

Homogeneous CO<sub>2</sub> Reduction by Ni(cyclam) at a Glassy Carbon Electrode

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## Supporting Information

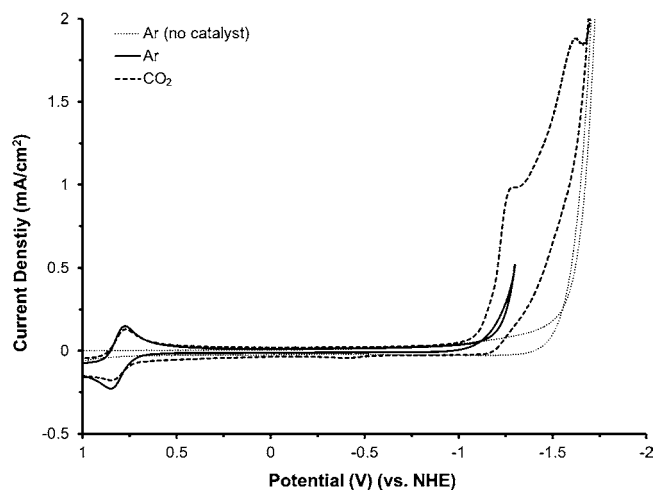
**ABSTRACT:** The homogeneous CO<sub>2</sub> reduction activity of several nickel cyclam complexes was examined by cyclic voltammetry and controlled potential electrolysis. CO production with high efficiency from unsubstituted Ni(cyclam) was verified, while the activity was found to be attenuated with methyl substitution of the amines on the cyclam ring. Reactivity with CO<sub>2</sub> was also probed using density functional theory (DFT) calculations. The relative CO<sub>2</sub> binding energies to the Ni<sup>I</sup> state obtained from DFT were found to match well with the experimental results and shed light on the possible importance of the isomeric form of Ni(cyclam) in determining the catalytic activity.

The photochemical and electrochemical conversion of CO<sub>2</sub> to higher-energy products has been a focus of research as a path to renewable fuels.<sup>1,2</sup> CO<sub>2</sub> can be electrochemically reduced directly on metal electrodes; however, either the potentials necessary are exceedingly negative or the metal surface is rapidly poisoned by the catalytic products or intermediates.<sup>3,4</sup> Transition-metal molecular catalysts have proven to efficiently and selectively reduce CO<sub>2</sub> with moderate overpotentials and high Faradaic efficiency, with the main reduction products being CO or formate.<sup>5</sup> Of these catalysts, Ni(cyclam)<sup>2+</sup> (cyclam = 1,4,8,11-tetraazacyclotetradecane) stands out because of its remarkable selectivity for CO production at a relatively low overpotential in aqueous solutions.<sup>6,7</sup> The active catalytic species is thought to be the one-electron-reduced species Ni(cyclam)<sup>+</sup>, with nickel in the 1+ formal oxidation state. Ni(cyclam)<sup>2+</sup> and analogues have been extensively studied by electrochemical methods. The majority of these reports have utilized a mercury electrode, most likely because of the large negative potential window possible with mercury in aqueous solutions. It has been shown that Ni(cyclam)<sup>+</sup> is adsorbed on the mercury electrode, thereby changing its reactivity with CO<sub>2</sub>.<sup>7,8</sup> The catalytic activity was shown to plateau with increasing catalyst concentration because of saturation of the adsorbed species on the electrode. This observation led to the conclusion that only the adsorbed species was catalytically active and the homogeneous activity of Ni(cyclam)<sup>+</sup> was thought to be only of minor importance.<sup>7</sup> Also, the homogeneous photocatalytic activity of Ni(cyclam)<sup>2+</sup> suffered from very low quantum yields, further supporting the claim for a lack of homogeneous activity.<sup>9</sup>

In contrast to the wealth of information on the catalytic activity of Ni(cyclam)<sup>2+</sup> on mercury, there are relatively few

reports studying CO<sub>2</sub> reduction on other electrode surfaces, and these studies did not report Faradaic efficiencies.<sup>10–13</sup> The inherent catalytic selectivity and apparent lack of homogeneous activity of Ni(cyclam)<sup>2+</sup> in previous reports were challenged by the findings of Kelly et al. The group used pulse radiolysis to generate e<sub>aq</sub><sup>-</sup>, CO<sub>2</sub><sup>•-</sup>, and H<sup>•-</sup>, which were used as the one-electron reducing agent for Ni(cyclam)<sup>2+</sup>.<sup>14,15</sup> CO<sub>2</sub> was found to interact with Ni(cyclam)<sup>+</sup> in a homogeneous fashion, and the apparent selectivity toward the reduction of CO<sub>2</sub> or protons was attributed to the concentrations of the two substrates at pH 4 (36 and 0.1 mM, respectively). In an effort to examine the homogeneous CO<sub>2</sub> reduction activity of Ni(cyclam)<sup>2+</sup>, an inert electrode material, glassy carbon (GC), was used for the present study.

Figure 1 shows the cyclic voltammogram (CV) of Ni(cyclam)<sup>2+</sup> in an aqueous KCl solution. Under argon, the



**Figure 1.** CV of 1 mM Ni(cyclam)<sup>2+</sup> in 0.1 M KCl(aq) (GC electrode; 100 mV/s scan rate).

Ni<sup>III/II</sup> couple is reversible (0.81 V vs NHE);<sup>16,17</sup> however, the Ni<sup>II/I</sup> couple is not observed because it is beyond the solvent window of GC in aqueous solution and the current response is dominated by proton reduction. When the solution is saturated with CO<sub>2</sub>, two irreversible reduction peaks emerge at -1.28 and -1.62 V. Because the Ni<sup>II/I</sup> couple is not visible under argon, a direct comparison between the Ni<sup>II/I</sup> reduction peak

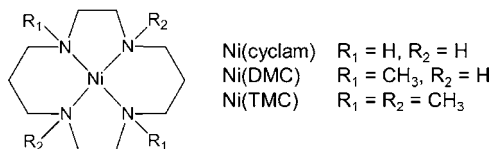
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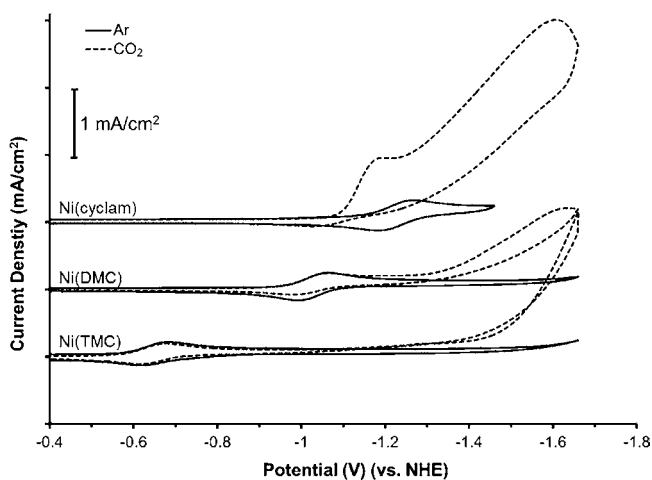
under argon and under CO<sub>2</sub> cannot be made. However, if the Ni<sup>III/II</sup> peak height is used to estimate the one-electron-reduction Faradaic current expected, the current is 5 times higher under CO<sub>2</sub> than under argon. To verify the reduction products, controlled potential electrolysis (CPE) was carried out under the same conditions as those in cyclic voltammetry and the head space of the electrochemical cell was sampled by gas chromatography. When held at -1.30 V for 1 h, the Faradaic efficiency was calculated to be 90% for CO (no H<sub>2</sub> was detected) with an average current density of 2.8 mA/cm<sup>2</sup>. When held at -1.60 V for 1 h, the Faradaic efficiency was calculated to be 90% for CO and 20%<sup>18</sup> for H<sub>2</sub> with an average current density of 4.1 mA/cm<sup>2</sup>. These results verify the previous finding that Ni(cyclam)<sup>2+</sup> will catalyze the homogeneous reduction of CO<sub>2</sub>.<sup>15</sup> Using the electrochemical method of Savéant,<sup>5</sup> a turnover frequency (TOF) of 90 s<sup>-1</sup> was found. The turnover number (TON) for long-term CPE was 4, establishing a catalytic reaction (see the Supporting Information for details).

Methylated analogues of Ni(cyclam)<sup>2+</sup>, Ni(DMC)<sup>2+</sup>, and Ni(TMC)<sup>2+</sup> (see Chart 1 for the structures) were also studied

**Chart 1. Structures of Ni(cyclam), Ni(DMC) (DMC = 1,8-Dimethyl-1,4,8,11-tetraazacyclotetradecane), and Ni(TMC) (TMC = 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)**



to understand the structural role of the cyclam ligand on the catalytic activity. The CV behaviors of the various cyclam complexes were investigated in a 1:4 water/acetonitrile mixed-solvent system in order to extend the solvent window so that the Ni<sup>II/I</sup> couple could be observed (Figure 2). The CV under argon shows that the Ni<sup>II/I</sup> couple is shifted positively with increased methylation of the amine groups on the cyclam ring, with the Ni<sup>II/I</sup> couples appearing at -1.23, -1.03, and -0.65 V for Ni(cyclam)<sup>2+</sup>, Ni(DMC)<sup>2+</sup>, and Ni(TMC)<sup>2+</sup>, respectively.



**Figure 2.** CVs of 1 mM Ni(cyclam)<sup>2+</sup>, Ni(DMC)<sup>2+</sup>, and Ni(TMC)<sup>2+</sup> in a 0.08 M tetrabutylammonium hexafluorophosphate electrolyte (1:4 water/acetonitrile; GC electrode; 100 mV/s scan rate).

This trend has been explained elsewhere.<sup>19,20</sup> When CO<sub>2</sub> is introduced, it appears that only Ni(cyclam)<sup>2+</sup> shows significant reactivity, as is apparent by the catalytic current increase at a potential corresponding to the reduction to Ni<sup>I</sup> as well as an anodic shift in the reduction peak. There is also the appearance of a second reduction peak at -1.61 V similar to the CV in Figure 1. Ni(DMC)<sup>2+</sup> appears to show no reactivity toward CO<sub>2</sub> near its Ni<sup>II/I</sup> couple potential because the current and peak potentials are similar to those under an argon atmosphere. However, Ni(DMC)<sup>2+</sup> does display a second reduction peak under CO<sub>2</sub> at a potential similar to that of Ni(cyclam)<sup>2+</sup>. This second reduction peak is not seen with Ni(TMC)<sup>2+</sup>. These results concerning the difference in the catalytic activity may be explained by the difference in the reduction potentials of the complexes. It is possible that the reduced Ni(DMC)<sup>+</sup> and Ni(TMC)<sup>+</sup> complexes do not have sufficient reductive power to react with CO<sub>2</sub>. Other structural arguments relating to the importance of the amine protons in hydrogen-bond stabilization of the CO<sub>2</sub> adduct may also be important.<sup>21</sup>

The catalytic activity in this mixed-solvent system was confirmed with CPE at two potentials corresponding to the two catalytic reduction peaks of Ni(cyclam)<sup>2+</sup> as well as for the second reduction peak of Ni(DMC)<sup>2+</sup>. High Faradaic efficiencies are maintained for Ni(cyclam)<sup>2+</sup> in the mixed-solvent system at the first reduction peak (see Table 1). CPE at

**Table 1. Results of CPE in 1:4 Water/Acetonitrile<sup>a</sup>**

complex	potential (V)	Faradaic efficiency (%)		current density (mA/cm <sup>2</sup> )
		CO	H <sub>2</sub>	
Ni(cyclam)	-1.21	90	0	1.8
Ni(cyclam)	-1.61	60	10	4.5
Ni(DMC)	-1.63	20	80	3.8

<sup>a</sup>Conditions: Held at the potential for 1 h, GC working electrode, 1 mM complex, 0.8 M tetrabutylammonium hexafluorophosphate electrolyte.

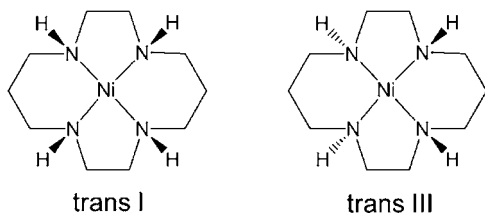
the potential of the second reduction peak shows a decline in the Faradaic efficiency for CO and some H<sub>2</sub> production. Ni(DMC)<sup>2+</sup> shows mainly H<sub>2</sub> production; however, CO is also observed with 20% Faradaic efficiency. The CPE results confirm that there is still CO<sub>2</sub> reduction activity at the potential where the second reduction peak is seen by cyclic voltammetry. The second reduction peak has been seen in other reports,<sup>10</sup> and its identity is still under investigation. Control experiments show that the second reduction peak only appears when the catalyst, CO<sub>2</sub>, and water are present. We cannot definitively assign its origin at this time, but it is most likely due to a different mechanism possible only at more negative potentials than the first nickel reduction.

These results prompted the use of density functional theory (DFT) calculations to study the effect of methylation of the cyclam ring on CO<sub>2</sub> binding. The functional BP86 was used because it was shown to be appropriate for first-row transition metals.<sup>22</sup> The CO<sub>2</sub> binding energy ( $\Delta E_{CO_2}$ ) was modeled by finding the difference in the total bonding energy (TBE) for geometry-optimized structures of LNi<sup>I</sup>, LNi<sup>I</sup>-CO<sub>2</sub>, and free CO<sub>2</sub> (L = cyclam, DMC, or TMC) and applying the relationship

$$\Delta E_{CO_2} = TBE_{LNi^I-CO_2} - (TBE_{LNi^I} + TBE_{CO_2})$$

The results, summarized in Table S1 in the Supporting Information, match well with the experiment. Ni(cyclam)<sup>+</sup> had a significantly more favorable  $\Delta E_{\text{CO}_2}$  than Ni(DMC)<sup>+</sup>. The geometry optimization of Ni(TMC)(CO<sub>2</sub>)<sup>+</sup> did not converge, with the DFT favoring the breaking of the Ni–CO<sub>2</sub> bond to reach a minimum energy structure. Of greater interest is the difference in  $\Delta E_{\text{CO}_2}$  between the isomers of Ni(cyclam)<sup>+</sup>. Ni(cyclam)<sup>2+</sup> is known to have five possible isomers; however, only trans I and trans III (see Chart 2) are present in solution

Chart 2. Structures of the Trans I and Trans III Isomers



in appreciable amounts (15% and 85%, respectively).<sup>23</sup> Therefore, these two were chosen for DFT calculations.

$\Delta E_{\text{CO}_2}$  was much more favorable for the trans I species by 21 kJ/mol. This large difference between the isomeric forms of Ni(cyclam) may be attributed to the CO<sub>2</sub> oxygens each interacting with two amine protons in the trans I isomer rather than just one in the trans III. Similar results were reported in a recent review.<sup>24</sup> This result may have some bearing on the literature. It has been reported that the adsorption on mercury initiates an isomerization process, which renders Ni(cyclam) more reactive toward CO<sub>2</sub> reduction.<sup>8</sup> However, mercury has also been suggested to lend electronic effects aiding in CO<sub>2</sub> binding to Ni.<sup>25,26</sup> More work is needed to verify these DFT results, as solvation and counteranions were ignored in these gas-phase calculations. Nonetheless, these computational and electrochemical results are encouraging. Ni(cyclam)<sup>2+</sup> will electrocatalytically reduce CO<sub>2</sub> to CO in a homogeneous fashion. Mechanistic studies of the electrocatalytic homogeneous process are needed to compare with the studies previously done on mercury.

Ni(cyclam)<sup>2+</sup> is one of the few CO<sub>2</sub> reduction catalysts that operates efficiently and selectively in water. However, it remains that the activity on mercury is much greater than that on other electrode materials, as is observed by CV peak current densities.<sup>10,13</sup> CV peak current densities on GC (Figure 1, peak at –1.28 V) and mercury<sup>7</sup> are 1.0 and 11 mA/cm<sup>2</sup>, respectively [1 mM Ni(cyclam); 100 mV/s]. The exact identity of the active species adsorbed on mercury remains to be identified but might explain this difference. If this species can be obtained without the use of such a toxic material as mercury, it would be a step closer to a more environmentally benign catalyst system.

## ■ ASSOCIATED CONTENT

### Supporting Information

Synthetic, TOF and TON determination, and DFT details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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- (16) The Ni<sup>II/III</sup> return oxidation peak is only reversible if the cathodic scan does not go more negative than –1.3 V. It is obscured by a large oxidative current if scanned more negative than –1.3 V (see Figure S1 in the Supporting Information).
- (17) All potentials have been converted to a normal hydrogen electrode (NHE).
- (18) The absolute error in the Faradaic efficiency measurements was not determined; however, we estimate the error to be approximately 10%.
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