrificial electron donor, and Ni(cyclam)$^{2+}$ as the catalyst has been only moderately successful.[9−11] In order to understand the factors responsible for the superior electrocatalytic activity of Ni(cyclam)$^{2+}$, extensive studies[2,4,6,7] have been carried out. While Ni(cyclam)$^{+}$ adsorbed on the surface of a mercury electrode is an active species, other aspects of the catalytic mechanism have remained unclear. Here we report the catalytic activity in aqueous solution and the CO$_2$ binding in acetonitrile of *RRSS*- and *RSSR*-NiHTIM(ClO$_4$)$_2$ (HTIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and NiDMC(ClO$_4$)$_2$ (DMC = *C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane) compared to those of Ni(cyclam)$^{2+}$. While *RSSR*-NiHTIM^{2+} is not, *RRSS*-NiHTIM^{2+} and NiDMC^{2+} are better catalysts than Ni(cyclam)$^{2+}$ in terms of their larger catalytic currents and more positive potentials. Since the catalytic activities of *RRSS*- and *RSSR*-NiHTIM^{2+} are quite different, structural differences may be a very important factor for adsorption onto a mercury electrode and CO$_2$ binding.



The *RRSS* and *RSSR* isomers of the square-planar nickel(II) complex of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradecane (HTIM) were prepared from the nickel(II) complex of 2,3,9,10-tetramethyl-1,4,8,11−tetraazacyclotetradeca-1,3,8,10-tetraene (TIM) by NaBH$_4$ reduction in aqueous solution and were purified by chromatography and recrystallization.[12] The crystal structures of *RRSS*-Ni^{II}HTIM(ClO$_4$)$_2$ and *RSSR*-Ni^{II}-HTIM(ClO$_4$)$_2$ have been determined.[12] Although the NiHTIM^{2+} complexes used for this study are pure isomers, both NiDMC^{2+} and Ni(cyclam)$^{2+}$ have various configuration isomers.[13] Each NH hydrogen atom can be above or below the plane of the four nitrogen atoms depending on the isomer.

Cyclic voltammograms of *RRSS*- and *RSSR*-NiHTIM(ClO$_4$)$_2$, NiDMC(ClO$_4$)$_2$, and Ni(cyclam)(ClO$_4$)$_2$ were recorded in 0.1 M aqueous KCl solution under Ar or CO$_2$ using a hanging mercury electrode (1.6 mg drop) vs Ag/AgCl. In the presence of Ar, reversible Ni$^{II/I}$ waves are observed at −1.52 V (*RRSS*-NiHTIM^{2+}), −1.48 V (*RSSR*-NiHTIM^{2+}), −1.51 V (NiDMC^{2+}), and −1.52 V (Ni(cyclam)$^{2+}$) at 100 mV s^{-1} scan rate with 10 s quiet time at −1.0 V. In the presence of CO$_2$, the Ni$^{II/I}$ reduction waves become irreversible and the cathodic currents increase 50−110 times ([Ni] = 0.5 mM). Our results for Ni(cyclam)$^{2+}$ are similar to previous results.[2−4,6,7] Cyclic voltammograms were recorded in aqueous solutions containing various concentrations of nickel complexes under CO$_2$. As can be seen from Figure 1, the observed peak current densities of the *RRSS*-NiHTIM^{2+} and NiDMC^{2+} complexes are higher than that of Ni(cyclam)$^{2+}$ when the catalyst concentration is less than 0.1 mM. The plateau is due to the limiting concentration of CO$_2$. In fact, when the 30, 10, and 3% CO$_2$ (balance: N$_2$ or Ar) are bubbled instead of pure CO$_2$, the plateau starts at lower NiL concentration and the plateau currents are linear with the CO$_2$ concentration. The peak currents for *RRSS*-NiHTIM^{2+} and NiDMC^{2+} also occurred at a more positive potential than for Ni(cyclam)$^{2+}$: 104 μA at −1.360 V for *RRSS*-NiHTIM^{2+}; 87 μA at −1.355 V for NiDMC^{2+}; 53 μA at −1.381 V for Ni(cyclam)$^{2+}$ ([Ni] = 20 μM). For a 7 μM solution of *RRSS*-NiHTIM^{2+}, when the quiet time at −1.0 V was changed from 10 to 120 s, the catalytic current increased from 77 to 92 μA and the peak potential shifted 50 mV more positive.

The above observations strongly support the following conclusions: (1) *RRSS*-NiHTIM^{2+} and NiDMC^{2+} are better catalysts for CO$_2$ reduction than Ni(cyclam)$^{2+}$ in terms of their larger catalytic currents and more positive potentials; (2) At high NiL

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(2) (a) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315−1316. (b) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.

(3) (a) Shionoya, M.; Kimura, E.; Iitaka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 9237. (b) Kimura, E.; Haruta, M.; Koike, T. Shionoya, M.; Takenouchi, K.; Iitaka, Y. *Inorg. Chem.* **1993**, *32*, 2779.

(4) (a) Fujihira, M.; Hirata, Y.; Suga, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *292*, 199−215. (b) Fujihira, M.; Nakamura, Y.; Hirata, Y.; Akiba, U.; Suga, *Denki Kagaku* **1991**, *59*, 532.

(5) Abbà, F; De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Lanfredi, A. M. M.; Pallavicini, P.; Poggi, A.; Ugozzoli, F. *Inorg. Chem.* **1994**, *33*, 1366.

(6) Balazs, G. B.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1992**, *322*, 325−345.

(7) Balazs, G. B.; Anson, F. C. *J. Electroanal. Chem. Interfacial Electrochem.* **1993**, *361*, 149−157.

(8) Smith, C. I.; Crayston, J. A.; Hay, R. W. *J. Chem. Soc., Dalton Trans.* **1993**, 3267−3269.

(9) (a) Craig, C. A.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1990**, *94*, 7957. (b) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2105.

(10) (a) Kimura, E.; Bu, X.; Shionoya, M.; Wada, S.; Maruyama, S. *Inorg. Chem.* **1992**, *31*, 4542. (b) Kimura, E.; Wada, S.; Shionoya, M.; Okazaki, Y. *Inorg. Chem.* **1994**, *33*, 770. (c) Fujita, E.; Milder, S. J.; Brunschwig, B. S. *Inorg. Chem.* **1992**, *31*, 2079.

(11) Matsuoka, S.; Yamamoto, K.; Ogata, T.; Kusaba, M.; Nakashima, N.; Fujita, E.; Yanagida, S. *J. Am. Chem. Soc.* **1993**, *115*, 601−609.

(12) Szalda, D. J.; Fujita, E.; Sanzenbacher, R.; Paulus, H.; Elias, H. *Inorg. Chem.*, in press.

(13) Connolly, P. J.; Billo, E. J. *Inorg. Chem.* **1987**, *26*, 3224−3226.

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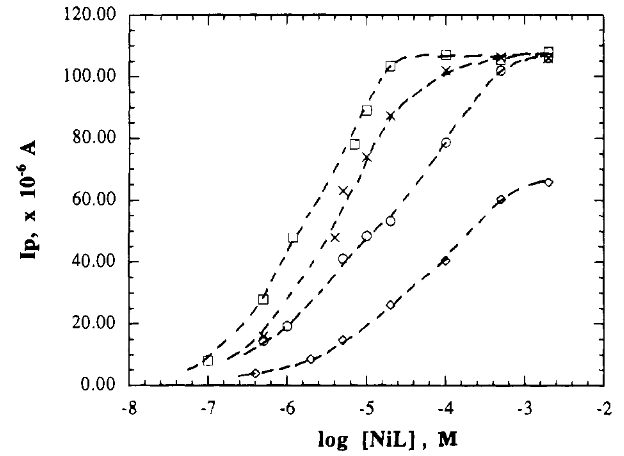

Figure 1. Cathodic peak current for CO_2 reduction on a mercury electrode vs the logarithm of the concentration of nickel complexes: 100 mV s^{-1} scan rate with 10 s quiet time at −1.0 V, CO_2-saturated 0.1 M KCl solutions. Key: (○) Ni(cyclam); (□) *RRSS*-NiHTIM; (◇) *RSSR*-NiHTIM; (×) NiDMC.

concentration, the current is controlled by the CO_2 concentration because of the fast catalytic reaction. (3) Adsorbed Ni(I) species are important for the catalytic reduction of CO_2. (4) The isomeric purity of *RRSS*-$NiHTIM^{2+}$ may contribute to the high catalytic activity through formation of a very stable Ni(I) species adsorbed on mercury. In fact, bulk electrolyses[14] with 5×10^{-6} M Ni(cyclam)$(ClO_4)_2$, *RRSS*-NiHTIM$(ClO_4)_2$, and NiDMC$(ClO_4)_2$ in 0.1 M KCl solutions confirmed that these two new complexes are excellent electrocatalysts for selective and efficient CO_2 reduction. CO production in a 4 h run: 2.1×10^{-4} mol for *RRSS*-$NiHTIM^{2+}$; 2.0×10^{-4} mol for $NiDMC^{2+}$; 1.5×10^{-4} mol for Ni(cyclam)$^{2+}$. Both the H_2 and formate produced are less than 1.5% of the CO for each nickel complex. It should be mentioned that the peak current density of *RSSR*-$NiHTIM^{2+}$, which is a geometric isomer of *RRSS*-$NiHTIM^{2+}$, is lower than that of Ni(cyclam)$^{2+}$. The axial methyl group of the *RSSR*-$NiHTIM^{2+}$ may sterically hinder CO_2 coordination to this complex and effective adsorption onto Hg.

In order to understand the CO_2 affinity of these complexes, we also recorded cyclic voltammograms of *RRSS*- and *RSSR*-NiHTIM$(ClO_4)_2$, NiDMC$(ClO_4)_2$, and Ni(cyclam)$(ClO_4)_2$ in CH_3CN containing 0.1 M $(C_3H_7)_4NClO_4$ and 1 mM nickel complex under Ar or CO_2 using a carbon fiber microelectrode (11 ± 2 μm) as the working electrode and a Ag/AgCl reference electrode with scan rates ranging from 0.1 to 51 V s^{-1}. In the presence of Ar, reversible $Ni^{II/I}$ waves were observed at −1.37 V (*RRSS*-$NiHTIM^{2+}$), −1.28 V (*RSSR*-$NiHTIM^{2+}$), −1.39 V ($NiDMC^{2+}$), and −1.38 V (Ni(cyclam)$^{2+}$) at 100 mV s^{-1} scan rate. (At scan rates of > 100 mV s^{-1}, the $E_{1/2}$ remain ± 2 mV.) On the other hand, in the presence of CO_2, the reduction became an irreversible wave, although the cathodic current density did not increase. The catalytic reaction was not observed in CH_3CN, because of lack of proton source. Such behavior has been reported for Ni(cyclam)$^{2+}$ in DMSO.[15] At a scan rate of 25.6–51.2 V s^{-1}, a reversible wave was observed under CO_2 and the wave was shifted about 20 mV more positive than the corresponding wave under Ar for all the nickel complexes except *RSSR*-$NiHTIM^{2+}$. The binding constants for CO_2 for these complexes in CH_3CN are estimated to be 4 ± 2 M^{-1} using equations previously reported.[16] Unfortunately the shifts of the potentials observed were quite small and no difference among these nickel complexes could be seen. In the case of *RSSR*-$NiHTIM^{2+}$, no positive shift of the potential was observed. Kelly et al.[17] recently measured a CO_2 dissociation constant of 0.062 M from Ni(cyclam)-CO_2^{+} in aqueous solution using pulse-radiolysis and flash-photolysis techniques. The binding constant of 16 M^{-1} in H_2O is larger than that (4 M^{-1}) in CH_3CN. Such a trend in CO_2 binding constants for cobalt macrocyclic complexes has been previously observed (4.5×10^8 M^{-1} in H_2O, 6×10^4 M^{-1} in CH_3CN for *rac*-CoL^+ where L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).[16,18,19] The square-planar Ni(I) complexes of HTIM, DMC, and cyclam, prepared in CH_3CN by Na–Hg reduction, have a d–d band at ~565 nm (ϵ = 36–80 $M^{-1}cm^{-1}$) and charge-transfer bands at ~384 (ϵ = 4000–4400) and ~270 (ϵ = 3400–4300).[12,20] The addition of ~700 Torr of CO_2 to the solution causes an ~80% decrease in intensity of all these absorptions and the appearance of a new peak at ~470 nm in the case of *RRSS*-$Ni^{I}HTIM^{+}$ (on the basis of the spectrum taken within 5 min after the addition). The difference spectrum for the *RRSS*-NiHTIM intermediate has absorption bands at 465 nm (ϵ ≥ 360) and 298 nm (ϵ ≥ 940), quite similar to the spectrum of the CO adduct.[12] The intermediate is unstable at room temperature, and these peak intensities decrease within 10 min together with the bands associated with the Ni(I) species. The final spectrum is featureless. Additional techniques including transient absorption and IR spectroscopies are needed to further characterize the nature of the intermediates in the electrocatalytic system.

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(14) The bulk electrolysis was carried out using a gastight three-necked flask equipped with two sidearms. The working electrode is 11 mL of mercury. The Pt counter electrode and the SCE were separated from the main compartment by two sets of medium glass frits. The pH of the solution was monitored during the electrolysis. The cell volume was 145 mL, 50 and 80 mL of which were occupied by the solution and gas, respectively. CO and H_2 were analyzed on a gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5A column at 60 °C using He and Ar as carrier gases, respectively. Formate was analyzed on an ion chromatograph equipped with an ion exclusion column.

(15) Schmidt, M. H.; Miskelly, G. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 3420–3426.

(16) Fujita, E.; Creutz, C.; Sutin, N.; Szalda, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 343 eq 6 and references therein.

(17) Kelly, C. A.; Mulazzani, Q. G.; Venturi, M.; Blinn, E. L.; Rodgers, M. A. To be submitted for publication.

(18) (a) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361. (b) Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 1153.

(19) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 4870.

(20) (a) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611. (b) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109. (c) Jubran, N.; Ginzburg, G.; Cohen, H.; Koresh, Y.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 251–258. (d) Jubran, N.; Meyerstein, D.; Cohen, H. *J. Chem. Soc., Dalton Trans.* **1986**, 2509.