Inorg. Chem. **1996,** *35,* 5127−5131

Properties of the Nickel(III) Complex with 1,4,8,11-Tetraazacyclotetradecane-1,4,8,11-tetraacetate in Aqueous Solution

Mahammad Ali,[†] Israel Zilbermann,[†,‡] Haim Cohen,[†,‡] Alexander I. Shames,[§] and Dan Meyerstein*,[†,||]

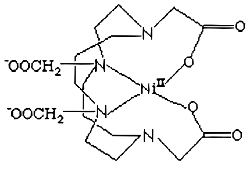
Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel, Nuclear Research Centre, Negev, Beer-Sheva, Israel, Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel, and The College of Judea and Samaria, Kedumim-Ariel, Israel

Received July 13, 1995[⊗]

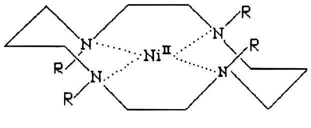
Oxidation of *trans*-**I**−$\mathrm{Ni^{II}L}$, or $\mathrm{Ni^{II}L_{out}}$, by $^{\bullet}\mathrm{OH}$ radicals was carried out by irradiating $\mathrm{N_2O}$ saturated solutions containing the complex, prepared by mixing equimolar concentrations of the metal ion and the ligand at pH 3.50. The intermediate thus formed has a strong absorption band at 310 nm and is stable for hours. That this unstable complex is a nickel(III) species was verified by EPR spectroscopy and its chemical reduction with ascorbic acid, which was found to be instantaneous. The most striking feature of the oxidation by $^{\bullet}\mathrm{OH}$ radicals, which are powerful single electron oxidizing agents, is that it produces a nickel(III) species which is different from the electrochemically produced one as manifested by their absorption spectra and EPR signals. The radiolytically produced nickel(III) species undergoes decarboxylation leading to the production of $\mathrm{CO_2}$, $\mathrm{CH_2O}$, $\mathrm{Ni^{II}L'}$ and $\mathrm{Ni^{II}L}$ ($\mathrm{L'}$ = the new ligand produced after oxidative degradation of one of the *N*-acetate groups of the ligand). The electrochemical oxidation of *trans*-**I**−$\mathrm{Ni^{II}L}$, or $\mathrm{Ni^{II}}_{\mathrm{out}}\mathrm{L}$, proceeds via the degradation of two of the acetate arms on average. The yield of $\mathrm{CH_2O}$ is ∼2.0 mol per mole of the nickel(II) complex in electrochemical oxidations. These observations point out that the two techniques produce different nickel(III) complexes which do not interconvert. The mechanisms leading to the production of $\mathrm{Ni^{II}L'}$ (oxidation by $^{\bullet}\mathrm{OH}$ radicals, radiolytically) and $\mathrm{Ni^{II}L''}$ (electrochemically) differ from that proposed in the literature.

Introduction

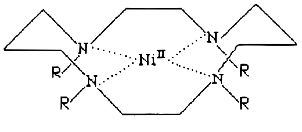
A high kinetic barrier is to be overcome for the insertion of divalent metal ions into the cavity of an N-substituted 14-membered tetraamine macrocyclic ligands though it is thermodynamically favorable.[1−4] Thus in the reaction of nickel(II) with 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetate L, the metal ion does not enter into the plane defined by the four nitrogen atoms of the macrocyclic ligand (metal in), but remains outside the cavity (metal out).[5] The exact structure of $\mathrm{Ni^{II}L_{out}}$ is not known; it was proposed on the basis of its UV−vis spectrum that the nickel is coordinated by two nitrogens and two carboxylates.[5b] However later the same authors suggested that the coordination of Ni(II) to L is octahedral, probably with a *cis* configuration, though the exact structure was not determined.[5c] It was suggested that the $\mathrm{Ni^{II}L_{in}}$ complex in the trans-**III** configuration can be prepared via the electrochemical oxidation of $\mathrm{Ni^{II}L_{out}}$, as the smaller $\mathrm{Ni^{III}}$ ion can insert into the macrocyclic cavity.[6] The proposed mechanism is as follows:



cis



trans III (RSRS)



trans I (RSSR)

$$\mathrm{Ni^{II}}_{\mathrm{out}}\mathrm{L} \xrightarrow{-e^-} \mathrm{Ni^{III}}_{\mathrm{out}}\mathrm{L} \xrightarrow{\mathrm{rds}} trans\text{-}\mathbf{III}\text{−}\mathrm{Ni^{III}L} \xrightarrow{+e^-} trans\text{-}\mathbf{III}\text{−}\mathrm{Ni^{II}L} \qquad (1)$$

Here, $\mathrm{Ni}^{n}{}_{\mathrm{out}}\mathrm{L}$ represents any of the "out" isomers of $\mathrm{Ni}^{n}\mathrm{L}$ and *trans*-III-$\mathrm{Ni}^{n}\mathrm{L}$ is the *trans*-isomer of $\mathrm{Ni}^{n}\mathrm{L_{in}}$.[7]

It seemed of interest to study the kinetics of the metal insertion (rate-determining step, rds) into the cavity of the macrocyclic ligand, L by producing $\mathrm{Ni^{III}L_{out}}$ via

$$\mathrm{Ni^{II}L_{out}} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{Ni^{III}L_{out}} + \mathrm{OH^-} \qquad (2)$$

This approach has two advantages: (i) The $^{\bullet}\mathrm{OH}$ radicals are powerful single electron oxidizing agents, and thus the process is clearly a single electron redox process. Furthermore $^{\bullet}\mathrm{OH}$

[†] Department of Chemistry, Ben-Gurion University of the Negev.
[‡] Nuclear Research Center.
[§] Department of Physics, Ben-Gurion University of the Negev.
[||] The College of Judea and Samaria.
[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

(1) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.
(2) D'Aniello, M. J.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.
(3) Freeman, G. M.; Barefield, E. K.; Derveer, D. G. V. *Inorg. Chem.* **1984**, *23*, 3092.
(4) Nakani, B. S.; Welsh, J. J. B.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 2956.
(5) (a) Madeyski, C. M.; Michael, J. P.; Hancock, R. D. *Inorg. Chem.* **1984**, *23*, 1487. (b) Hafliger, H.; Kaden, T. A. *Helv. Chim. Acta* **1979**, *62*, 683. (c) Riesen, A.; Zehnder, M.; Kaden, T. A. *Helv. Chim. Acta* **1986**, *69*, 2067.
(6) Kimura, E.; Koike, T.; Yamaoka, M.; Kodama, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1341.
(7) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

S0020-1669(95)00871-8 CCC: $12.00

radicals were shown to oxidize various nickel(II) complexes to the corresponding nickel(III) species via processes which have rates approaching the diffusion-controlled limit.[8−10] (ii) The pulse-radiolysis setup in Jerusalem enables one to produce *ca.* 20 μM of $^{\bullet}$OH radicals within 1 μs. Thus observable concentrations of $Ni^{III}L_{out}$ can be prepared within few microseconds. The results obtained clearly point out that $Ni^{III}L_{out}$ does not convert into *trans*-**III**−$Ni^{III}L$ prior to the ligand oxidation, which takes several hours.

Experimental Section

Materials. The ligand 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetate (L) was synthesized by the reported method[11] and characterized by ^{1}H and ^{13}C NMR methods.[11] $Ni^{II}L_{out}$ was prepared by mixing equimolar concentrations of $NiCl_2 \cdot 6H_2O$ and the ligand, L. All other chemicals were of reagent grade and were used without further purification. All solutions were prepared with heat distilled water which was further purified by passing through a Millipore Milli-Q water purification system. N_2O was purified from trace amounts of oxygen by bubbling through two washing bottles containing VSO_4 in dilute H_2SO_4 followed by a washing bottle containing triply distilled water.

Procedures. In all experiments a constant ionic strength, $I = 0.50$ M Na_2SO_4, was maintained. Na_2SO_4 was chosen as the supporting electrolyte as it was used in the previous study describing the preparation of *trans*-**III**−$Ni^{II}L$.[6] In that study it was shown that sulfate does not act as an axial ligand of *trans*-**III**−$Ni^{III}L$ due to the high binding constants of the intramolecular acetate groups.[6]

Cyclic voltammetric studies were carried out using an EG & G Princeton Applied Research potentiostat/galvanostat, Model 263, operated by Research Electrochemistry Software EG & G PARC, using a three-electrode assembly consisting of a glassy carbon working electrode, a platinum counter electrode, and saturated calomel as a reference electrode.

The EPR measurements were carried out with a Varian E-12 X-band EPR spectrometer and a Varian E-257 variable temperature accessory at room temperature and 113 K. To get more precise *g*-factor values, the magnetic field was calibrated using a Bruker B-NM 20 tracking NMR magnetometer and the frequency was calibrated using the standard signal of 4-hydroxy-TEMPO (4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy) free radical in solution with $g = 2.0059 \pm 0.0001$. The *g*-factor and peak-to-peak line width (ΔH_{pp}) errors were found to be ±0.001 and ±0.10 mT for room temperature and ±0.005 and ±0.50 mT for 113K experiments, respectively.

The pulse radiolysis experiments were carried out at the linear electron accelerator facility of the Hebrew University of Jerusalem using 0.5−1.50 μs and 200 mA pulses. The dose per pulse was in the range 1000−3000 rads/pulse. The experimental setup and techniques used for evaluating the results have been described elsewhere[12] in detail. γ-Irradiations were carried out using a ^{60}Co source with a dose rate of 1300 rads/min.

Analysis. The yield of CO_2 was determined by gas chromatography on a Varian 3700 (the error limit is ±10% of the experimental value). The gaseous samples were taken through a rubber septum using a gastight syringe and were analyzed on a Poropak column using a TCD gas detector, calibrated with the necessary standard. The yield of CH_2O was measured by mixing equal volumes of the solutions to be analyzed and acetylacetone in an acetic acid−ammonium acetate buffer medium and measuring the absorbance at 410 nm and comparing it with the standard calibration curve constructed by reacting equal volumes of different known concentrations of CH_2O and acetylacetone in an acetic acid−ammonium acetate buffer medium.[13]

Slow reactions were followed spectrophotometrically with an HP 8452-A diode array spectrophotometer. For these experiments N_2O saturated solutions were irradiated in syringes and transferred after irradiation into a flow through 1 cm optical cell made of quartz. The reference cell contained identical unirradiated solutions.

Results and Discussion

The radiolysis of water produces hydroxyl radicals and hydrated electrons with similar yields, along with a small (<10%) yield of hydrogen atoms[14]

$$H_2O \xrightarrow{e^-,\gamma} e_{aq}^{\,-}\ (2.65),\ {}^{\bullet}H\ (0.60),\ {}^{\bullet}OH\ (2.65),\ H_2\ (0.45),\ H_2O_2\ (0.75) \qquad (3)$$

The yield of respective products are given in *G* values (defined in terms of number of molecules of the product formed by the absorption of 100 eV by the sample) in parentheses.

The hydrated electron reacts with N_2O to produce $^{\bullet}$OH radicals[14]

$$e_{aq}^{\,-} + N_2O \rightarrow N_2 + O^{\bullet -} \qquad k_4 = 8.7 \times 10^9\ M^{-1}\ s^{-1} \qquad (4)$$

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^- \qquad (5)$$

In neutral solutions saturated with N_2O, 2.2×10^{-2} M, the yield of $^{\bullet}$OH radicals is therefore 5.30 (a somewhat higher yield is obtained due to the effect of N_2O on $G(H_2)$ and $G(-H_2O)$).[14] When N_2O-saturated solutions containing $(1.00-10.0) \times 10^{-4}$ M $Ni^{II}L_{out}$, prepared by mixing equimolar quantities of $NiCl_2 \cdot 6H_2O$ and L at pH 3.50−7.00 are irradiated with a short pulse from the linear accelerator, the formation of a relatively long lived species is observed. This intermediate clearly is the product of reaction between $Ni^{II}L_{out}$ and $^{\bullet}$OH radicals. The rate of this process is very high, with $k > 5.0 \times 10^9$ M^{-1} s^{-1}, approaching the diffusion-controlled limit. The formation of the intermediate is followed by two processes of transformation obeying first-order rate laws with $k_{f1} = (3.20 \pm 0.50) \times 10^3$ s^{-1} and $k_{f2} = (40 \pm 5)$ s^{-1} yielding a species which is stable for hours. The latter processes cause only slight changes in the absorption spectrum of the product which has a strong absorption band at 310 nm (Figure 1a). The molar extinction coefficients of the initially formed and the final relatively stable species at 310 nm are as follows: (8100 ± 800) M^{-1} cm^{-1} and (9700 ± 900) M^{-1} cm^{-1} respectively. The spectrum is not affected by the addition of Na_2SO_4 so that $I = 0.50$ M.

The intermediate thus formed by the oxidation by $^{\bullet}$OH radicals is relatively stable and undergoes a slow first-order decomposition reaction with $k_d = (7.10 \pm 0.20) \times 10^{-5}$ s^{-1}. The reaction of $^{\bullet}$OH radicals with $Ni^{II}L_{out}$ might in principle be one of the following:

---

(8) Lati, J.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1978**, 1105.

(9) Lati, J.; Meyerstein, D. *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 611.

(10) Lati, J.; Meyerstein, D. *Inorg. Chem.* **1972**, *11*, 2397.

(11) Maury, M. R.; Zaluzec, E. J.; Pavkovic, S. F.; Herlinger, A. W. *Inorg. Chem.* **1991**, *30*, 3657.

(12) Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1992**, *31*, 2439.

(13) Nash, T. *Nature* **1952**, *170*, 976.

(14) Matheson, M. S.; Dorfman, L. M. *Pulse Radiolysis*; MIT Press: Cambridge, MA, 1967.

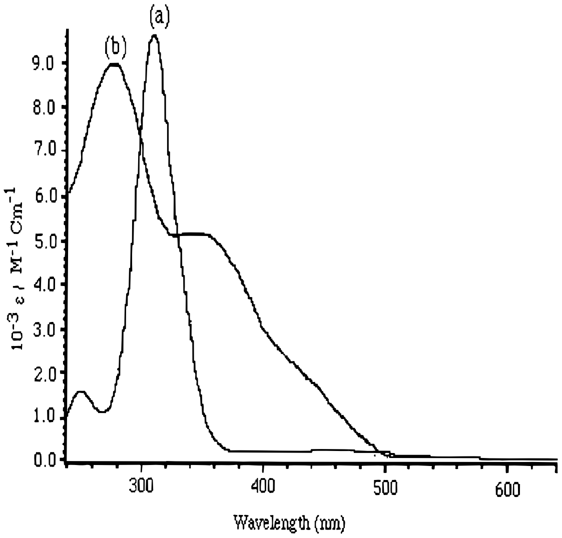


Figure 1. Absorption spectra of the nickel(III) complexes generated from $Ni^{II}L_{out}$ by (a) pulse-radiolytic oxidation at pH 3.50 in N_2O saturated solution and (b) electrochemical oxidation using 2.00×10^{-3} M of the complex at pH = 3.50 and $I = 0.50$ M (Na_2SO_4).

1. Electron transfer may take place from one of the carboxylate groups to the $^{\bullet}OH$, followed by decarboxylation and binding of the alkyl radical formed to the central nickel ion, *i.e.*, the intermediate observed would contain the ($>N-CH_2-Ni^{III}$) unit.

2. Hydrogen abstraction from the ligand may take place, forming substituted alkyl radicals. The latter might react with the central nickel ion, provided the steric factors permitted, to form a transient of the type ($R_1R_2-CH-Ni^{III}$).

3. Oxidation of the central metal ion to form $Ni^{III}L_{out}$ may occur.

The experimental observations support the third process. This conclusion is based on the following arguments:

1. No alkyl radical, including those with α-carboxylates or amine substituents, has an absorption band with $\epsilon_{max} \sim 9000$ $dm^3\ mol^{-1}\ cm^{-1}$ in the near-UV region.

2. All alkyl radicals react with dioxygen in a process with rates approaching the diffusion-controlled limit.[15] However opening the sample to air after the irradiation, *i.e.* exposing it to dioxygen, hardly affects the kinetics of decomposition of the intermediate. Also when solutions containing $Ni^{II}L_{out}$, 1.3×10^{-4} M O_2, and 1.1×10^{-2} M N_2O were irradiated, conditions under which all the hydrated electrons react via reaction 4, the same transient is formed. The slight effect of dioxygen on the kinetics of decomposition might be due to its reaction with $Ni^{II}L'\text{-}CH_2{}^{\bullet}{}_{out}$, or with another intermediate formed in the decomposition process (Scheme 1), forming a peroxyl complex which might react with $Ni^{III}L_{out}$ and thus affect slightly the observed kinetics of decomposition.

3. The decomposition of the complex H_3C-Ni^{III}(cyclam) is considerably accelerated by dioxygen and proceeds via the homolytic insertion of the dioxygen into the Ni−carbon σ-bond.[16]

4. The $^{\bullet}OH$ radicals were shown to oxidize the central nickel(II) ion in Ni^{II}(nta),[8] Ni^{II}(edta),[9] $[Ni^{II}(en)_3]^{2+}$,[10] $[Ni^{II}(glycine)_3]^-$,[10] $[Ni^{II}$(1,4,8,11-tetraazacyclotetradecane)],[17] $[Ni^{II}$(1,4,7,10,13-pentaazacyclopentadecane)],[18] $[Ni^{II}$(1,4,7,10-tetraazacyclotridecane)][19], $[Ni^{II}$(1,4,7,12-tetraazacyclopentadecane)][19] and $[Ni^{II}$(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)][20,21] and analogous complexes.[19] Thus it is reasonable that $^{\bullet}OH$ free radicals will oxidize the central cation in an analogous way to form $Ni^{III}L_{out}$.

5. All the known analogous nickel(III) complexes have strong absorbance bands in the near-UV region.[8−10,17−21]

6. The EPR spectra of the intermediate (vide infra) clearly indicate that the unpaired electron resides on a low spin state of the metal ion.

7. The intermediate was found to oxidize ascorbate immediately upon mixing.

All these observations suggest that the intermediate formed is a nickel(III) complex. Furthermore, the yield of CO_2 formed by γ-radiation is time dependent. The amount of CO_2 formed immediately after irradiation is negligibly small in comparison with that found after 2 days. After 2 days, *i.e.*, after full decomposition of the nickel(III) complex $G(CO_2) \sim 2.50$, which is around half of $G(^{\bullet}OH)$. The relatively low yield of CO_2, which is explained below, again rules out the possibility of electron transfer from a carboxylate group to $^{\bullet}OH$ radicals in the first reaction. The results thus indicate that the oxidation of $Ni^{II}L_{out}$ by $^{\bullet}OH$ radicals forms $Ni^{III}L_{out}$ in an unstable form. This complex rearranges in two consecutive steps into a relatively stable isomer of $Ni^{III}L_{out}$, and the UV and EPR spectra of the latter isomer differ considerably from those of the product of the electrochemical oxidation of $Ni^{II}L_{out}$; see below. Similar rearrangement reactions were also reported for $[Ni^{III}(nta)]$,[8] $[Ni^{III}(edta)]^-$,[9] and $[Cu^{III}(edta)]^-$ [8] complexes. The relatively stable isomer decomposes via a first-order process, which probably involves decarboxylation, as CO_2 is a product, followed by a fast oxidation by a second $Ni^{III}L$ complex as outlined in Scheme 1,

Scheme 1

$$Ni^{II}L_{out} + {}^{\bullet}OH \xrightarrow{\text{very fast}} Ni^{III}L_{out} + OH^-$$

$$Ni^{III}L_{out} \xrightarrow{\text{rearrangement}} [Ni^{III}L_{out}]' \qquad k_{f1} = (3.20 \pm 0.20) \times 10^3\ s^{-1}$$

$$[Ni^{III}L_{out}]' \xrightarrow{\text{further rearrangement}} [Ni^{III}L_{out}]'' \qquad k_{f2} = (40.0 \pm 5.00)\ s^{-1}$$

$$[Ni^{III}L_{out}]'' \rightarrow Ni^{II}L'-CH_2{}^{\bullet}{}_{out} + CO_2 \qquad k_d = (7.10 + 0.20) \times 10^{-5}\ s^{-1}$$

$$Ni^{III}L'\text{-}CH_2{}^{\bullet}{}_{out} + [Ni^{III}L_{out}]'' + H_2O \xrightarrow{\text{fast}} Ni^{II}L'_{out} + Ni^{II}L_{out} + CH_2O$$

(where L′ is the ligand L with only three *N*-acetate groups).

This mechanism accounts also for the yield of CO_2 and CH_2O during the decomposition of $Ni^{III}L_{out}$ which equals $\sim 0.50G(^{\bullet}OH)$. Similar mechanisms were proposed previously for the decomposition of $[Ni^{III}(glycine)_3]$, $[Ni^{III}(en)_3]^{3+\prime}$, $[Ni^{III}(nta)]$, $[Ni^{III}(edta)]^-$, and analogous copper(III) complexes.[8−10]

---

(15) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 413.

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

(17) Zeigerson, E.; Ginzburg, G.; Meyerstein, D.; Kirschenbaum, L. J. *J. Chem. Soc. Dalton Trans.* **1980**, 1243.

(18) Fabbrizzi, L.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2125.

(19) Jubran, N.; Meyerstein, D.; Koresh, Y.; Cohen, H. *J. Chem. Soc., Dalton Trans.* **1986**, 2509.

(20) Cohen, H.; Kirschenbaum, L. J.; Zeigerson, E.; Jaacobi, M.; Fuchs, E.; Ginzburg, G.; Meyerstein, D. *Inorg. Chem.* **1979**, *18*, 2763.

(21) Zeigerson, E.; Ginzburg, G.; Becker, J. Y.; Kirschenbaum, L. J.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1981**, *20*, 3988.

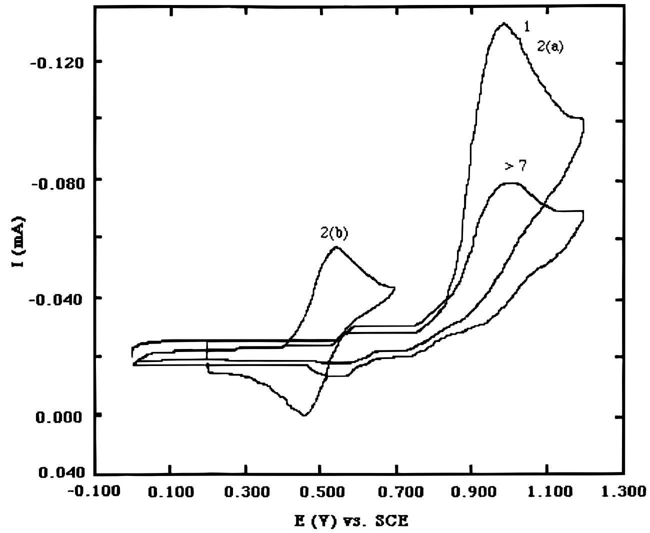


Figure 2. Cyclic voltammograms of (a) $Ni^{II}L_{out}$ and (b) Ni^{II}(Cyclam) complexes on a glassy carbon electrode at pH 5.00 and 1.60, respectively, with a scan rate of 200 mV s^{-1} using 2.00×10^{-3} M of complexes and $I = 0.50$ M Na_2SO_4 as supporting electrolyte. The numbers 1 and >7 indicate the first scan and more than seven scans, respectively.

The pulse-radiolysis experiments thus clearly do not support the mechanism proposed in the literature.[6] It was therefore decided to restudy the electrochemical oxidation of $Ni^{II}L_{out}$ and to compare the physical properties of the nickel(III) complexes obtained in these two different routes. The cyclic voltammogram of 2.00×10^{-3} M solution of $Ni^{II}L_{out}$ (freshly prepared by mixing equimolar quantities of $NiCl_2 \cdot 6H_2O$ and the ligand (L), at pH 3.50 and 5.00) showed waves similar to those reported by Kimura and co-workers,[6] Figure 2a. The spectrum of the nickel(III) complex obtained after preparative electrolysis at +1.20 V vs SCE is plotted in Figure 1b. This spectrum clearly proves that the radiolytic and electrochemical oxidations yield different nickel(III) complexes. Comparison of the integral anodic current of $Ni^{II}L_{out}$ to that of $[Ni^{II}(cyclam)]^{2+}$ (measured under identical concentrations of substrates and electrolyte but at different pH (vide supra)), which corresponds to a $1e^-$ oxidation,[22] reveals that the process consumes *ca.* $5e^-$ per nickel complex. The appearance of a large current at +1.00 V may be due to one of two sources.

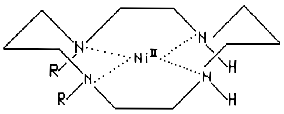
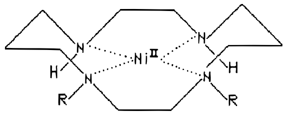
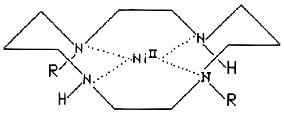
1. The first is a "catalytic oxidation of water" as proposed in the literature,[6] which may occur by the electrochemical oxidation of $Ni^{II}L_{out}$ adsorbed on the electrode surface to $Ni^{III}L_{out}$ which then reacts with water in a fast step to produce $Ni^{II}L_{out}$ and oxygen:

$$Ni^{II}L_{out} \rightarrow Ni^{III}L_{out} + e^- \qquad (6)$$

$$2Ni^{III}L_{out} + H_2O \xrightarrow{\text{fast}} 2Ni^{II}L_{out} + 2H_3O^+ + {}^1/_2O_2 \qquad (7)$$

If this is the situation then the diffusion current should not decrease with repeated number of scans provided that the regenerated $Ni^{II}L_{out}$ is also involved in catalysis. As there is a decrease in the diffusion current on repeating the number of scans the low number of the catalytic cycles has then to be attributed to a fast isomerization of the nickel(III) complex lowering its redox potential and inhibiting the catalytic cycle. It should however be remembered that $Ni^{III}L_{out}$ does not isomerize into *trans*-**III**-$Ni^{III}L$ as it has not been observed in the pulse-radiolysis studies.

2. The second is nickel(III) ion catalyzed autooxidation of the ligand during the electrochemical process. In order to check this, $Ni^{II}L_{out}$ was oxidized at a potential of +1.20 V vs SCE, reduced back to nickel(II) at a potential of 0.00 V, and then the yield of CH_2O formed was measured. The results point out that indeed after quantitative electrochemical oxidation at +1.20 V the solutions contain (1.97 ± 0.20) mol of CH_2O per mole of the complex whereas the yield is lower if incomplete electrolytic oxidation is performed. It was not possible to measure the yield of CO_2 released, as it escapes during the electrolysis process. But in a controlled preliminary experiment the oxidation of the nickel(II) complex by potassium persulfate showed evolution of CO_2. All these observations confirm that the electrochemical oxidation of $Ni^{II}L_{out}$ is accompanied by the oxidative decarboxylation of *ca.* two acetate arms of the ligand leading to an overall $5e^-$ transfer for each molecule of the complex with the resulting formation of $Ni^{III}L''_{out}$ (where, L'' = cyclamdiacetate). This then isomerises via a fast process to *trans*-**III**−$Ni^{III}L''$ as now two of the donor nitrogens are secondary ones. It is reasonable to expect that L'' would be a mixture of several isomers depending on which acetate groups are oxidized. A mixture of the following isomers is expected (where $R = CH_2COO^-$), the drawing is for the *trans*-**I** isomer of $Ni^{II}L''_{out}$ though as stated above probably the *cis* isomer is present in the solutions.

Naturally when these isomers rearrange into the corresponding *trans*-**III** isomers, a complex mixture of isomers is probably formed.

The EPR data point out that the electronic state of the Ni(III) complexes obtained both by electrochemical and by γ-ray irradiation is the low spin state (d^7, $S = {}^1/_2$).[23] The room temperature EPR spectrum of the electrochemically generated $Ni^{III}L$ species, at pH 3.50, 5.00, and 7.00 at an ionic strength of 0.50 M (Na_2SO_4) consists of a single line with a symmetric lorentzian-shape with $g_{iso} = 2.126$ and $\Delta H_{pp} = 1.72$ mT (Figure 3A). The spectrum of identical frozen solutions (113 K) is a superposition of two signals with integral intensities of the same order (Figure 3a). One of the signals may be associated with a $Ni^{III}L''$ complex with an axial distorted ligand field with $g_\perp = 2.166$, $g_\| = 2.028$, and $g_{av} = 2.120$, which is very similar to the reported one.[6] The second signal is a broad singlet with $g = 2.124$ and $\Delta H_{pp} = 10$ mT. For comparison purposes the EPR spectrum of the electrochemically generated $[Ni^{III}(cyclam)]^{3+}$ complex at pH 1.60 was remeasured (Figure 3B) and found to have $g_{iso} = 2.157$ and $\Delta H_{pp} = 2.40$ mT at room temperature. At 113 K a spectrum with $g_\perp = 2.221$, and $g_\| = 2.022$, and $g_{av} = 2.155$ is observed (Figure 3b). The EPR spectrum of $Ni^{III}L'$ obtained by γ-ray irradiation at pH 3.50 and 5.00, is significantly different from that of the spectrum of $Ni^{III}L''$ obtained by electrochemical oxidation. Thus the room temperature singlet line shifts to a low field $g_{iso} = 2.179$, and

---

[22] Zeigerson, E.; Ginzburg, G.; Kirschenbaum, L. J.; Meyerstein, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *127*, 113.

[23] One of the reviewers suggested that due to the quality of the EPR spectra they might be due to Ni^IL and not to Ni(III) complexes. This possibility is ruled out by the observation that all Ni(I) complexes of this type react with dioxygen in reactions with rates approaching the diffusion-controlled limit.

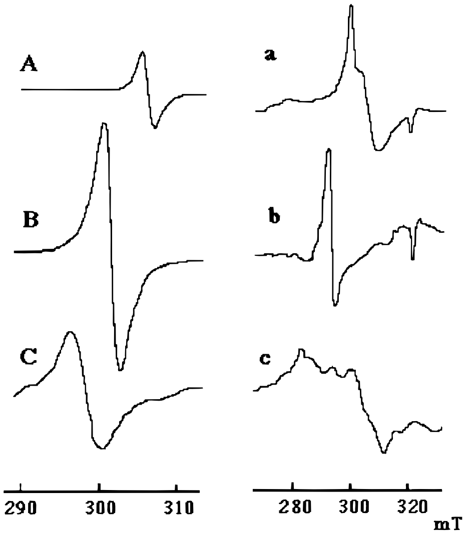
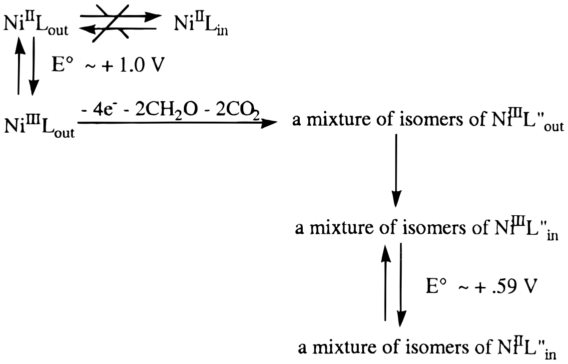


Figure 3. X-band EPR spectra of nickel(III) complexes at room temperature and, at $\nu = 9.093$ GHz, generated in different ways: (a) $Ni^{III}L$ generated by electrochemical oxidation at pH 5.00, I = 0.50 M (Na_2SO_4); (b) Ni^{III}(cyclam) generated by electrochemical oxidation, at pH = 1.60, I = 0.50 M (Na_2SO_4); (c) $Ni^{III}L$ generated by γ irradiation at pH 5.00 and at room temperature. Plots a, b, and c are the corresponding spectra at 113 K.

broadens up to $\Delta H_{pp} = 3.94$ mT. The integral intensity of this line increases nonlinearly with time of irradiation probably due to the decomposition of the species formed with time and by interaction with H_2O_2 and/or with radicals. At 113 K the peak to peak signal intensity decreases, and a very broad line with hard to distinguish characteristic points at $g_1 = 2.30$, $g_2 = 2.13$, and $g_3 = 2.04$, and $\Delta H_{pp} = 30$ mT is observed (Figure 3c).

The spectra of frozen samples indicate that the electrochemical oxidized complex is a mixture of at least two isomers or conformers which differ from each other by the value of axial distortion. The more distorted configuration is responsible for the well-distinguished *g*-factors. The other configuration has a broad symmetric line. The width of the line can be explained by the distribution of the distortions in frozen solution. This conclusion is supported by the room temperature spectra. Indeed, the value of $g_{iso} = 2.126$ is higher than the g_{av} value calculated from the first signal; this deviation is out of experimental error. Comparing the data with those of $[Ni^{III}(cyclam)]^{3+}$ point out that both $Ni^{III}L''$ isomers are less distorted than the former ($g_{av} = 2.157$). The EPR spectra of the $Ni^{III}L$ complex obtained by the γ-ray irradiation are in accord with the presence of this complex in a mixture of isomeric forms leading to different extent of distortions which leads to the line broadening and decreases the peak-to-peak signal intensity. The room temperature spectra, which show both a wide shift in a *g*-factor toward low field and a considerable line broadening, also support this proposition.

Scheme 2



A plausible mechanism for the electrochemical oxidation of $Ni^{II}L_{out}$ leading to the production of a *trans*-**III**−$Ni^{III}L''$ species (where L″ represents cyclamdiacetate) and two molecules of CH_2O per molecule of the complex is outlined in Scheme 2. The above reactions scheme indicates that it is reasonable to expect several isomers of *trans*-**III**−$Ni^{III}L''$ formed via electrochemical oxidation. Finally, two points should be reemphasized.

1. The oxidation of $Ni^{II}L_{out}$ by •OH radicals yields a different nickel(III) product than the electrochemical oxidation. This difference arises due to the fact that •OH radicals are single electron oxidizing agents whereas the electrode process is capable of being a multiple electron transfer process.

2. The reduction of the mixture of the nickel(III) complexes produced electrochemically does not yield *trans*-**III**−$Ni^{II}L$ as reported previously but a mixture of isomers of *trans*-**III**−$Ni^{II}L''$ which differs from the former by the number of acetate arms attached to the N-atoms on the parent cyclam ligand.

Acknowledgment. This study was supported by a grant from the Budgetting and Planning Committee of the Council of Higher Education and the Israeli Atomic Energy Committee. M.A. acknowledges a postdoctoral fellowship from the Budgetting and Planning Committee of the Council of Higher Education. D.M. wishes to express his thanks to Mrs. Irene Evenes for her ongoing interest and support.

IC950871N