# Oxidatively Induced Isomerization of Square-Planar [Ni(1,4,8,11-tetraazacyclotetradecane)](ClO₄)₂

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Previous proton NMR and electronic spectroscopy studies have demonstrated that the square-planar complex of Ni(II) and 1,4,8,11-tetraazacyclotetradecane (cyclam) exists in two stable isomeric conformations, namely the *R,S,R,S* form or *trans*-I isomer and the *R,R,S,S* form or *trans*-III isomer. Electrochemical analysis of the *trans*-I isomer of Ni(II)−cyclam has demonstrated rapid conversion to the *trans*-III cyclam conformation following oxidation to Ni(III). The mechanism and kinetics for this oxidatively-induced isomerization were studied by the technique of cyclic voltammetry (CV) with simulation of CV traces by finite-difference computations. The most crucial mechanistic indicator was found to be the transient *trans*-I-Ni(III) species. This intermediate was detected by CV over a pH range 2−4 and was found to have an apparent half-life of ca. 400 ms at room temperature. Remarkably, this life-time was approximately a billionfold shorter than the corresponding *trans*-I-Ni(II) species. Measurements made at varied solution temperature and pH demonstrated that the oxidatively induced isomerization followed an apparent square-scheme, where the *trans*-I/III isomerization process of Ni(III) was independent of pH. This finding precluded a base-catalyzed isomerization process that has been previously identified for the Ni(II) system. Arrhenius plots of the forward isomerization rate constant allowed the extraction of activation parameters for the Ni(III) process. These parameters are discussed with respect to possible rate-determining steps.

## Introduction

There are five possible conformational isomers of planar complexes of the macrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane): *RSRS* (++++), *RSRR* (+−++), *RRSS* (+−−+), *RSSR* (++−−), and *RRRR* (+−+−), where + indicates that the hydrogen of the NH is above the plane of the macrocycle and − indicates that it is below the plane (see Figure 1). These forms were designated *trans*-I to *trans*-V, respectively, by Bosnich, Poon, and Tobe,[2] and this nomenclature will be used in the present paper.

Wagner and Barefield[3] isolated the *trans*-I and *trans*-III forms of nickel(II)−tetramethylcyclam (tetramethylcyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), but in the case of the unsubstituted macrocycle, only complexes of the *trans*-III form could be prepared. Semiquantitative estimates of the relative strain energies of the five isomers of cyclam by Bosnich *et al.*[2] and later Whimp *et al.*[4] indicated that the *trans*-III form was the most stable. Subsequently, molecular mechanics calculations on nickel(II)−cyclam by Hancock *et al.*[5] indicated that the strain energies of the *trans*-I and *trans*-III forms of the nickel(II) complex were comparable, and the authors commented that "... it will be of considerable interest to see whether both forms can be detected in solution, or isolated in the solid form."

Connolly and Billo reported the observation, by proton NMR, of the *trans*-I isomer of [Ni(cyclam)]²⁺ in equilibrated aqueous
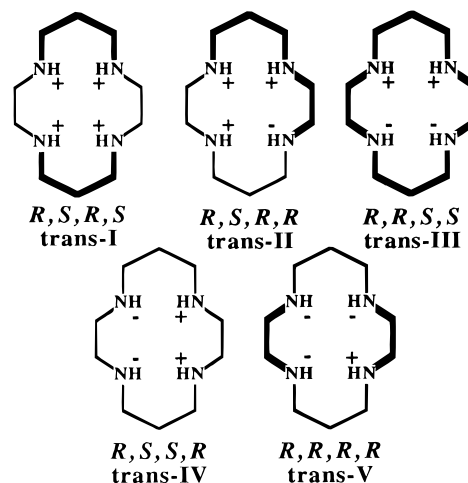


**Figure 1.** Five possible conformational isomers of cyclam.

solutions of *trans*-III-[Ni(cyclam)]²⁺.[6] The *trans*-I isomer comprised approximately 15% of the total complex at 25 °C and was found to isomerize to the *trans*-III species under basic conditions. The half-life of the *trans*-I complex was approximately 2 h at pH 7. At pH less than 3 the *trans*-I complex was found to be extremely inert. In fact, by extrapolation of the rate of isomerization from measurements made at pH 7, the half-life of the *trans*-I complex at pH 2 was estimated to be on the order of 20 years at room temperature. Recently, a procedure was developed to isolate the pure *trans*-I isomer and studies have been initiated to investigate further the conformational lability associated with the *trans*-I complex.

In this paper, we wish to report a billionfold enhancement in the rate of *trans*-I/III isomerization when *trans*-I-[Ni(cyclam)]²⁺ is oxidized to its 3+ state at low solution pH. The kinetics

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and mechanism of this oxidation have been probed by cyclic voltammetry (CV) and finite-difference simulation.[7] While CV has become a standard method for screening the redox behavior of metal complexes[8] and many other inorganic systems,[9] traces that are perturbed by kinetic complications such as conformational intermediates or slow heterogeneous electron transfer can be difficult to diagnose by standard one- or two-point analysis of peak potentials or currents.[10] Finite-difference computations permit an entire CV waveform to be simulated for a particular set of mechanistic (kinetic and thermodynamic) and experimental (solution and cell) conditions. By the fitting of all or, at least, most points of a computed CV trace to an experimental trace, the likelihood of misdiagnosing a complicated mechanism is decreased significantly. It is also advisable to establish proper fits for wide variations of experiential conditions that impact the kinetic process under study (e.g., solvent, electrolyte, concentration, sweep rate, multiple cycles, electrode material, and/or temperature).

We have used CV to detect the metastable *trans*-I isomer that is generated by oxidation of *trans*-I-[Ni(cyclam)]$^{2+}$. Detection of such an intermediate provides conclusive evidence that the oxidatively induced isomerization proceeds by a sequential or "square" mechanism, where the electron transfer event and structural rearrangement occur in distinct, consecutive steps.[11] This mechanism and its variations have been fully described in two recent theoretical treatments.[12,13] Both models have inspired much recent experimental work on Cu(II/I) systems by Kano *et al.*[14] and especially by Rorabacher.[15−19]

Unlike copper systems, relatively few investigations have addressed the effects that structural rearrangements have on redox processes of nickel complexes,[20−23] and presently no information is available for complexes possessing square-planar geometry. The present study represents the first detailed kinetic investigation of redox-induced structural rearrangement for a square-planar nickel center in aqueous media and provides insight into the sequential nature of the process.[24]

## Experimental Section

**Materials.** [Ni(cyclam)](ClO$_4$)$_2$ was prepared according to Barefield *et al.*[25] All aqueous solutions were prepared with 18-MΩ Milli-Q reagent water (Millipore Corp.). Sodium perchlorate monohydrate (+99.8%, Aldrich) and 70% HClO$_4$ (analytical reagent, Mallinckrodt, Inc.) were used to prepare electrolyte solutions used in all electrochemical studies. NMR spectra were recorded in D$_2$O which was 0.01 M in DClO$_4$ (Aldrich).

**R,S,R,S-[Ni(cyclam)](ClO$_4$)$_2$.** A sample of Ni(cyclam)(ClO$_4$)$_2$ (0.50 g, 1.1 mmol) in 20 mL of water was made basic (pH ca. 10) and heated in a boiling water bath for several minutes. The hot solution was acidified to pH 2−3 with perchloric acid and allowed to cool to room temperature, and 0.16 g of KSCN (1.6 mmol) was added. The violet precipitate was removed by filtration, 3 g of NaCl was added to the filtrate, and the solution was extracted with several 5-mL portions of chloroform. The aqueous layer was then extracted with 5-mL portions of nitromethane until the aqueous layer was colorless. The nitromethane extracts were evaporated to dryness under reduced pressure. The *trans*-I isomer can be recrystallized from aqueous solution (pH 2−3) Yield: approximately 15%. *Caution! Perchlorate salts are potentially explosive.* ¹H NMR (D$_2$O, 0.01 M DClO$_4$): δ (in ppm) 1.30 (q, 2H), 1.96 (d, 2H), 2.48 (m, 4H), 2.62 (m, 8H), 3.16 (q, 4H), 3.62 (br s, ~3.5 H, NH). UV/vis (0.01 M HClO$_4$): $\lambda_{max}$ 439 nm, $\epsilon_{max}$ 59 M$^{-1}$ cm$^{-1}$. Anal. Calcd for C$_{10}$H$_{24}$Cl$_2$N$_4$O$_8$Ni: C, 26.23; H, 5.28; N, 12.24. Found: C, 26.06; H, 5.29; N, 12.07 (Desert Analytics).

**Spectroscopy.** UV−visible spectra of solutions recovered from controlled potential electrolysis experiments were acquired with a Shimadzu UV-270 recording spectrophotometer and were reference to a blank electrolyte containing 3.5 M NaClO$_4$ and 0.01 M HClO$_4$. ¹H-NMR data were acquired with a Varian XL300 spectrometer using a 5 mm broad-band probe. The spectral width was widened to 10 kHz to include the region in which peaks of the paramagnetic *trans*-III isomer occurred.

**Electrochemistry.** CV measurements of [Ni(cyclam)]$^{2+}$ solutions were performed using a glass titration cell (10 mL, Brinkman Instrument, Inc.) equipped with either a glassy carbon or gold working electrode, a platinum wire counter electrode, and a silver quasi-reference electrode (AgQRE) that was in ionic contact with the tested solution through a porous ceramic frit. The potential of the AgQRE was referenced to the reversible *trans*-III-[Ni(cyclam)]$^{2+/3+}$ couple ($E_{1/2}$ = +0.772 versus a 3.5 M NaCl calomel electrode)[26] which was added to the test solution at the conclusion of each experiment. Solutions generally contained the tested isomer at 0.50−3.0 mM concentrations in a stock electrolyte of 3.5 M NaClO$_4$ that was acidified to pH 1.0−4.0. Experiments were initiated by deoxygenating the test solution with humidified nitrogen and were continued under a nitrogen blanket. Variable solution temperatures were monitored to within ±0.2 °C by a mercury thermometer immersed directly in the test solution. Sub-ambient temperatures to 0 °C were obtained by partially immersing the cell bottom in an ice-cooled brine. By this method, test solution temperatures were stable to with ±0.5 °C. Computer simulation of all CV waveforms was performed with a potential increment of 2 mV using the implicit finite-difference algorithm of Rudolph and Feldberg (DigiSim version 2.0, Bioanalytical Systems, Inc.).[27]

Coulometry associated with the controlled potential electrolysis (CPE) of [Ni(cyclam)]$^{2+}$ solutions was performed with a large-area, working electrode made of reticulated vitreous carbon (RVC). The RVC cylinder was positioned concentrically around a glass tube that contained a coiled platinum wire counter electrode. The counter electrode was in ionic contact with the test solution through a medium-porosity glass frit that blocked the end of the tube. A AgQRE was also present in the cell but was separated from the test solution by a smaller fritted tube. Stirred solution voltammograms were recorded at a stationary glassy carbon disk electrode before and after CPE to analyze solution composition and were performed with a potential sweep rate of 0.02 V s$^{-1}$. Both CV and CPE measurements were controlled by an EG&G Model 273A potentiostat that was interfaced to a microcomputer.

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## Results and Discussion

**Isolation of the *Trans*-I Isomer.** A previous study,[6] which demonstrated the existence of the *trans*-I isomer in aqueous solution in equilibrium with the *trans*-III isomer, provided information which was used to develop a procedure to isolate the pure *trans*-I isomer. Since the rate of equilibration is rapid at high pH but extremely slow in acidic solution, and the position of equilibrium is shifted to produce more of the *trans*-I isomer at higher temperature, the *trans*-I complex in a hot basic solution can be "locked-in" by acidifying the solution. As well, NMR and other evidence indicated that, unlike the *trans*-III isomer, the *trans*-I isomer has an extremely small tendency to add axial ligands. We exploited this difference by precipitating most of the remaining *trans*-III isomer from solution as *trans*-[Ni(cyclam)](SCN)$_2$. The final traces of the *trans*-octahedral complex were removed by solvent extraction. The *trans*-I complex could then be extracted into nitromethane and isolated as a yellow powder.

**Characterization of the *Trans*-I Isomer.** The NMR spectrum of the *trans*-I isomer (in equilibrium with the *trans*-III isomer) has been discussed previously;[28] the *trans*-I configuration was assigned to the complex largely on the basis of NMR coupling constants. In the present work, two new spectral features are evident. First, the spectrum contains a new peak at $\delta$ 3.62 attributable to the NH protons. Although the spectrum was recorded in D$_2$O, the NH protons do not exchange at low pH; exchange presumably occurs *via* deprotonation, which is base-catalyzed. Second, the peak at $\delta$ 3.16, which was a triplet in the previously published spectrum,[28] is here a quartet, consistent with coupling to the N−H proton (the quartet is actually a pair of overlapping triplets; $J_{HCNH} \sim 12$ Hz). This coupling confirms the previous assignment of the $\delta$ 3.16 protons to the N−CH(axial) of the six-membered rings, since the *trans*-diaxial relationship between the protons H−N−C−H is consistent with a coupling constant of 12 Hz. When the pH of the solution is raised by addition of NaOD, the N−H peak disappears and the quartet collapses to a triplet.

The electronic spectrum of the *trans*-I isomer exhibits a single peak in the visible region, characteristic of square-planar nickel(II). Spectra were identical when measured in either 0.01 M HClO$_4$ or 0.01 M HClO$_4$ + 3 M NaClO$_4$, with $\lambda_{max}$ 439 nm, $\epsilon_{max}$ 58 ± 1 M$^{-1}$ cm$^{-1}$. The absence of a significant increase in molar absorptivity when the perchlorate concentration is increased demonstrates that there is no appreciable concentration of high-spin *trans*-I-[Ni(cyclam)(H$_2$O)$_2$]$^{2+}$ in equilibrium with the planar *trans*-I-[Ni(cyclam)]$^{2+}$, in agreement with the NMR results.

**Electrochemical Behavior of the [Ni(cyclam)]$^{2+/3+}$ Couples.** Previous voltammetry of *trans*-III-[Ni(cyclam)]$^{2+}$ carried out by Fabrizzi *et al.*[26] has shown that the Ni(II/III) couple is centered at +0.772 V versus a 3.5 M NaCl calomel reference electrode (NaCE). We found the same oxidation to be diffusion-controlled as well as chemically reversible on the CV time scale at both glassy carbon and gold electrode surfaces. The process did not show evidence of slow electron transfer or "quasi-reversibility" at either electrode surface, and a diffusion coefficient of 5.6 × 10$^{-6}$ cm$^2$ s$^{-1}$ (294 K) was measured for the Ni(II) species. CPE conclusively demonstrated that the process involved the transfer of only one electron per molecule of the complex ($n_{app}$ = 0.92) and that the Ni(III) species was stable in solution at ambient temperatures for over 10 min.

Cyclic voltammograms recorded for the *trans*-I-[Ni(cyclam)]$^{2+}$ showed an oxidative behavior that was very different
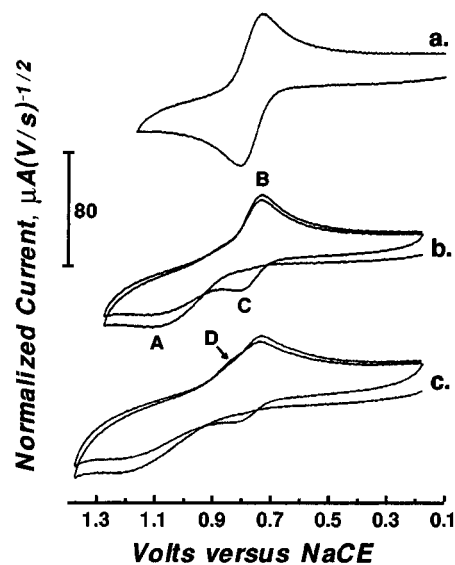


**Figure 2.** CV of 3 mM *trans*-III-[Ni(cyclam)]$^{2+}$ (a) and 3 mM *trans*-I-[Ni(cyclam)]$^{2+}$ (b) in 3.5 M NaClO$_4$ (pH 2) recorded at 21 °C at a glassy carbon disk electrode with a sweep rate of 0.2 V s$^{-1}$. For comparison, a CV of the same 3 mM *trans*-I-[Ni(cyclam)]$^{2+}$ solution recorded at 20 °C at a glassy carbon disk electrode with a sweep rate of 1.0 V s$^{-1}$ is shown in (c). Peaks labeled A−D are described in the text.

from the *trans*-III isomer. Figure 2a,b compares voltammograms recorded for the two isomers at 0.2 V s$^{-1}$ and under the same cell and solution conditions.

At the glassy carbon electrode, the *trans*-I isomer showed a broad oxidation on the first cycle (peak labeled A in Figure 2b) that yielded a reduction wave (labeled B) at +0.74 V. Significantly, on the second cycle a new oxidation peak (labeled C) appeared at +0.81 V. This new oxidation was found to be directly coupled to peak B by clipping the positive voltage ramp of the second cycle just before peak A. At 1 V s$^{-1}$ (Figure 2c), the initial oxidation peak A of the *trans*-I voltammogram demonstrated a significant positive potential shift. Also, the current associated with new oxidation peak C, when normalized for sweep rate, was significantly decreased. The CV at 1 V s$^{-1}$ also showed a new, ill-defined wave (labeled D in Figure 3c) that appeared on the positive shoulder of the main reduction peak B.

Since the coupled peaks C and B were centered around the same potential as the *trans*-III-Ni(II/III) process, it was suspected that oxidation of the *trans*-I species caused a rapid isomerization to the *trans*-III conformation. Conversion to the C/B couple was confirmed by bulk-scale electrolysis of the *trans*-I complex.[29] Coulometry indicated that the oxidation only consumed one electron per molecule of the starting *trans*-I isomer ($n_{app}$ = 1.02). Following bulk-reduction of the solution, which also required one electron per molecule of the original *trans*-I complex ($n_{app}$ = 0.93), a UV−visible spectrum of the electrolysis mixture indicated a square planar Ni(II) product ($\lambda_{max}$ 442 nm, $\epsilon_{max}$ 60 M$^{-1}$ cm$^{-1}$). However, these results were not conclusive regarding the ultimate conformation of the final complex because of the similarity of the *trans*-I- and *trans*-III-Ni(II) chromophores. The ultimate product of the *trans*-I electrolysis was characterized by bulk oxidation and reduction of a *trans*-I solution containing 3.5 M NaClO$_4$ in D$_2$O that was acidified to pD 2 with D$_2$SO$_4$. $^1$H-NMR of the final electrolysis solution showed definitively that the final product was *trans*-III-[Ni(cyclam)]$^{2+}$.[6]

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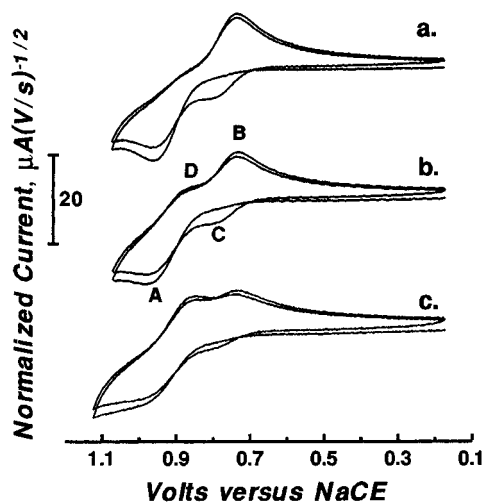
(29) Results provided as Supporting Information.

**Figure 3.** CV of 3 mM *trans*-I-[Ni(cyclam)]$^{2+}$ in 3.5 M NaClO$_4$ (pH 2) recorded at 21 °C at a gold disk electrode with sweep rates of 0.05 (a), 0.2 (b), and 1.0 (c) V s$^{-1}$. Peaks labeled A−D are described in the text.



**Figure 4.** CV of 3 mM *trans*-I-[Ni(cyclam)]$^{2+}$ in 3.5 M NaClO$_4$ (pH 2) recorded at a gold disk electrode with a sweep rate of 0.2 V s$^{-1}$ and solution temperatures of +12 (a), +8 (b), and +1 °C (c). Peaks labeled A−D are described in text.

It was suspected that the reduction peak D observed at sweep rates above 0.5 V s$^{-1}$ (Figure 2c) was directly coupled to the primary oxidation peak A, thus providing evidence of a short-lived Ni(III) complex in the *trans*-I conformation. However, the extreme breadth of peak A ($E_p - E_{p/2}$ ca. 200 mV at 1 V s$^{-1}$) and the large separation between the coupled peaks A and D ($\Delta E_p$ ca. 500 mV at 1 V s$^{-1}$) suggested that the A/D couple was electrochemically sluggish on the CV time scale. Since it is well-known that glassy carbon working electrodes are prone to display slow electron transfer,[30] especially for certain metal complexes,[31] voltammetry of *trans*-I isomer was further investigated at a gold working electrode.

Figure 3 shows a series of cyclic voltammograms recorded at a gold disk working electrode over a sweep rate range from 0.05 to 1 V s$^{-1}$. Through the series, peak A showed only a small positive shift at higher sweep rates, indicating that the oxidation was a much faster process at gold. Because peak separations were significantly smaller, the coupled reduction of *trans*-I-Ni(III) (peak D) was not obscured by the reduction of *trans*-III-Ni(III) (peak B). Sweep rates above 0.2 V s$^{-1}$ allowed the formal potential for the A/D couple to be estimated at $[E_{p,A} + E_{p,D}]/2 = +0.92$ V versus NaCE. Comparison of sweep-rate normalized peak currents also showed that growth of the *trans*-I reduction peak D occurred at the expense of both *trans*-III peaks, B and C. On the basis of the CV at 1 V s$^{-1}$ (Figure 3c), which shows approximately the same reduction peak currents and therefore the same electrode concentrations for the *trans*-I- and *trans*-III-Ni(III) species, it was possible to estimate a crude room-temperature half-life for the *trans*-I-Ni(III) isomer of ca. 400 ms.

To measure the influences of thermal activation and base catalysis on the isomerization, CV traces were recorded at solution temperatures of 20 °C down to 1 °C and pH from 1 to an upper limit of ca. 4.0. Changes observed by lowering the solution temperature (Figure 4) were similar to the changes noted by increasing the CV sweep rate. However, it was found that smaller normalized currents were the result of higher solution viscosity on the diffusion-controlled electrode reactions. Tests were not performed on solutions with pH greater than 4 because of significant *trans*-I to *trans*-III conversion in the Ni(II) state.
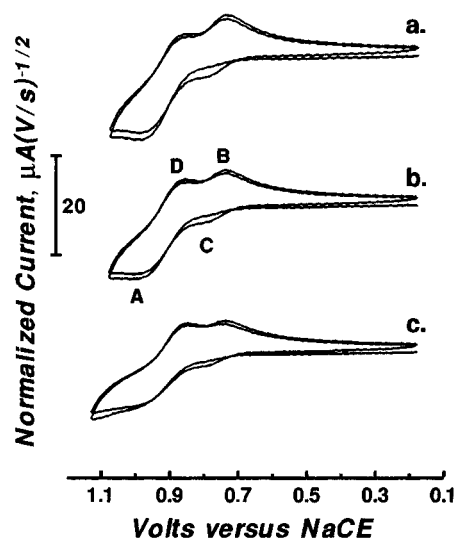
Remarkably, CV traces showed little or no change with pH. Had a proton-coupled mechanism been active, the half-life of the *trans*-I-Ni(III) species would have changed by approximately one decade for each unit pH increase.[32] Because the currents observed for peaks B and D were nearly the same over the entire pH range (for a particular temperature), base or acid catalysis did not appear to influence isomerization of the complex in its higher oxidation state.

A final effect apparent in voltammograms recorded using gold electrodes was excessive oxidative current near the positive potential limit of each sweep (Figures 3 and 4). This effect was especially evident at lower temperatures and higher sweep rates and was probably caused by oxidation of the gold electrode surface. While voltammograms of the blank electrolyte showed the coupled peaks associated with gold surface oxidation and reduction,[33] it was clear that redox waves for the *trans*-I and *trans*-III complexes would be largely unaffected by gold surface reaction except at the positive extreme of the potential sweep.[29] Conditions that favored current generation by the gold surface oxidation over any diffusion-controlled processes, such as high sweep rates, high pH, and low temperatures, enhanced the artifact.

**Mechanism and Kinetics of Oxidatively Induced Isomerization.** To measure the kinetics of the *trans*-I/III isomerization process, experimental voltammograms recorded with a wide range of sweep rates (0.05−5 V s$^{-1}$), temperatures (20−1 °C), and pH (1−4) were compared to voltammograms computed with the fast implicit finite-difference algorithm of Rudolf and Feldberg.[27] Prior to computation, the algorithm was assigned boundary conditions that matched the experimental conditions of the real voltammogram being fit. Other parameters included a mechanism describing all electrode and solution reactions, diffusion coefficients for all species participating in these reactions, and constants (both thermodynamic and kinetic) that governed all reaction steps.

The mechanism indicated by CV as well as CPE of the *trans*-I-[Ni(cyclam)]$^{2+}$ system was the square scheme shown in Scheme 1. Several thermodynamic and kinetic constants in Scheme 1 were known prior to fitting. Formal potentials of the *trans*-I- and *trans*-III-Ni(II/II) couples as well as the half-
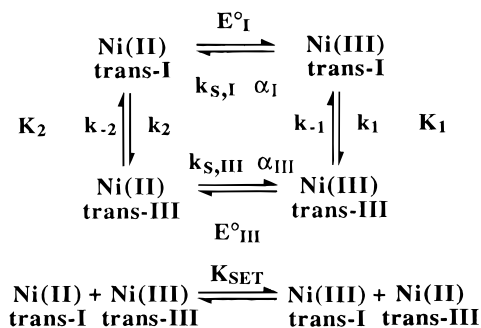
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**Scheme 1.** Electrode and Solution Reactions Proposed for the Oxidatively Catalyzed Isomerization of *trans*-I-[Ni(cyclam)]$^{2+}$

life of the *trans*-I-Ni(III) species were initially estimated from one- or two-point CV measurements. Enthalpic and entropic energy changes measured by $^1$H-NMR for the Ni(II) isomerization equilibrium[6,28] allowed $K_2$ to be estimated at various temperatures (e.g., $K_2 = 5 \pm 2$ at 298 K). The rate constants for this process ($k_2$ and $k_{-2}$) were assigned values of zero since it has been shown that the Ni(II) isomerization is effectively blocked on CV time scales at pH levels less than 4.[6] Using estimates for $K_2$ and the formal potentials $E°'_I$ and $E°'_{III}$, values for $K_1$ and $K_{SET}$ were calculated from the thermodynamic relationships $K_2/K_1 = K_{SET} = \exp[(E°'_{III}-E°'_I)F/RT]$. The solution electron transfer (SET) reaction was included as a dynamic equilibrium (i.e., no rate limitations on the CV time scale) since there is ample precedent for fast SET reactions in most square or ECE-type systems.[34] Finally, diffusion coefficients for all species were assumed to be equal to the value measured for *trans*-III-[Ni(cyclam)]$^{2+}$. Coefficients at subambient temperatures ($D_T$) were estimated from the relationship $D_T \propto T\eta_T^{-1}$, where $\eta_T$ is viscosity at various temperatures, $T$.

Figure 5 shows representative final fits. Values of kinetic and thermodynamic parameters that required optimization are listed in Table 1. With the exception of systematic deviations at the most positive voltages of the CV traces, which were probably caused by surface oxidation of the gold electrode, the mechanism described by Scheme 1 and the data in Table 1 yielded a good match to all experimental waveforms.

Values of $k_{-1}$ were not fit but were computed from $K_1$ and the optimized value of $k_1$ ($k_{1,obsd}$ in Table 1). The precision of $k_{-1}$ was poor (RSD > 20%) because of errors compounded from $k_{1,obsd}$, $K_2$, $E°'_{III}$, and $E°'_I$. To check the relative accuracy of $k_{-1}$, CV traces were simulated without an isomerization step for Ni(II). This omission was valid since $k_2$ and $k_{-2}$ were always assigned values of zero in the square-scheme simulations. The mechanism without $K_2$ defined an $\overset{\rightarrow}{ECE}$ process[34] that permitted $k_{-1}$ to be optimized without altering the value of $k_{1,obsd}$. $\overset{\rightarrow}{ECE}$ fits were identical to square-scheme fits when $k_{-1}$ was zero or below a limiting value. This result established that the reverse isomerization was slow on CV time scale and did not influence the recorded traces. $\overset{\rightarrow}{ECE}$ simulations also provided an optimized limit for $k_{-1}$ when its value was increased until poor fits were observed. Under all conditions, this limit (listed as $k_{-1,obsd}$ in Table 1) agreed with the absolute values computed using a square-scheme.

The simulations demonstrated that *trans*-I to -III isomerization of nickel−cyclam was both energetically favored and kinetically faster with nickel in its 3+ oxidation state. At room temperature, the free energy change for the Ni(III) pathway was
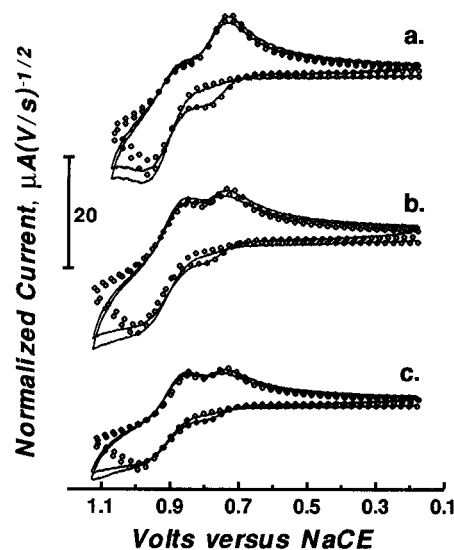
(34) Evans, D. H. *Chem. Rev.* **1990**, *90*, 739.

**Figure 5.** Experimental voltammograms (solid lines) and final fits (open circles) obtained by digital simulation of the mechanism described in Scheme 1. Experimental conditions corresponded to 3 mM *trans*-I-[Ni(cyclam)]$^{2+}$ in 3.5 M NaClO$_4$ (pH = 2) at solution temperatures of +21 (a, b) and +1 °C (c). Experimental votammograms were recorded at sweep rates of 0.2 (a, c) and 1.0 V s$^{-1}$ (b).

**Table 1.** Final Equilibrium and Rate Constants Defined in Scheme 1[a] and Obtained by Finite-Difference Simulation of CV Traces

| conditions[b] | | | optimized parameters[c] | | | | | |
|---|---|---|---|---|---|---|---|---|
| $C_I$, mM | $T$, K | pH | $E°'_I$, V | $k_{s,I,app}$, cm s$^{-1}$ | $\alpha_I$ | $k_{1,obsd}$,[d] s$^{-1}$ | $10^3 k_{-1}$,[d] s$^{-1}$ | $k_{-1,obsd}$,[e] s$^{-1}$ |
| 1.4 | 294 | 2.0 | 0.91 | 0.6 | 0.5 | 1.3(1) | 0.8(3) | [<80] |
| 2.8 | 294 | 2.0 | 0.91 | 0.1 | 0.5 | 2.0(1) | 1.2(4) | |
| 3.3 | 294 | 3.0 | 0.91 | 0.2 | 0.5 | 2.1(2) | 1.3(4) | |
| 2.8 | 294 | 3.6 | 0.90 | 0.2 | 0.5 | 1.5(1) | 1.4(5) | |
| 1.4 | 291 | 2.0 | 0.91 | 0.8 | 0.5 | 0.8(2) | 0.5(2) | [<60] |
| 3.3 | 289 | 3.0 | 0.91 | 1.7 | 0.5 | 1.7(1) | 1.0(5) | |
| 2.8 | 289 | 3.6 | 0.92 | 1.6 | 0.5 | 1.3(1) | 0.5(4) | |
| 1.4 | 284 | 2.0 | 0.91 | 0.8 | 0.5 | 0.70(5) | 0.4(2) | [<50] |
| 2.8 | 285 | 2.0 | 0.92 | 0.8 | 0.5 | 0.9(1) | 0.3(1) | |
| 3.3 | 284 | 3.0 | 0.91 | 0.8 | 0.5 | 1.2(1) | 0.7(3) | |
| 2.8 | 284 | 3.6 | 0.91 | 1.3 | 0.5 | 1.05(8) | 0.6(2) | |
| 2.8 | 281 | 2.0 | 0.92 | 0.6 | 0.5 | 0.6(1) | 0.2(1) | [<50] |
| 1.4 | 278 | 2.0 | 0.90 | 0.8 | 0.5 | 0.5(1) | 0.4(2) | [<50] |
| 2.8 | 278 | 2.0 | 0.91 | 0.3 | 0.5 | 0.5(1) | 0.3(1) | |
| 3.3 | 279 | 3.0 | 0.91 | 0.3 | 0.5 | 0.8(2) | 0.4(2) | |
| 2.8 | 278 | 3.6 | 0.91 | 0.5 | 0.5 | 0.8(1) | 0.4(2) | |
| 2.8 | 274 | 2.0 | 0.91 | 0.2 | 0.5 | 0.33(8) | 0.17(6) | [<30] |

$^a$ Because a nonisothermal reference electrode was employed for CV measurements, $E°'_{III}$ was assigned a constant value of 0.77 V vs NaCE at all temperatures. $K_2$ was derived from ref 6. $K_{SET}$ and $K_1$ were calculated by $K_2/K_1 = K_{SET} = \exp[(E°'_{III}-E°'_I)/RT]$. The rate constants $k_{s,III,app} > 10$ cm s$^{-1}$, $k_{SET} > 1 \times 10^5$ M$^{-1}$ s$^{-1}$, and $k_2 = 0$ s$^{-1}$ were assumed in all cases (see text for explanations). $^b$ CV traces were recorded for solutions of *trans*-I-[Ni(cyclam)]$^{2+}$ in 3.5 M NaClO$_4$ at a gold disk electrode. $^c$ Each entry represents an average of final fits for sweep rates of 0.1−1.0 V s$^{-1}$. $^d$ Values in parentheses given the absolute precision of last reported digit. $^e$ Values in brackets indicate the lowest average rate constant to perturb the fit with the $\overset{\rightarrow}{ECE}$ mechanism (see text for explanation).

approximately five times more negative than that of the Ni(II) pathway. More remarkable was the proton independence of the Ni(III) isomerization rate constant and its large magnitude compared to the Ni(II) system. Below a pH of 3, the Ni(III) reaction was more than a billion times faster than the Ni(II) pathway. The Ni(III) process clearly differed from the Ni(II) isomerization that Connolly and Billo found to be base-catalyzed.[6]

The simulations also detected an apparently slow heterogeneous charge transfer for the *trans*-I isomer. This sluggish behavior was not an artifact of uncompensated solution resistance since the measured rate constant ($k_{s,I,app}$) did not vary consistently with concentration and the *trans*-III couple was nearly Nernstian at the same sweep rates. Because both isomers possess similar molecular size and charge, their divergence in $k_s$ could not have been solely the result of Frumkin effects or solvation differences between the couples. Although some inner-sphere structural rearrangement may have occurred during the *trans*-I electron transfer and thereby slowed the reaction in Marcus fashion, the most significant contributions to low $k_{s,I,app}$ values were probably from surface effects. These effects probably included mild surface adsorption of a *trans*-I species and/or partial passivation of the gold electrode by surface oxide formation. No other processes could have caused the distinctly different charge transfer behavior exhibited by the *trans*-I couple at gold and carbon electrodes or could have induced the observed variations of $k_{s,I,app}$ with concentration and pH.

Temperature dependence of $k_{1,obsd}$ provided an opportunity to more deeply probe the unusual Ni(III) isomerization mechanism. Since statistical analysis of $k_{1,obsd}$ values for 3 mM solutions did not accord any significant proton dependence, the average rate constant for each temperature was plotted in Arrhenius fashion and activation parameters were calculated from absolute rate expressions. The positive enthalpy change ($\Delta H^{\ddagger}_{298} = 57 \pm 7$ kJ mol$^{-1}$) and large negative entropy change ($\Delta S^{\ddagger}_{298} = -54 \pm 7$ J K$^{-1}$ mol$^{-1}$) were consistent with an increase in bonding during the isomerization. This would be expected for a rate-determining step involving change from four-coordinate Ni(II) to six-coordinate Ni(III). A shorter atomic radius of, and stronger bonding by, Ni(III) would also likely make the macrocycle ligand more rigid and reinforce the observed trend in activation energies.

The minimal influence of pH on the rate of isomerization (<50% within the temperature range available for study) is intriguing and suggests that a conjugate base mechanism is not involved in the rate-determining step of the Ni(III) system. Yet proton inversion at two nitrogen centers must occur in order for the *trans*-I and *trans*-III isomers to interconvert. Thus it

seems likely that either the rate of base-catalyzed nitrogen inversion has ceased to be rate limiting or inversion occurs by some other means that is consistent with Ni(III) forming a six-coordinate structure. Without more definitive structural information for both isomers of the Ni(III) complex, possibly by simultaneous CPE−EPR measurements, it is impossible to speculate further on the actual inversion pathway.

## Conclusions

With the *trans*-I form of [Ni(cyclam)] in the 2+ state and in solutions near a pH of 2−3, the halflife for the *trans*-I species has been estimated to be ca. 20 years at room temperature. However, oxidation of *trans*-I-[Ni(cyclam)] to the 3+ state provides a dramatic enhancement to the rate of isomerization. Cyclic voltammetry has confirmed that this isomerization proceeds from a transient *trans*-I-Ni(III) species that has a room-temperature halflife of ca. 400 ms. Variable-temperature measurements of the *trans*-I/III isomerization rate constant of [Ni(cyclam)]$^{3+}$ have provided activation enthalpy and entropy changes which support a rate-determining step involving change from four- to six-coordinate Ni(III). However, because base- or acid-catalyzed proton inversion of the cyclam ring was not found to limit the rate of isomerization and because structures of the short-lived Ni(III) species could not be determined, the exact nature of the isomerization pathway is still unknown.

**Supporting Information Available:** Stirred solution voltammograms recorded before and after electrolysis of *trans*-I-[Ni(cyclam)]$^{2+}$ (Figure S-1) and CV traces recorded with a gold electrode in a blank electrolyte (3.5 M NaClO$_4$, pH 2) and in electrolyte with *trans*-I-[Ni(cyclam)]$^{2+}$ (Figure S-2) (3 pages). Ordering information is given on any current masthead page.

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