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The Thermodynamics and Kinetics of CO_2 and H^+ Binding to Ni(cyclam)$^+$ in Aqueous Solution

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Abstract: Pulse radiolysis and laser flash photolysis have been used to generate and characterize Ni(cyclam)$^+$, where cyclam is 1,4,8,11-tetraazacyclotetradecane, in aqueous solution. Reduction of Ni(cyclam)$^{2+}$ was carried out at ambient temperature (22 ± 2 °C) by solvated electrons, e_{aq}^-, hydrogen atoms, $H^\bullet$, and carbon dioxide radical anions, $CO_2^{\bullet-}$. Reduction by e_{aq}^- occurs with a rate constant of $(4.1 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} ($I \le 2 \times 10^{-4}$ M). Reduction by $CO_2^{\bullet-}$ and $H^\bullet$ proceeds via an inner-sphere mechanism to yield [Ni(cyclam)(CO_2)]$^+$ and [Ni(cyclam)(H)]$^{2+}$, with rate constants of $(6.7 \pm 0.2) \times 10^9$ and $(5 \pm 2) \times 10^9$ M^{-1} s^{-1}, respectively. Decomposition of the adducts, to yield Ni(cyclam)$^+$ and CO_2 or H^+, proceeds with rate constants of $(2.0 \pm 0.2) \times 10^6$ and $(5.3 \pm 0.7) \times 10^5$ s^{-1}, respectively. Carbon dioxide and proton dissociation constants for [Ni(cyclam)(CO_2)]$^+$ and [Ni(cyclam)(H)]$^{2+}$ were found to be $(6.2 \pm 0.3) \times 10^{-2}$ and $(1.6 \pm 0.4) \times 10^{-2}$ M, respectively. The rate constants for the addition of CO_2 and H^+ to Ni(cyclam)$^+$ were calculated to be $(3.2 \pm 0.4) \times 10^7$ and $(3 \pm 1) \times 10^7$ M^{-1} s^{-1}, respectively. The selective reduction of CO_2 by Ni(cyclam)$^+$ in the presence of protons at pH 4 is rationalized.

Introduction

The conversion of abundant and inexpensive carbon dioxide into fuels and organic chemicals has been a subject of long standing interest.[2] The complex Ni(cyclam)$^{2+}$, where cyclam is 1,4,8,11-tetraazacyclotetradecane, was first shown by Sauvage and co-workers to be an efficient and selective catalyst for the electrochemical reduction of carbon dioxide in acidic (pH 4) aqueous solution.[3] This system has subsequently been studied in some detail by two other groups, with special emphasis on the strong adsorption of Ni(cyclam)$^+$ to the surface of mercury electrodes.[4,5] The use of Ni(cyclam)$^{2+}$ as a *homogeneous* mediator for CO_2 reduction has also been demonstrated using a photochemical system, although the quantum efficiency for the formation of CO was quite small.[6] An insightful theoretical account of the binding and reduction of CO_2 by a Ni(cyclam)$^+$ model has been reported by Sakaki.[7] Several reports have appeared on the electrocatalytic activity of nickel(II) complexes in which the cyclam structure has been modified[8] or covalently linked to another Ni(cyclam)$^{2+}$ subunit, Ni_2(biscyclam)$^{4+}$.[9] Most of these modifications resulted in lower catalytic activity than Ni(cyclam)$^{2+}$, in terms of the magnitude of their catalytic currents.[3,8] Interestingly, catalytic activity similar to Ni(cyclam)$^{2+}$ can be achieved, provided the macrocycle maintains a 5,6,5,6 chelate ring sequence.[8] Recently, Fujita et al. reported catalytic activity somewhat greater than that of Ni(cyclam)$^{2+}$ from two nickel(II) complexes in which the cyclam ligand was modified by methylation of the carbon backbone.[8b]

The importance of the metal complex may be understood by considering that the Ni(cyclam)$^{2+/+}$ couple, $E^0 = -1.33$ V,[3b] is insufficient to reduce CO_2 by outer-sphere electron transfer ($E^0(CO_2/CO_2^{\bullet-}) = -1.90$ V),[10] eq 1.

$$\mathrm{Ni(cyclam)^+ + CO_2 \rightarrow Ni(cyclam)^{2+} + CO_2^{\bullet-}} \qquad (1)$$

Without a viable outer-sphere pathway, the reduction of CO_2 must proceed by an inner-sphere mechanism. Consequently, a crucial reaction step for the reduction of CO_2 to CO by Ni(cyclam)$^+$ would seem to be the addition of the Lewis acid, CO_2, to an axial coordination site of the nucleophilic metal complex, eq 2.

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$$\mathrm{Ni(cyclam)^+ + CO_2 \rightleftharpoons [Ni(cyclam)(CO_2)]^+} \qquad (2)$$

The formation of the adduct, $[Ni(cyclam)(CO_2)]^+$, would allow the sequential two electron reduction and protonation to proceed without the formation of the high energy $CO_2^{\bullet -}$ intermediate. Recently, Balazs and Anson have placed a lower limit on the rate constant for the addition of CO_2 to $Ni(cyclam)^+$ adsorbed on the surface of a mercury electrode to be $>6 \times 10^5$ M^{-1} s^{-1} using a mercury-coated gold rotating disk electrode.[5b] Fujita et al. have reported the CO_2 binding constant to $Ni(cyclam)^+$ at a carbon fiber microelectrode to be 4 ± 2 M^{-1} in acetonitrile.[8b]

In acidic aqueous solution, the proton might be expected to be a more effective Lewis acid than the "inert" CO_2 molecule. In fact, protic media is often avoided in studies of potential CO_2 reducing agents since proton reduction often competes with CO_2 reduction. One of the most intriguing questions regarding the reactivity of $Ni(cyclam)^+$ is the selectivity it displays, under certain conditions, toward CO_2 reduction in acidic solution.[3,6b] Considering that protons are involved in the two electron reduction of CO_2, a better understanding of the reactivity of $Ni(cyclam)^+$ toward protons is clearly of importance.

Despite considerable interest in the reduction of carbon dioxide by $Ni(cyclam)^+$ in water, thermodynamic and kinetic information regarding the binding of CO_2 and H^+ to this complex is lacking. The very low quantum efficiency for the reduction of CO_2 by $Ni(cyclam)^{2+}$ in the photochemical system[6b] and the importance of $Ni(cyclam)^+$ adsorbed on the electrode surface for the electrochemical CO_2 reduction,[5b] raises questions concerning the differences in catalytic activity between homogeneous and electrode adsorbed $Ni(cyclam)^+$. In the current work, we report the kinetics of the reduction of $Ni(cyclam)^{2+}$ by $CO_2^{\bullet -}$ and $H^\bullet$ and the binding of CO_2 and H^+ by $Ni(cyclam)^+$. This data provides insight into intermediates which are undoubtedly involved in the CO_2 reduction mechanism and allows for a detailed comparison with the related complex CoL^+, where L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, which has previously been studied in detail by Creutz et al.[11]

Experimental Section

Materials. $Ni(ClO_4)_2$, $HClO_4$, $NaClO_4$, $NaCO_2H$, and $Na_2C_2O_4$ were reagent grade and were used as received. Water was obtained from Nanopure II or Millipore (Milli-Q) water purification systems. The compounds $Ni(cyclam)(ClO_4)_2$ and $Ni(cyclam)Cl_2$ were prepared by the published procedures.[12] The compounds were purified by repeated recrystallization from water and acetone. Solutions were purged with Ar or saturated with N_2O or CO_2. In some cases, solutions were saturated with Ar/CO_2 mixtures of known composition, allowing the concentration of CO_2 to be varied. Unless otherwise indicated, measurements were taken at ambient temperature, 22 ± 2 °C. The solubility of CO_2 in water at 1 atm partial pressure as a function of temperature was taken from the literature with the value at 22 ± 2 °C taken to be $(3.6 \pm 0.2) \times 10^{-2}$ M.[13] Although the total concentration of CO_2 (i.e., $CO_2 + H_2CO_3 + HCO_3^- + CO_3^{2-}$) increases with increasing pH, the concentration of CO_2 itself is independent of pH.[14] The concentration of CO_3^{2-} is negligible and H_2CO_3 represents <0.3% of the total CO_2 concentration under the conditions of the current work.[14] The concentration of HCO_3^- is ca. 10% of the total CO_2 concentration at pH 5.2 and ca. 1% at pH 4.3.[14] However, as $Ni(cyclam)^+$ is unreactive toward HCO_3^- and the dehydration of HCO_3^- is slow, τ = 0.18 and 1.8 s at pH 4 and 5 respectively, its concentration is neglected.[3b,14] Solution pH was adjusted using $HClO_4$ or NaOH. Ionic strength adjustments were made by the addition of $NaClO_4$.

Laser Flash Photolysis. Pulsed laser excitation was carried out at the Center for Photochemical Sciences, Bowling Green State University, at ambient temperature using the frequency quadrupled output from a Quantel 660B Q-switched Nd:YAG laser (266 nm). The ca. 7 ns pulse energies were on the order of 30 mJ/pulse. Typically, 3−10 shots were averaged with a 15−45 s delay between shots. The computer controlled, time resolved UV−vis spectrophotometer has been previously described.[15] Samples were contained in 10 mm × 10 mm quartz cuvettes. Ground state spectra of the solutions were obtained with a Perkin Elmer Lambda Array 3840.

Variable temperature experiments were carried out using a home built water jacketed cuvette holder. A water/ethylene glycol solution was circulated through the water jacket by a Lauda RC 6 constant temperature bath. Temperature was monitored by a thermocouple positioned in a well adjacent to the cuvette. The cell temperature was allowed to equilibrate for 15−30 min and is considered to be accurate to within 0.2 °C.

Pulse Radiolysis. Pulse radiolysis was performed using the 12 MeV electron linear accelerator of the FRAE-CNR Institute in Bologna. The irradiations were carried out at ambient temperature on samples contained in Spectrosil cells of 2 cm optical pathlength. Solutions were protected from the analyzing light by means of a shutter and appropriate cutoff filters. The bandwidth used throughout the pulse radiolysis experiments was 5 nm. The radiation dose per pulse was monitored by means of a charge collector placed behind the irradiation cell and calibrated with a N_2O-saturated solution containing 0.1 M HCO_2^- and ~0.5 mM methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dication; MV^{2+}) using $G\epsilon = 9.32 \times 10^4$ at 602 nm.[16] G(X) represents the number of molecules of species X formed per 100 eV of energy absorbed by the system.

Results

The Pulse Generation of Reducing Environments. The radiolysis of aqueous solutions generates e_{aq}^-, $H^\bullet$, and $^\bullet OH$, and molecular products (H_2 and H_2O_2) according to eq 3, where the numbers in parentheses represent the G values for the individual species.[17]

$$\mathrm{H_2O \rightsquigarrow e_{aq}^-(2.6),\ H^\bullet\ (0.6),\ {}^\bullet OH\ (2.7),\ H_2\ (0.45),\ H_2O_2\ (0.7)} \qquad (3)$$

In the current work, reducing conditions were created in Ar-purged solutions by scavenging the hydroxyl radical with either *tert*-butyl alcohol, eq 4,[17]

$$\mathrm{{}^\bullet OH + (CH_3)_3COH \rightarrow {}^\bullet CH_2C(CH_3)_2OH\ (95.7\%) + (CH_3)_3CO^\bullet\ (4.3) + H_2O} \qquad (4)$$

with $k_4 = 6.0 \times 10^8$ M^{-1} s^{-1}, or with formate, eqs 5 and 6,

$$\mathrm{{}^\bullet OH + HCO_2^- \rightarrow CO_2^{\bullet -} + H_2O} \qquad (5)$$

$$\mathrm{{}^\bullet OH + HCO_2H \rightarrow {}^\bullet CO_2H + H_2O} \qquad (6)$$

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where $k_5 = 3.2 \times 10^9\ M^{-1}\ s^{-1}$ and $k_6 = 1.3 \times 10^8\ M^{-1}\ s^{-1}$.[17,18] Under a carbon dioxide atmosphere, the hydrated electron may be scavenged, eq 7,

$$e_{aq}^- + CO_2 \rightarrow CO_2^{\bullet -} \tag{7}$$

with $k_7 = 7.7 \times 10^9\ M^{-1}\ s^{-1}$.[17] Under acidic conditions, the hydrated electron will be scavenged by protons to yield the hydrogen atom, eq 8,

$$e_{aq}^- + H^+ \rightarrow H^\bullet \tag{8}$$

with $k_8 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}$.[17]

The species e_{aq}^-, $CO_2^{\bullet -}$, and $H^\bullet$ are strong reducing agents, $E^0 = -2.87$, -1.90, and -2.30 V, respectively,[10,19] whereas the radical $^\bullet CH_2C(CH_3)_2OH$ is a weak reducing agent, $E^0 = -0.1$ V.[20] The species e_{aq}^-, $H^\bullet$, $CO_2^{\bullet -}$, and $^\bullet CH_2C(CH_3)_2OH$ are all known to decay by bimolecular processes for which values of $2k = 5.5 \times 10^9\ M^{-1}\ s^{-1}$,[17] $1.55 \times 10^{10}\ M^{-1}\ s^{-1}$,[17] $1.3 \times 10^9\ M^{-1}\ s^{-1}$ ($I = 0.1$ and pH 7)[21] and $1.4 \times 10^9\ M^{-1}\ s^{-1}$,[22] respectively, have been reported.

The Reduction of Ni(cyclam)$^{2+}$ by e_{aq}^-. Pulse radiolysis (dose per pulse = 24 Gy) of Ar-purged solutions containing 0.1 mM Ni(cyclam)$^{2+}$ and 0.5 M *tert*-butyl alcohol at pH 7 results in the formation of e_{aq}^- as the primary reducing agent, eqs 3 and 4. The *tert*-butyl alcohol radical formed in eq 4 is thermodynamically incapable of reducing Ni(cyclam)$^{2+}$, vide supra. Under these conditions reaction 9 is expected, as originally reported by Jubran et al.[23]

$$Ni(cyclam)^{2+} + e_{aq}^- \rightarrow Ni(cyclam)^+ \tag{9}$$

Consistent with expectation, the rate constant observed for the decay of e_{aq}^- is linearly related to the concentration of Ni(cyclam)$^{2+}$, yielding the bimolecular rate constant for reaction 9, $k_9 = (4.1 \pm 0.2) \times 10^{10}\ M^{-1}\ s^{-1}$ ($I \leq 2 \times 10^{-4}$ M). This value is consistent with the previously reported value of $3.8 \times 10^{10}\ M^{-1}\ s^{-1}$.[23] Reaction 9 was also studied in the presence of 0.1 M formate where $k_9 = (2.6 \pm 0.1) \times 10^{10}\ M^{-1}\ s^{-1}$ was obtained. Following the decay of e_{aq}^-, a spectrum is observed exhibiting a maximum at 380 nm, Figure 1, attributed to Ni(cyclam)$^+$.

The lifetime of Ni(cyclam)$^+$ is limited, with a value dependent upon the nature of the solution. The decay kinetics of Ni(cyclam)$^+$, monitored at 380 nm, were complex in all systems investigated. Additionally, the lifetime is a sensitive function of both proton and CO_2 concentration. However, as a result of the complexity of these systems and their relevance to the more involved issue of the two electron reduction mechanism of protons and CO_2, an account of the decay kinetics will be deferred to a separate publication.[24] For the purposes of the present study, the decay kinetics are sufficiently resolved in time from the events studied that they are either neglected or the initial decay was approximated to an exponential.

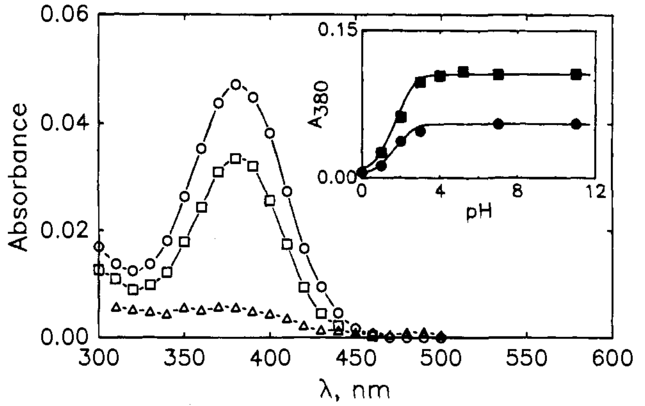

Figure 1. Spectra obtained from pulse radiolysis of Ar-purged solutions containing 0.1 mM Ni(cyclam)$^{2+}$ and 0.5 M *tert*-butyl alcohol at (open circles) pH 7, (open squares) pH 3 and (open triangles) pH 1. Optical path = 2.0 cm, dose per pulse = 24 Gy. Inset: values of A_{380} as a function of pH for Ar-purged solutions containing 0.5 mM Ni(cyclam)$^{2+}$ and (solid circles) 0.5 M *tert*-butyl alcohol or (solid squares) 0.1 M formate.

The pH Dependent Yield of Ni(cyclam)$^+$. Decreasing the pH below about 4, in the presence of *tert*-butyl alcohol, results in a decrease in the intensity of the 380 nm absorbance, Figure 1, and yields an inflection point at pH 1.8, Figure 1 inset. This pH dependence suggests an equilibrium of the type given by eq 10

$$Ni(cyclam)(H)^{2+} \rightleftharpoons Ni(cyclam)^+ + H^+ \tag{10}$$

where the pK_a of Ni(cyclam)(H)$^{2+}$ is 1.8 ± 0.1.

In order to check whether the apparent pK_a estimated above was due to an artifact of the conversion of the hydrated electron into hydrogen atoms, eq 8, the pH dependence on the yield of Ni(cyclam)$^+$, i.e., the absorbance maximum at 380 nm, was studied using pulse radiolysis of Ar-purged solutions of Ni(cyclam)$^{2+}$ and 0.1 M formate. Under these conditions both e_{aq}^- and $CO_2^{\bullet -}$ are produced by eqs 3, 5, and 6, approximately doubling the reducing equivalents per pulse. Consistent with expectation, the intensity of the absorbance monitored at 380 nm was about twice that observed in the presence of *tert*-butyl alcohol, Figure 1 inset, over the pH range investigated. Again an inflection point was observed at pH 1.8. The observation of the same pH dependent absorbance behavior with two different systems supports the nature of eq 10.

The Reduction of Ni(cyclam)$^{2+}$ by H$^\bullet$. At low pH, e_{aq}^- is effectively converted to $H^\bullet$ according to eq 8. At pH 2, in the presence of 0.5 M *tert*-butyl alcohol (Ar saturated), under conditions such that more than 92% of e_{aq}^- are scavenged by H^+ to give $H^\bullet$ (based on competition for e_{aq}^- by H^+ and Ni(cyclam)$^{2+}$), two important changes occur in the absorbance growth at 380 nm. First, the rate of growth is much slower than that observed at pH 7. Secondly, the growth does not obey first-order kinetics. The latter point was determined by two observations. First, the fit of the growth to first-order kinetics is less than perfect due to the presence of an induction period or time-lag during the initial portion of the growth. Second, approximating the growth to first-order kinetics results in a nonlinear dependence on Ni(cyclam)$^{2+}$ concentration which approaches a limiting value. However, as noted above, the absorbance spectrum does not change shape with decreasing pH, suggesting that Ni(cyclam)$^+$ is still formed at this pH. These observations suggest that $H^\bullet$ is reducing Ni(cyclam)$^{2+}$ to Ni(cyclam)$^+$, but the formation of the latter species is preceded, and consequently delayed, by the formation of an intermediate. The implication is that the reaction proceeds by an inner-sphere

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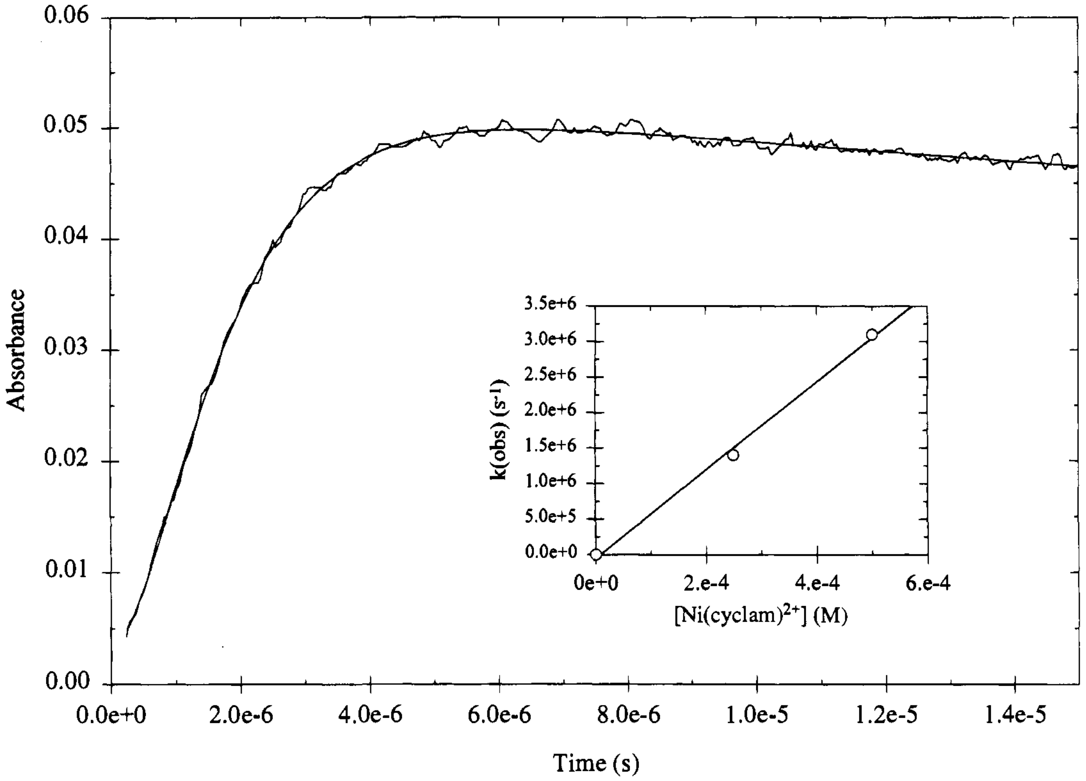

Figure 2. Growth of the absorbance monitored at 380 nm following pulse radiolysis of an Ar-purged solution containing 0.5 mM $Ni(cyclam)^{2+}$ and 0.5 M *tert*-butyl alcohol at pH 2. The smooth line is a fit of the data. Inset: plot of the observed first order rate constant for the growth as a function of $Ni(cyclam)^{2+}$ concentration. The point located at the origin is not experimental data but was used in the fit.

mechanism, i.e., eq 11 followed by eq 10.

$$Ni(cyclam)^{2+} + H^{\bullet} \rightarrow Ni(cyclam)(H)^{2+} \qquad (11)$$

In the presence of excess $Ni(cyclam)^{2+}$, both reaction 11 and the approach to equilibrium 10 will follow first-order kinetics. Such a reaction may be treated as an $A \rightarrow B \rightarrow C$ reaction scheme in which the $A \rightarrow B$ rate constant, eq 11, will be linearly dependent upon the concentration of the excess reagent, $Ni(cyclam)^{2+}$, and the $B \rightarrow C$ rate constant, eq 10, will be independent of the concentration of $Ni(cyclam)^{2+}$, at a given pH. The $B \rightarrow C$ rate constant is the sum of the forward and reverse rate constants of equilibrium 10, k_{10f} and $k_{10r}[H^+]$. The decay of $Ni(cyclam)^+$ was significant on the time scale investigated, and therefore it was necessary to approximate the initial decay to first-order kinetics. The absorbance at 380 nm was fit by nonlinear least squares, to a sequence of three consecutive first-order reactions,[25] Figure 2. The rate of reaction 11 became too large at $Ni(cyclam)^{2+}$ concentrations greater than ca. 0.5 mM to obtain reliable fits of the data. That is, when the rate of reaction 11 is sufficiently rapid, the formation of $Ni(cyclam)^+$ becomes rate-limited by the approach to equilibrium 10. Under such conditions iterative fitting of the data failed to converge. The lower concentration data was fit yielding (a) a $Ni(cyclam)^{2+}$ concentration independent rate constant, $k_{10} = k_{10f} + k_{10r}[H^+] = (8.5 \pm 0.9) \times 10^5\ s^{-1}$ and (b) a $Ni(cyclam)^{2+}$ concentration dependent rate constant from which $k_{11} = (5 \pm 2) \times 10^9\ M^{-1}\ s^{-1}$ was obtained, Figure 2 inset. With knowledge of $K_{10} = (1.6 \pm 0.4) \times 10^{-2}$ M, then $k_{10f} = (5.3 \pm 0.7) \times 10^5\ s^{-1}$ and $k_{10r} = (3 \pm 1) \times 10^7\ M^{-1}\ s^{-1}$. The binding constant for eq 11 may be evaluated from the reduction potentials of $Ni(cyclam)^{2+}$ and H^+ and from K_{10} to yield, $K_{11} = 1.7 \times 10^{18}\ M^{-1}$.

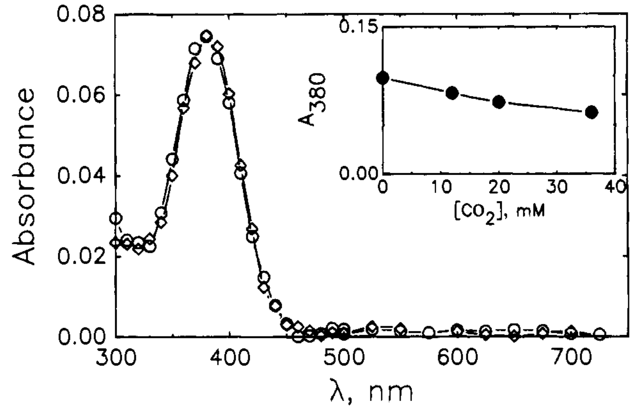

Figure 3. Spectra obtained from pulse radiolysis of solutions containing 0.5 mM $Ni(cyclam)^{2+}$ and (open diamonds) 0.5 M *tert*-butyl alcohol, Ar-purged at pH 7 or (open circles) 0.1 M formate, CO_2 saturated at pH 5.2. The spectra are normalized at 380 nm. Inset: dependence of A_{380} on the concentration of CO_2 in solutions containing 0.5 mM $Ni(cyclam)^{2+}$ and 0.1 M formate at pH 5.2. Optical path = 2.0 cm, dose per pulse = 24 Gy.

The CO_2 Dependent Yield of $Ni(cyclam)^+$. Attempts to scavenge e_{aq}^- by dissolved CO_2, to study the reduction of $Ni(cyclam)^{2+}$ in the absence of e_{aq}^-, resulted in a diminished yield of $Ni(cyclam)^+$ monitored at 380 nm, Figure 3 inset. The shape of the spectrum, however, was independent of CO_2 concentration ($[CO_2]$ = 0−36 mM) over the spectral range 300−700 nm, Figure 3. Behavior of this type suggests the presence of an equilibrium of the type given by eq 12.

$$Ni(cyclam)(CO_2)^+ \rightleftharpoons Ni(cyclam)^+ + CO_2 \qquad (12)$$

The CO_2 adduct apparently does not absorb significantly in the

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(24) Kelly, C. A.; Mulazzani, Q. G.; Blinn, E. L.; Rodgers, M. A. J., manuscript in preparation.

(25) Connors, K. A. *Chemical Kinetics;* VCH: Weinheim, 1988; pp 73−75.

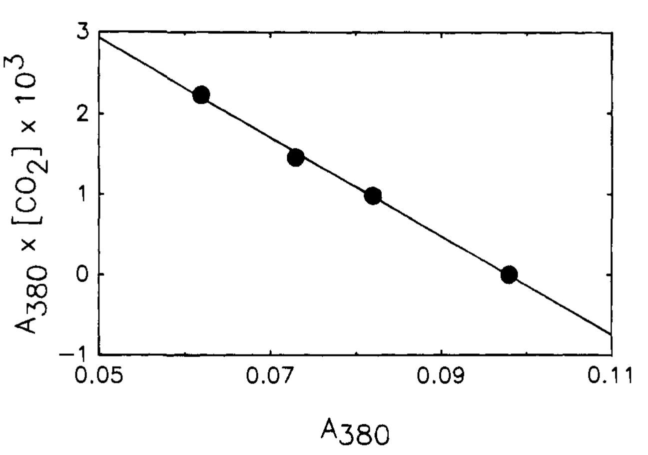

Figure 4. Plot of $A_{380} \times [CO_2]$ vs A_{380}, the data is the same as Figure 3, inset.

300−700 nm region. In the presence of only one absorbing species, the following relation holds,

$$A[CO_2] = KA_0 - KA \qquad (13)$$

where A is the maximum absorbance of Ni(cyclam)$^+$ at a given concentration of CO_2, A_0 is the maximum absorbance of Ni(cyclam)$^+$ in the absence of CO_2, and K is the equilibrium constant for eq 12. A plot of $A \times [CO_2]$ vs A, Figure 4, where the absorbance was monitored at 380 nm, yielded $K_{12} = 0.062 \pm 0.003$ M.

The Reduction of Ni(cyclam)$^{2+}$ by Laser Flash Photolysis. Pulsed laser excitation of aqueous solutions of oxalate ($pK_1 = 1.271$, $pK_2 = 4.272$)[26] at 266 nm, leads to the formation of e_{aq}^- and oxidized oxalate by a multiphoton mechanism, eq 14.[27] Oxidized oxalate is believed to undergo decarboxylation with a rate constant $>10^8$ s^{-1} to give $CO_2^{\bullet-}$ and CO_2, eq 15.[27]

$$(HC_2O_4^-/C_2O_4^{2-}) + 2h\nu \rightarrow e_{aq}^- + (HC_2O_4^{\bullet}/C_2O_4^{\bullet-}) \qquad (14)$$

$$(HC_2O_4^{\bullet}/C_2O_4^{\bullet-}) \rightarrow CO_2^{\bullet-} + CO_2\,(+\,H^+) \qquad (15)$$

Oxalate is an effective scavenger of the hydrated electron, eqs 16 and 17,

$$e_{aq}^- + C_2O_4^{2-} \rightarrow C_2O_4^{\bullet 3-} \qquad (16)$$

$$e_{aq}^- + HC_2O_4^- \rightarrow HC_2O_4^{\bullet 2-} \qquad (17)$$

which proceed with rate constants, $k_{16} = 3.2 \times 10^9$ M^{-1} s^{-1} and $k_{17} = 1.3 \times 10^8$ M^{-1} s^{-1}.[17]

Pulsed laser excitation at 266 nm of an Ar-purged solution containing 10 mM oxalate at pH 4.3 resulted in the prompt formation of the absorption band of the hydrated electron[17] according to eq 14. Under these conditions, e_{aq}^- decays by first-order kinetics as a result of eqs 16 and 17, with an observed rate constant of 1.0×10^7 s^{-1} ($I = 0.1$ M). In the presence of Ni(cyclam)$^{2+}$, an absorbance growth is observed at 380 nm composed of two kinetic components, Figure 5. The spectrum observed following the slow growth possesses the same shape as that observed following the slow growth and is similar to that observed in the pulse radiolysis experiments except for an enhanced absorbance at wavelengths less than ca. 350 nm. Presumably the additional absorbance is due to the tailing absorbance of reduced oxalate, eqs 16 and 17. The initial growth is consistent with the formation of Ni(cyclam)$^+$ by e_{aq}^-, eq 9. The rate constant for the decay of e_{aq}^- as a function of Ni(cyclam)$^{2+}$ concentration yielded the bimolecular rate constant, $k_9 = (3.1 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} ($I = 0.025$ M) . The slow portion of the growth is presumably due to reduction of Ni(cyclam)$^{2+}$ by $CO_2^{\bullet-}$, where $CO_2^{\bullet-}$ is formed by eq 15.

The Reduction of Ni(cyclam)$^{2+}$ by $CO_2^{\bullet-}$. The slow component of the growth at 380 nm following flash photolysis at pH 4.3 does not follow first-order kinetics, displaying an initial time-lag or sigmoidal growth kinetics before approaching exponential kinetics at longer times. The sigmoidal rise of the 380 nm absorbance was also observed following pulse radiolysis in the presence of formate in Ar-purged or CO_2-saturated solution at pH > 4. This kinetic form, taken with the presence of equilibrium 12, supports the idea that the mechanism for the reduction of Ni(cyclam)$^{2+}$ by $CO_2^{\bullet-}$ proceeds via an inner-sphere mechanism, i.e., eq 18 followed by equilibrium 12.

$$\mathrm{Ni(cyclam)}^{2+} + CO_2^{\bullet-} \rightarrow \mathrm{Ni(cyclam)(CO_2)}^+ \qquad (18)$$

The kinetics for the reduction of Ni(cyclam)$^{2+}$ by $CO_2^{\bullet-}$ is therefore analogous to that observed for the H$^\bullet$ reduction, with the exception that the decay of Ni(cyclam)$^+$ was negligible on the time scale of the growth. Fitting the growth as a series of two reactions ([Ni(cyclam)$^{2+}$] = 0.1−0.8 mM, Figure 5) yielded a rate constant that was linearly dependent on the concentration of Ni(cyclam)$^{2+}$, Figure 5 inset, leading to a bimolecular rate constant $k_{18} = (6.7 \pm 0.2) \times 10^9$ M^{-1} s^{-1} and a first-order rate constant $k_{12} = (2.0 \pm 0.2) \times 10^6$ s^{-1}, which is the sum of k_{12f} and $k_{12r}[CO_2]$. Knowledge of the equilibrium constant, K_{12}, allows the evaluation of $k_{12f} = (2.0 \pm 0.2) \times 10^6$ s^{-1} and $k_{12r} = (3.2 \pm 0.4) \times 10^7$ M^{-1} s^{-1}. The binding constant for eq 18 may be evaluated from the one electron reduction potentials of Ni(cyclam)$^{2+}$ and CO_2 and from K_{12}, yielding $K_{18} = 7.1 \times 10^{10}$ M^{-1}.

A variable temperature investigation (2−50 °C) without added CO_2, i.e., under conditions such that reaction 12r is negligible, yielded $\Delta H^{\ddagger} = 6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6$ cal K^{-1} mol^{-1} for the addition of $CO_2^{\bullet-}$ to Ni(cyclam)$^{2+}$, eq 18, Figure 6A, and $\Delta H^{\ddagger} = 11$ kcal mol^{-1} and $\Delta S^{\ddagger} = 8$ cal K^{-1} mol^{-1} for the dissociation of CO_2 from Ni(cyclam)$^+$, eq 12f, Figure 6B. From these values, and from the equilibrium constants K_{12} and K_{18}, the activation free energies for equilibria 12 and 18 can be estimated: $\Delta G_{12f}^{\ddagger} = 8.6$, $\Delta G_{12r}^{\ddagger} = 6.9$, $\Delta G_{18f}^{\ddagger} = 4.2$, and $\Delta G_{18r}^{\ddagger} = 19$ kcal mol^{-1}.

Pulse radiolysis was used to measure the extinction coefficient of Ni(cyclam)$^+$ at 380 nm, pH 7, in the presence of *tert*-butyl alcohol. Assuming G(Ni(cyclam)$^+$) = $G(e_{aq}^-)$ + G(H$^\bullet$) = 3.2, then $\epsilon_{380} = 3650 \pm 150$ M^{-1} cm^{-1}.[28]

Discussion

Radical Addition to Ni(cyclam)$^{2+}$. The current work provides direct evidence for an inner-sphere mechanism for the reduction of Ni(cyclam)$^{2+}$ by both H$^\bullet$ and $CO_2^{\bullet-}$. The strongly reducing radicals H$^\bullet$ and $CO_2^{\bullet-}$ were observed to add to Ni(cyclam)$^{2+}$ with rate constants approaching the diffusion limit. Reduction of Ni(cyclam)$^{2+}$ by $CO_2^{\bullet-}$ was previously reported

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[26] (26) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985, pp 5−52.

[27] Prasad, D. R.; Hoffman, M. Z.; Mulazzani, Q. G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1986**, *108*, 5135−5142.

[28] The extinction coefficient of Ni(cyclam)$^+$ reported herein of $\epsilon_{380} = 3650$ M^{-1} cm^{-1} is somewhat in disagreement with the value of $\epsilon_{375} = 4500$ M^{-1} cm^{-1} reported previously by Jubran et al., ref 23. The difference in ϵ_{max} may arise from different assumptions concerning the value of G(Ni(cyclam)$^+$) where the role of H$^\bullet$ as a precursor to Ni(cyclam)$^+$ may not have been recognized.

[29] Tait, A. M.; Hoffman, M. Z.; Hayon, E. *Inorg. Chem.* **1976**, *15*, 934−939.

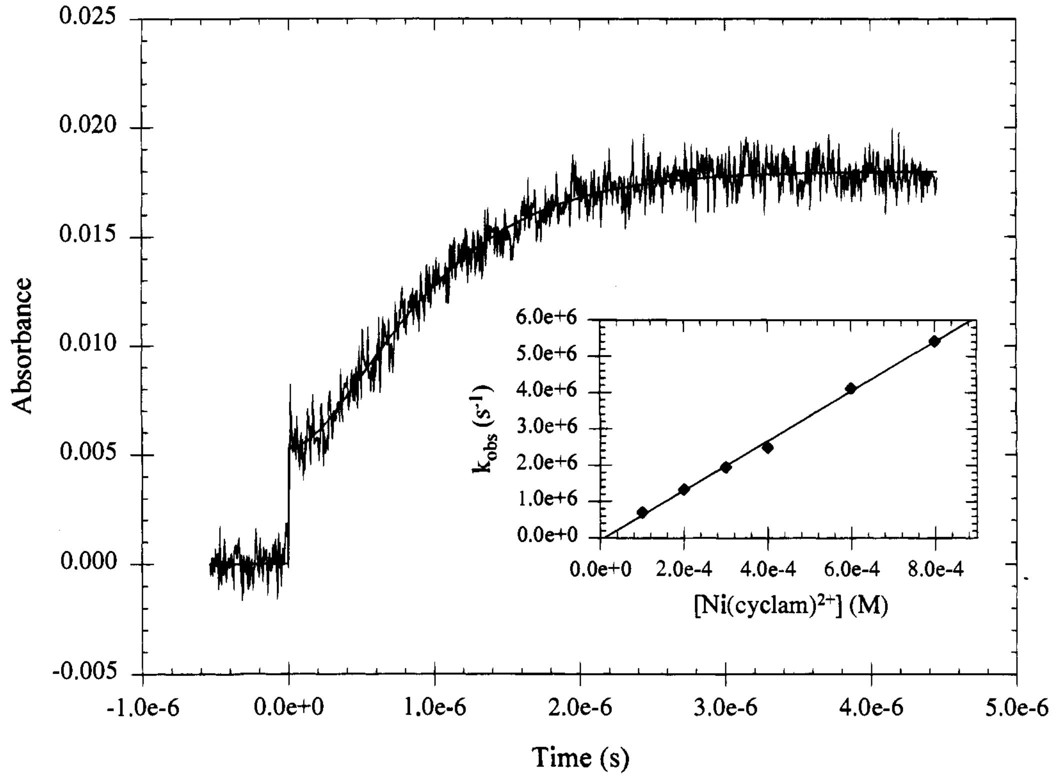

Figure 5. Growth of the absorbance monitored at 380 nm following flash photolysis of an Ar-purged solution containing 0.3 mM Ni(cyclam)$^{2+}$ and 10 mM oxalate at pH 4.3. The smooth line is a fit of the data. Inset: plot of the observed first order rate constant for the growth as a function of Ni(cyclam)$^{2+}$ concentration.

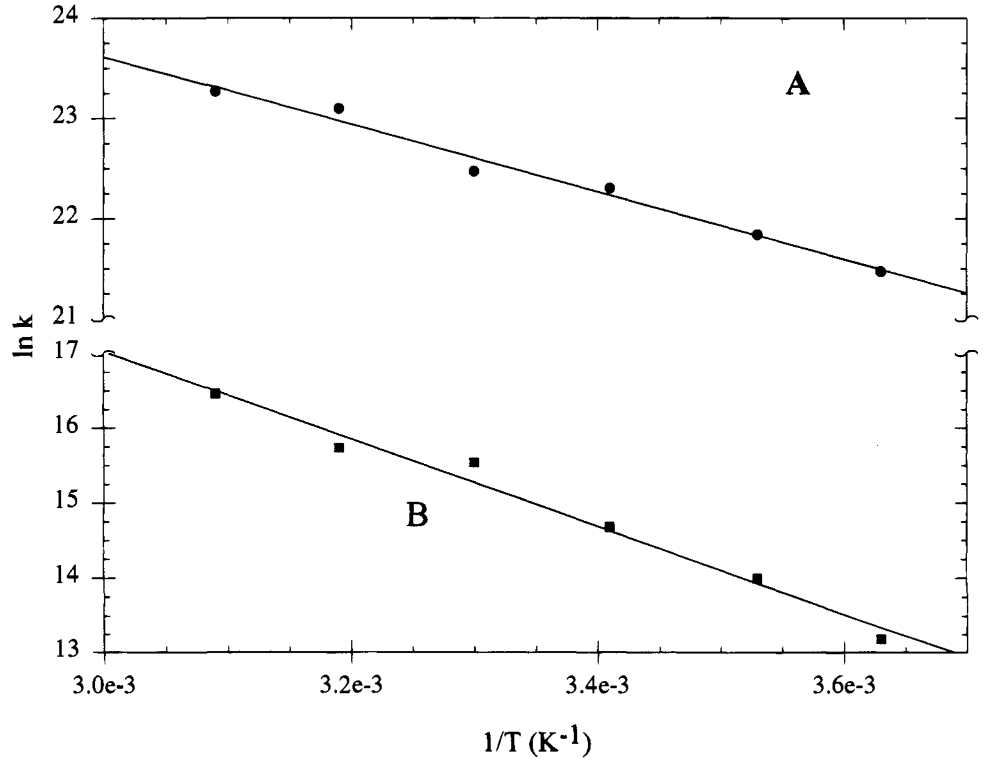

Figure 6. Temperature dependence for (A) $CO_2^{\bullet -}$ addition to Ni(cyclam)$^{2+}$ and (B) dissociation of CO_2 from [Ni(cyclam)(CO_2)]$^+$. The data was obtained by laser flash photolysis of Ar-purged solutions containing 0.1—0.5 mM Ni(cyclam)$^{2+}$ and 10 mM oxalate at pH 4.3.

as a simple bimolecular electron transfer with a rate constant, $k = 5.2 \times 10^9$ M^{-1} s^{-1}.[23] However, it was suggested that the reduction may proceed by an inner-sphere mechanism due to the observation that the rate constant for the reduction of Ni(DMC)$^{2+}$, where DMC is the ligand *C-meso*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane, by $CO_2^{\bullet -}$ ($k = 4 \times 10^6$ M^{-1} s^{-1}), was much lower than the rate constant for the reduction of Ni(cyclam)$^{2+}$, even though the driving force for reduction is greater in the former case by 60 mV.[23] Therefore, shielding of the Ni^{2+} by the axial methyl groups of the DMC ligand was proposed to hinder axial ligation of the approaching $CO_2^{\bullet -}$, slowing the reduction.[23]

To the best of our knowledge, no report has appeared on the $H^\bullet$ reduction of Ni(cyclam)$^{2+}$. Two closely related nickel(II) macrocycles were studied by Tait et al. using pulse radiolysis methods.[29] These authors did not invoke an inner-sphere mechanism for either $H^\bullet$ or $CO_2^{\bullet-}$ reduction in their systems, although they did speculate on the formation of nickel hydrides during the reaction of the nickel(I) complexes with proton donors.[29] Muonium atoms, a light hydrogen atom isotope, have been observed to react with Ni(cyclam)$^{2+}$ in a reaction attributed to reduction of the nickel(II) complex to Ni(cyclam)$^+$ with a rate constant $\leq 5 \times 10^8$ M^{-1} s^{-1}.[30]

While the kinetics for the formation of Ni(cyclam)$^+$ from $CO_2^{\bullet-}$ and $H^\bullet$ demonstrate the inner-sphere nature of the reaction, Marcus theory provides insight into the advantage of the inner-sphere pathway.[31] The self-exchange rate constants for eqs 19 and 20

$$CO_2 + CO_2^{\bullet-} \rightarrow CO_2^{\bullet-} + CO_2 \qquad (19)$$

$$\text{Ni(cyclam)}^{2+} + \text{Ni(cyclam)}^{+} \rightarrow \text{Ni(cyclam)}^{+} + \text{Ni(cyclam)}^{2+} \qquad (20)$$

have been previously reported with $k_{19} = 1.4 \times 10^{-3}$ M^{-1} s^{-1} and $k_{20} = 1 \times 10^{-3}$ M^{-1} s^{-1}, respectively.[23,32] The equilibrium constant for the hypothetical outer-sphere reduction, eq 21,

$$\text{Ni(cyclam)}^{2+} + CO_2^{\bullet-} \rightleftharpoons \text{Ni(cyclam)}^{+} + CO_2 \qquad (21)$$

may be evaluated from the known reduction potentials of the reactants yielding $K_{21} = 4.4 \times 10^9$. From these values,[33] the Marcus cross relation yields $k_{21f} = 30$ M^{-1} s^{-1}. The observed rate of formation of Ni(cyclam)$^+$, limited by the [Ni(cyclam)(CO_2)]$^+$ dissociation rate constant of 2×10^6 s^{-1}, is likely taking advantage of the greater electronic coupling offered by the inner-sphere channel to accelerate the reaction rate.

While the hydrogen atom is known to be an extremely poor outer-sphere reducing agent,[34] the $H^+/H^\bullet$ self exchange rate constant has not been previously reported. Based on the rate constant for the reduction of Fe^{3+} by $H^\bullet$, for which $k < 2 \times 10^6$ M^{-1} s^{-1},[35] the Fe^{3+}/Fe^{2+} self-exchange rate constant, 4.0 M^{-1} s^{-1},[36] and reduction potential, $E^0(Fe^{3+}/Fe^{2+}) = 0.771$ V,[37] then the self-exchange rate constant, $k(H^+/H^\bullet)$, can be estimated as $< 3 \times 10^{-26}$ M^{-1} s^{-1}.[38] This self-exchange rate constant, the smallest yet reported,[39] corresponds to a reorganization energy, λ, of >200 kcal mol^{-1}.[40] The solvation energy difference between the very strongly solvated proton, $\Delta G_{solv}(H^+)_{aq} = -260$ kcal mol^{-1},[41] and the hydrophobic hydrogen atom, $\Delta G_{solv}(H^\bullet)_{aq} = 4.4$ kcal mol^{-1},[19] clearly indicates the importance of solvation/desolvation during the electron transfer. The outer-sphere electron transfer rate constant for $H^\bullet$ reduction of Ni(cyclam)$^{2+}$, eq 22,

$$\text{Ni(cyclam)}^{2+} + H^\bullet \rightarrow \text{Ni(cyclam)}^{+} + H^+ \qquad (22)$$

can therefore be placed at $<2 \times 10^{-7}$ M^{-1} s^{-1}. An outer-sphere mechanism for the formation of Ni(cyclam)$^+$ by eq 22 is consequently ruled out.

Table 1. Comparison of $H^\bullet$ and $CO_2^{-\bullet}$ Addition Rate Constants in Aqueous Solution

reaction	k, M^{-1} s^{-1}	ref
Ni(cyclam)$^{2+}$ + $H^\bullet \rightarrow$ Ni(cyclam)(H)$^{2+}$	5×10^9	*a*
N-meso-CoL^{2+} + $H^\bullet \rightarrow$ *N-meso*-CoL(H)$^{2+}$	1.3×10^9	*b*
N-rac-CoL^{2+} + $H^\bullet \rightarrow$ *sec-N-rac*-CoL(H)$^{2+}$	1.1×10^9	*b*
Ni(cyclam)$^{2+}$ + $CO_2^{-\bullet} \rightarrow$ Ni(cyclam)(CO_2)$^+$	6.7×10^9	*a*
N-meso-CoL^{2+} + $CO_2^{-\bullet} \rightarrow$ *N-meso*-CoL(CO_2)$^+$	3×10^9	*b*
N-rac-CoL^{2+} + $CO_2^{-\bullet} \rightarrow$ *sec-N-rac*-CoL(CO_2)$^+$	8.5×10^8	*b*

[a] Values obtained in this work. [b] Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361.

Table 1 compares the rate constants for the addition of $H^\bullet$ and $CO_2^{\bullet-}$ to Ni(cyclam)$^{2+}$ and closely related CoL^{2+} complexes. The reduction potentials of the nickel and cobalt complexes are nearly identical, $E^0(CoL^{2+}/CoL^+) \approx -1.32$ V,[11] allowing comparison to be made based on equal driving force. However, the hexamethylated ligand, L, is expected to impose greater steric repulsion toward approaching reactants than cyclam. The factor of two to eight difference in radical addition rate constants between Ni(cyclam)$^{2+}$ and CoL^{2+} is therefore attributed to ligand steric differences.

Equilibria Involving the Uptake of H^+ and CO_2 by Ni(cyclam)$^+$. The maximum yield of the 380 nm absorbing Ni(cyclam)$^+$ clearly decreased with increasing concentration of either H^+ or CO_2. The decrease is not due to increasing concentrations of $H^\bullet$ or $CO_2^{\bullet-}$, since both species are effective at reducing Ni(cyclam)$^{2+}$ to Ni(cyclam)$^+$. The decrease in yield can only be attributed to the binding of H^+ or CO_2 by Ni(cyclam)$^+$ to give nonabsorbing species at the wavelength of interest, i.e., equilibria 10 and 12. It should be noted that the proton equilibrium is not due to deprotonation of a cyclam secondary amine proton. Such an equilibrium is known to occur for the oxidized complex Ni(cyclam)$^{3+}$, which has been reported to possess a pK_a of 7.1.[42] It is expected that, as the oxidation state of the central metal ion is decreased, the protonic nature of the coordinated amine hydrogen will be diminished. Consequently, deprotonation of the coordinated amine is expected to occur at higher pH for the lower oxidation state nickel complex, inconsistent with the present results.

It is of interest that neither [Ni(cyclam)(H)]$^{2+}$ nor [Ni(cyclam)(CO_2)]$^+$ possess significant absorbance in the 300–700 nm range.[43] The oxidized complex, Ni(cyclam)$^{3+}$, written neglecting additional ligands, is known to absorb strongly in the 300–400 nm wavelength range.[23] The lack of absorbance by the "H" or "CO_2" adducts provide some evidence that the +3 oxidation state of nickel is not reached in these complexes. In contrast, the spectrum of the Ni(cyclam)$^{2+}$ methyl radical adduct, [(cyclam)Ni-CH_3]$^{2+}$, provides convincing evidence for

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(31) Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.

(32) Venturi, M.; Mulazzani, Q. G.; D'Angelantonio, M.; Ciano, M.; Hoffman, M. Z. *Radiat. Phys. Chem.* **1991**, *37*, 449–456.

(33) The cross reaction rate constant was calculated iteratively from $k_{22} = k_{12}2/(k_{11}K_{12}f_{12})$ where $\ln f_{12} = (1/4)(\ln K_{12}2/\ln (k_{11}k_{22}/Z^2)$ assuming a collision frequency, Z, of 10^{11} s^{-1}. Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322.

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(35) Baxendale, J. H.; Dixon, R. S.; Stott, D. A. *Trans. Faraday Soc.* **1968**, *64*, 2398–2401.

(36) Silverman, J.; Dodson, R. W. *J. Phys. Chem.* **1952**, *56*, 846–852.

(37) Latimer, W. M. *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, 2nd ed.; Prentice-Hall: New York, 1952.

(38) Schwarz, H. A. Brookhaven National Laboratory, personal communication, 1994.

(39) Hung, M.-L.; McKee, M. L.; Stanbury, D. M. *Inorg. Chem.* **1994**, *33*, 5108–5112.

(40) The $H^+/H^\bullet$ self-exchange rate constant should be regarded only as a rough estimate due to the rather large magnitude of the driving force for the cross reaction, $\Delta G = -70$ kcal mol^{-1}. It should be noted that despite the large reaction driving force, $-\lambda < \Delta G < \lambda$ and therefore the cross reaction is in the normal free-energy region. Sutin, N. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1983; pp 441–498.

(41) Farrell, J. R.; McTigue, P. *J. Electroanal. Chem.* **1982**, *139*, 37–56.

(42) De Santis, G.; Fabbrizzi, L.; Poggi, A.; Taglietti, A. *Inorg. Chem.* **1994**, *33*, 134–139.

(43) Absorption bands with extinction coefficients less than ca. 200 M^{-1} cm^{-1}, i.e., $d-d$ transitions, would not have been observable.

Table 2. Comparison of pK_a's and H^+ Addition and Dissociation Rate Constants in Aqueous Solutuion

reaction	const	value	ref
$Ni(cyclam)(H)^{2+} \rightleftharpoons Ni(cyclam)^+ + H^+$	pK_a	1.8	a
	k_f	$5 \times 10^5\ s^{-1}$	a
	k_r	$3 \times 10^7\ M^{-1}\ s^{-1}$	a
N-meso-$CoL(H)^{2+} \rightleftharpoons$ *N-meso*-$CoL^+ + H^+$	pK_a	>13.9	b
	k_f	$<10^{-4}\ s^{-1}$	b
	k_r	$2.4 \times 10^9\ M^{-1}\ s^{-1}$	b
prim-N-rac-$CoL(H)^{2+} \rightleftharpoons$ *N-rac*-$CoL^+ + H^+$	pK_a	11.4	b
	k_f	$1.2 \times 10^{-2}\ s^{-1}$	b
	k_r	$3.1 \times 10^9\ M^{-1}\ s^{-1}$	c

[a] Values obtained in this work. [b] Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361. [c] Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 86.

Table 3. Comparison of Dissociation Constants and CO_2 Addition and Dissociation Rate Constants in Aqueous Solution

reaction	const	value	ref
$Ni(cyclam)(CO_2)^{2+} \rightleftharpoons Ni(cyclam)^+ + CO_2$	K	0.062 M	a
	k_f	$2.0 \times 10^6\ s^{-1}$	a
	k_r	$3.2 \times 10^7\ M^{-1}\ s^{-1}$	a
N-meso-$CoL(CO_2)^+ \rightleftharpoons$ *N-meso*-$CoL^+ + CO_2$	K	1.7×10^{-7} M	b
	k_f	$2.7\ s^{-1}$	b
	k_r	$1.6 \times 10^7\ M^{-1}\ s^{-1}$	b
prim-N-rac-$CoL(CO_2)^+ \rightleftharpoons$ *N-rac*-$CoL^+ + CO_2$	K	2.2×10^{-9} M	b
	k_f	$0.38\ s^{-1}$	b
	k_r	$1.7 \times 10^8\ M^{-1}\ s^{-1}$	b

[a] Values obtained in this work. [b] Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361.

Table 4. Comparison of Homolytic Bond Dissociation Free Energies in Solution

reaction	$\Delta G°_{aq}$, kcal mol^{-1}	ref
$Ni(cyclam)(H)^{2+} \rightleftharpoons Ni(cyclam)^{2+} + H^•$	25	a
$Ni(cyclam)(CO_2)^+ \rightleftharpoons Ni(cyclam)^{2+} + CO_2^{•-}$	15	a
$Ni(cyclam)(CH_3)^{2+} \rightleftharpoons Ni(cyclam)^{2+} + CH_3^•$	9.6, 9.5	b, c
prim-N-rac-$CoL(H)^{2+} \rightleftharpoons$ *N-rac*-$CoL^{2+} + H^•$	38	d
sec-N-rac-$CoL(H)^{2+} \rightleftharpoons$ *N-rac*-$CoL^{2+} + H^•$	38	d
prim-N-rac-$CoL(CO_2)^+ \rightleftharpoons$ *N-rac*-$CoL^{2+} + CO_2^{•-}$	25	d
N-meso-$CoL(H)^{2+} \rightleftharpoons$ *N-meso*-$CoL^{2+} + H^•$	>41	d
N-meso-$CoL(CO_2)^+ \rightleftharpoons$ *N-meso*-$CoL^{2+} + CO_2^{•-}$	23	d

[a] This work. [b] Sauer, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 4578. [c] Kelley, D. G.; Marchaj, A.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 7583. [d] Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361.

Table 5. Comparison of Heterolytic Bond Dissociation Free Energies in Solution

reaction	$\Delta G°_{aq}$, kcal mol^{-1}	ref
$Ni(cyclam)(H)^{2+} \rightleftharpoons Ni(cyclam)^+ + H^+$	2.4	a
$Ni(cyclam)(CO_2)^+ \rightleftharpoons Ni(cyclam)^+ + CO_2$	1.6	a
prim-N-rac-$CoL(H)^{2+} \rightleftharpoons$ *N-rac*-$CoL^+ + H^+$	15	b
sec-N-rac-$CoL(H)^{2+} \rightleftharpoons$ *N-rac*-$CoL^+ + H^+$	16	b
prim-N-rac-$CoL(CO_2)^+ \rightleftharpoons$ *N-rac*-$CoL^+ + CO_2$	12	b
N-meso-$CoL(H)^{2+} \rightleftharpoons$ *N-meso*-$CoL^+ + H^+$	>19	b
N-meso-$CoL(CO_2)^+ \rightleftharpoons$ *N-meso*-$CoL^+ + CO_2$	9	b

[a] This work. [b] Creutz, C.; Schwarz, H. A.; Wishart, J. F.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1991**, *113*, 3361.

the formation of "Ni^{3+}".[44] Interestingly, the spectra of the $CoL(H)^{2+}$ and $CoL(CO_2)^+$ complexes suggest the formation of the Co^{3+} oxidation state.[11]

Tables 2 and 3 compare the pK_a and CO_2 dissociation constants of the adducts $Ni(cyclam)(H)^{2+}$, $CoL(H)^{2+}$, $Ni(cyclam)(CO_2)^+$, and $CoL(CO_2)^+$, along with the associated rate constants. Adduct bond strengths can be evaluated by the homolytic and heterolytic bond dissociation free energies in aqueous solution, $\Delta G°_{hom}(Ni{-}X)_{aq}$ and $\Delta G°_{het}(Ni{-}X)_{aq}$, of the $[(cyclam)Ni{-}H]^{2+}$ and $[(cyclam)Ni{-}(CO_2)]^+$ bonds and compared with the closely related $CoL(X)^{n+}$ systems. The $Ni^{3+}{-}CH_3$ bond strength of the interesting $[(cyclam)Ni{-}CH_3]^{2+}$ complex is also included for comparison from data given by two groups.[44,45] Typically, values of $\Delta G°_{hom}$ are within a few kcal/mol of the gas phase BDE and have the benefit of avoiding errors associated with the estimation or neglect of solvation and entropy terms.[46] Based on the $Ni(cyclam)^+$ binding constants to H^+ and CO_2 and on the known one electron reduction potentials of $Ni(cyclam)^{2+}$, H^+ and CO_2, the aqueous phase homolytic and heterolytic bond dissociation free energies may be estimated, Tables 4 and 5. For comparison, values determined from the work of Creutz et al. for the closely related CoL^{n+} complexes are also listed in Tables 4 and 5.

From Tables 4 and 5, it is clear that CoL^+ forms much more stable complexes with CO_2 and H^+ than $Ni(cyclam)^+$. The formation of stronger bonds suggests greater charge transfer in the former case. This observation forces the realization that the one-electron reduction potentials are insufficient to characterize the reactivity of the reduced metal complexes. That is, differences in product bond strengths cannot be due simply to differences in the 2+/+ reduction potential of the complexes, which are quite similar. Rather, the bond strength differences appear to depend on the 3+/2+ potential as well, for which $E_{1/2}(CoL^{3+}/CoL^{2+}) = -0.2$ V vs SCE in acetonitrile[11] ≈ −0.2 V vs NHE in water,[47] compared with the oxidation of $Ni(cyclam)^{2+}$, $E^0(Ni(cyclam)^{3+}/Ni(cyclam)^{2+}) = 0.97$ V[42]. That is CoL^+ is a stronger two electron reducing agent than $Ni(cyclam)^+$, with $E^0(CoL^{3+}/CoL^+) \approx -0.76$ V and $E^0(Ni(cyclam)^{3+}/Ni(cyclam)^+) = -0.18$ V.

The data from Tables 2−4 provide insight into mechanistic details that have not been addressed directly, but are worth commenting on. Thermodynamic driving force plays a critical role in controlling the activation energy for a chemical reaction.[48] Consequently, as the metal−adduct bond energy increases, it is anticipated that the dissociation rate constant will decrease and the addition rate constant will increase, other factors being equal. This expectation is borne out for all the observed reactions except CO_2 addition. The addition rate constants, which are not diffusion limited, are similar for $Ni(cyclam)^+$ and the CoL^+ complexes despite the much larger driving force in the latter systems. This effect suggests that CO_2 addition to the reduced metal complexes is rate limiting. A subsequent fast step may stabilize $CoL(CO_2)^+$ to a greater extent than $Ni(cyclam)(CO_2)^+$. A number of stabilizing pathways are possible, for example, isomerization of the macrocycle or coordinated CO_2, or possibly protonation of the bound CO_2. Too much speculation beyond this point is not warranted. However, the possibility of structural rearrangement upon addition remains an open and important question.

Relevance to the CO_2 Reduction Mechanism. The current work provides insight into the nature of the activated intermediate involved in CO_2 reduction. The reason for the highly selective and efficient reactivity of $Ni(cyclam)^+$ toward CO_2 in

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(44) Sauer, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 4578−4581.

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(47) The reduction potential vs SCE in acetonitrile is assumed to be approximately equal to the reduction potential vs NHE in water. Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815−4824.

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mildly acidic aqueous solution compared to the CoL$^+$ complexes is evident. Based on the known CO_2 and H^+ binding constants, Table 1 and 2, protonation is favored over CO_2 binding at pH < 8.6, 4.2, and 2.0 for *meso*-CoL$^+$, *prim-rac*-CoL$^+$, and Ni(cyclam)$^+$, respectively. Protonation undoubtedly leads to proton reduction in competition with CO_2 reduction. Therefore, Ni(cyclam)$^+$ can function as a selective CO_2 reduction catalyst over a larger pH range than the CoL$^+$ complexes.

The above points are important in the design of improved catalytic systems. For example, it is well known that Ni(cyclam)$^{3+}$ is stabilized by the presence of coordinating anions.[49] Stabilization of the +3 oxidation state would lead to a lowering of the two electron reduction potential of Ni(cyclam)$^{3+}$, perhaps leading to a more stable bond to CO_2. Such stabilization is supported by the theoretical calculations of Sakaki.[7] It is also likely that such stabilization will lead to a strengthening of the Ni−H bond, though in an unpredictable way. If the Ni−H bond strength increases more than the Ni−CO_2 bond strength then there will be a decrease in the *selective* CO_2 reduction pH range. However, it is not clear that increasing the bond strength to CO_2 will improve the efficiency of the two electron reduction.

Conclusions

Reduction of Ni(cyclam)$^{2+}$ by both H$^\bullet$ and $CO_2^{\bullet-}$ has been shown to proceed by an inner-sphere mechanism. The adducts thus formed, [Ni(cyclam)(H)]$^{2+}$ or [Ni(cyclam)(CO_2)]$^+$, rapidly come to equilibrium with free Ni(cyclam)$^+$ and H^+ or CO_2. The binding of CO_2 does not proceed by insertion into a Ni−H bond. The species [Ni(cyclam)(H)]$^{2+}$ and [Ni(cyclam)(CO_2)]$^+$ are proposed to be intermediates in the two electron reduction of H^+ and CO_2 by Ni(cyclam)$^+$.

Binding constants for the addition of protons and CO_2 to Ni(cyclam)$^+$ reveal that formation of the CO_2 adduct is favored in CO_2 saturated solution at pH > 2.0. It is this property that is responsible for the exceptional selectivity for CO_2 reduction over H^+ reduction by Ni(cyclam)$^+$ at pH 4.

The origin of the efficiency by which Ni(cyclam)$^+$ reduces CO_2 is not entirely clear. The proposed intermediate in CO_2 reduction, [Ni(cyclam)(CO_2)]$^+$, which forms from CO_2 and Ni(cyclam)$^+$ with a reasonably large bimolecular rate constant, possesses a lifetime of only 500 ns before regenerating the starting materials. Such a short lifetime for the reactive intermediate would not seem to be ideal for promoting reaction efficiency. Favoring efficiency, however, is the relatively low pH at which Ni(cyclam)$^+$ can exist before protonation competes with CO_2 binding. This property allows the reduction to be proton assisted.

Clearly, a number of issues remain concerning the mechanism of CO_2 reduction. A time resolved investigation into the reactivity of [Ni(cyclam)(CO_2)]$^+$ and [Ni(cyclam)(H)]$^{2+}$ and the mechanism of CO and H_2 evolution will be the subject of a separate publication.[24]

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