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Article

Reduction of the Allylic Substituents in Ni^I(1,8-dipropenyl-1,4,8,11-tetraazacyclotetradecane)$^+$ by the Central Ni(I) in Aqueous Solutions

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The complex Ni^{II}(1,8,-di-2-propenyl-1,4,8,11-tetraazacyclotetradecane)$^{2+}$, $(NiL^1)^{2+}$, was synthesized. X-ray crystallography demonstrates that the complex obtained is the *trans*-III isomer. The allylic substituents shift the redox couples $(NiL^1)^{3+/2+}$ and $(NiL^1)^{2+/+}$ anodically relative to the corresponding couples for Ni^{II}(1,4,8,11-tetraazacyclotetradecane)$^{2+}$, $(NiL^2)^{2+}$, as expected. Surprisingly, the lifetime of $(NiL^1)^+$ in neutral aqueous solutions is shorter than that of $(NiL^2)^+$. Pulse radiolysis experiments reveal that the allylic substituents are reduced by the central Ni(I) ion. The first step in this reduction is a general acid catalyzed process. The results suggest that this step involves schematically the reaction $\mathrm{Ni(I)\!-\!NCH_2CH\!=\!CH_2^+ + H^+ \rightarrow \underbracket{Ni(III)\!-\!NCH_2CH_2CH_2}^{2+}}$. The latter transient decomposes slowly with a half-life time of several minutes. Preliminary results support the suggestion that $(NiL^2)^+$, or other Ni(I)L complexes of this family, might reduce many alkenes present in the solution.

Introduction

During a systematic effort to develop new, relatively stable, single electron reducing reagents, it was decided to synthesize the complex Ni^{II}(1,8,-di-2-propenyl-1,4,8,11-tetraazacyclo-tetradecane)$^{2+}$, $(NiL^1)^{2+}$. It was expected that the allylic substituents, or at least one of them, would axially bind to the central Ni(I) ion, thus shifting the redox potential of the couple $(NiL^1)^{2+/+}$ anodically relative to that of $(NiL^2)^{2+/+}$,[1] L^2 = (1,4,8,11-tetraazacyclotetradecane−cyclam). Furthermore, it was expected that also kinetically $(NiL^1)^+$ will be more stable then $(NiL^2)^+$.

Another reason for initiating this study is the recent interest in the redox chemistry of nickel complexes due to their role in a variety of enzymes[2] and electrocatalytic processes.[3]

Surprisingly enough, the results indicated that the redox potentials of the couples $(NiL^1)^{2+/+}$ and $(NiL^3)^{2+/+}$ (L^3 = 1,8-dimethyl-1,4,8,11-tetraazacyclotetradecane) are similar.[4] Furthermore, the results point out that $(NiL^1)^+$ is short-lived in aqueous solutions due to the reduction of the allylic substituents by the central Ni(I) ion. Due to the importance of the reduction of alkenes in aqueous solutions, it was decided to study in detail the mechanism and kinetics of this process.

Experimental Section

Materials. All chemicals used in this study were of A.R. grade, purchased from Aldrich or Fluka. These chemicals were used without further purification. Aqueous solutions were prepared from deionized water which was further purified by passing through a Milli-Q-Millipore setup, final resistance $>10^7 \Omega$.

Helium was purified from traces of dioxygen by passing it through two washing bottles containing 0.1 M VSO_4 in dilute H_2SO_4 over a Zn amalgam, followed by a washing bottle containing purified water.

Synthesis of $[Ni(II)L^1]^{2+}$. From the cyclam ligand, synthesized according to the literature procedure,[5] the ligand (1,4,8,11-tetra-

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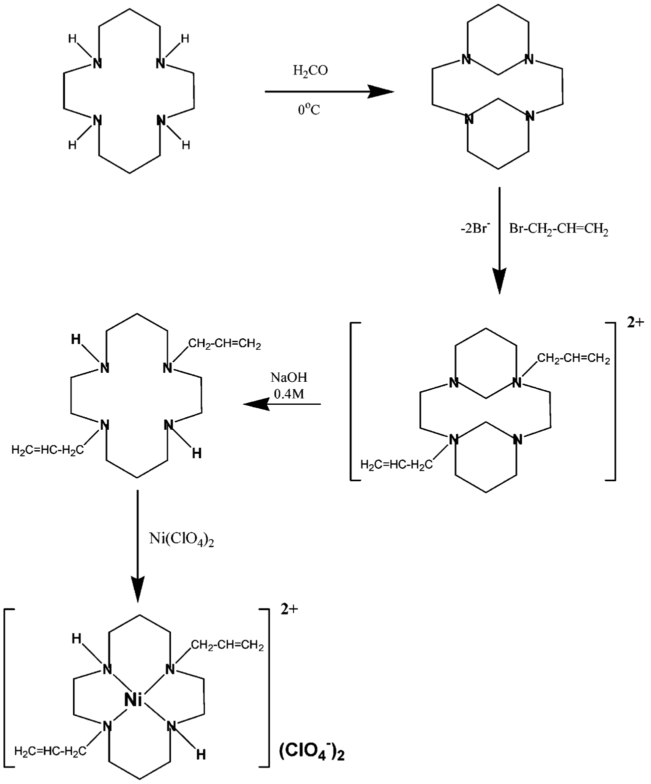
Scheme 1. Synthesis of $[Ni(II)L^1]^{2+}$



azatricyclo[9.3.1]hexadecane)[6] was synthesized and characterized by NMR analysis.

Forming two bridges between two pairs of nitrogen atoms within the macrocyclic ring is an efficient technique for binding functional “arms” to the cyclam.[6] These bridges prevent the binding of more than two substituents, which bind to the *trans* positions.

To a 50 mL CH_3CN solution containing 5 g of this ligand was added 6.7 g of liquid allyl bromide. After 3 h of stirring, the white precipitate was collected (yield 90%). A 3 g portion of the precipitate is then dissolved in 150 mL of 0.4 M NaOH solution. After 2 h of stirring and evaporation until dryness, the final ligand is extracted by 3 × 100 mL portions of dichloromethane, and distilled in a vacuum (0.5 mmHg), at 130−140 °C (yield 40%).

$Ni(ClO_4)_2 \cdot 6H_2O$ (1.55 g) was dissolved in 100 mL of ethanol. This ethanol solution was added to 100 mL of ethanol solution containing 1 g of the distilled ligand. A green suspension was obtained. After about 30 min, an orange solution was obtained. The solution was refluxed for 24 h while stirring, and the orange precipitate was collected after filtering the ethanol. The complex was recrystallized from a mixture of hot water and ethanol. The synthetic steps are summed up in Scheme 1.

Warning. *Perchlorate salts of transition metal complexes, and organic perchlorates, are potentially explosive and have to be handled with care.*

Spectrophotometry. All spectra were collected on an HP8452A spectrophotometer in an anaerobic UV−vis quartz cell.

Electrochemistry. Cyclic votammograms were recorded under the following conditions: An EG&G Princeton Applied Research potentiostat and galvanostat model 263A driven by Power CV electrochemistry software was used in connection with the HMDE mode of model 303A SMDE (Ag/AgCl reference electrode) or with a glassy carbon PVC coated electrode (SCE reference electrode, counter electrode was platinum wire).

NMR. NMR spectra were recorded on a Bruker DMX-500 spectrometer operating at 500.130 and 125.758 MHz, respectively, for ^1H and ^{13}C.

Pulse Radiolysis. Pulse radiolysis experiments were carried out using the Varian 7715 linear electron accelerator of the Hebrew University of Jerusalem. The pulse duration was 0.1−1.5 μs with a 200 mA current of 5 MeV electrons. The dose per pulse was 3−30 Gy. Irradiations were carried out in a 4 cm spectrosil optical cell, and the analyzing light was passed three times through the cell. A 150 W xenon arc produced the analyzing light. The experimental setup was identical with that described elsewhere in detail.[7] For dosimetry, an N_2O-saturated solution containing 1×10^{-3} M $Fe(CN)_6^{4-}$ was used. The yield was measured by using $\epsilon(Fe(CN)_6^{3-})_{420} = 1000\ M^{-1}\ cm^{-1}$. The values of the molar extinction coefficients calculated from the dosimetry measurements have error limits of ±15% due to the scatter in the pulse intensity and due to the uncertainties in *G* values.

γ-Irradiations were carried out using a ^{60}Co γ-source with a dose rate of 4 Gy/min.

Production of Radicals. The radiolysis of water in dilute aqueous solutions can be summarized as follows:[8]

$$H_2O \xrightarrow{e^-,\gamma} \cdot OH\ (2.65),\ \cdot H\ (0.60),\ e^-_{aq}\ (2.65),\ H_2\ (0.45),\ H_2O_2\ (0.75) \quad (1)$$

(The values in parentheses are the relative yields of the products, expressed as *G* values which are defined as the number of molecules of each product per 100 eV radiation absorbed by the solution.)[8] In concentrated solutions, the yield of the radicals is slightly higher and those of H_2O_2 and H_2 are somewhat lower. At pH > 3, the contribution of •H atoms to the total free radical yield is less than 10%.

The redox potential of the formate radical $CO_2{\cdot}^-$ is −1.9 V.[9] This radical is produced by irradiating a He saturated solution containing formate. Under these conditions, the •OH and H• radicals react with the formate according to the reaction:[10]

$$H\cdot/\cdot OH + HCOO^- \rightarrow CO_2{\cdot}^- + H_2/H_2O$$

$$k_{\cdot OH} = 3.2 \times 10^9\ M^{-1}\ s^{-1}\ ^{10}$$

$$k_{H\cdot} = 2.1 \times 10^8\ M^{-1}\ s^{-1}\ ^{10}$$

Under these conditions, the $CO_2{\cdot}^-$ radical and e^-_{aq} are the reducing agents formed in the solution.

The e^-_{aq} reacts faster than the formate radical; therefore, the reaction with each of them can be separately identified.

Irradiations. γ-Irradiations were carried out in a ^{60}Co γ-source, Noratom, with a dose rate of ≈4.0 Gy/min, which was determined by means of Fricke dosimetry, using a *G*-value of *G* = 15.6.[11]

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Table 1. Crystallographic Data for $[NiL^1]^{2+}$

empirical formula	$C_{16}H_{32}Cl_2N_4NiO_8$
color	dark orange
fw	538.07
T	298(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimension	$a = 8.592(3)$ Å, $\alpha = 68.159(5)°$ $b = 8.960(3)$ Å, $\beta = 74.482(7)°$
Volume	572.9(3) $Å^3$
Z	1
D (calcd)	1.559 Mg/m^3
abs coeff	1.129 mm^{-1}
$F(000)$	282
cryst size	$0.1 \times 0.2 \times 0.3$ mm^3
θ range for data collection	2.45−23.25°
index ranges	$-8 \leq h \leq 9$ $-8 \leq k \leq 9$ $-9 \leq l \leq 10$
reflns collected	2882
indep reflns	1639 [R(int) = 0.0269]
completeness to $\theta = 23.25°$	99.5%
abs correction	semiempirical
max and min transm	1 and 0.63
refinement method	full-matrix least-squares on F^2
data/restraints/params	1693/0/146
GOF on F^2	0.999
final R indices [$I > 2\sigma(I)$]	R1 = 0.0536, wR2 = 0.1338
R indices (all data)	R1 = 0.0697, wR2 = 0.1437
largest diff peaks	1.116 and −0.823 e $Å^{-3}$

Results and Discussion

X-ray Structure Determination. X-ray diffraction data of the complex were collected at room temperature on a Bruker Smart System diffractometer with a 6KCCD detector, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A summary of the crystallographic data and structure refinement parameters is given in Table 1.

The structure was solved by direct methods[12] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference Fourier map and refined isotropically. All calculations were carried out using the SHELXL-97 program.[13] Selected bond distances and angles are given in Table 2.

The X-ray characterization points out that the isomer *1R,4R,8S,11S* (also known as *trans*-III) was obtained (see Figure 1). The bond angles for N(2)−Ni−N(1) of 92.58° prove that the central nickel atom retains its planar coordination sphere, formed by the four nitrogen atoms. Furthermore, the bond Ni−N(1), 1.967 Å (the tertiary nitrogen), is longer than the bond Ni−N(2), 1.943 Å, as expected. Comparing these data with the analogous data for the symmetric Ni^{II}(1,4,8,11-tetramethyl-1,4,8,11-tetraazatetracyclodecane)$^{2+}$, $(NiL^4)^{2+}$,[14] demonstrates that the allylic substituents do not induce a larger steric hindrance than the methyl substituents in $(NiL^4)^{2+}$. However, binding of the allylic substituents to the central Ni(I) ion might impose considerable steric constraints.

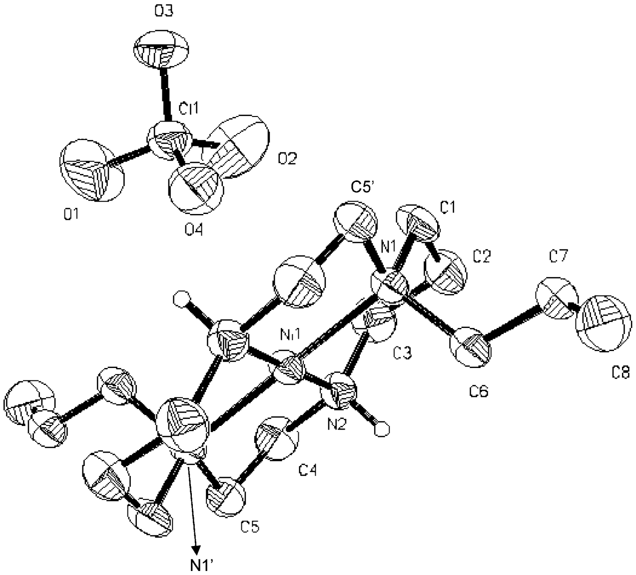

Figure 1. Crystallographic structure of $[NiL^1]^{2+}$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[NiL^1]^{2+}$

Ni(1)−N(2)	1.943(4)	C(5)−N(1)′	1.502(6)
Ni(1)−N(1)	1.967(4)	C(6)−C(7)	1.497(6)
C(1)−N(1)	1.503(6)	C(6)−N(1)	1.511(6)
C(1)−C(2)	1.505(8)	C(7)−C(8)	1.301(7)
C(2)−C(3)	1.510(7)	C(1)−O(1)	1.405(5)
C(3)−N(2)	1.501(7)	Cl(1)−O(3)	1.419(4)
C(4)−C(5)	1.490(8)	Cl(1)−O(4)	1.430(5)
C(4)−N(2)	1.499(6)	Cl(1)−O(2)	1.435(5)
N(2)−Ni(1)−N(2)	92.58(16)	C(5)′−N(1)−Ni(1)	105.7(3)
N(2)−Ni(1)−N(1)′	87.42(16)	C(1)−N(1)−Ni(1)	116.1(3)
N(1)−C(1)−C(2)	114.1(4)	C(6)−N(1)−Ni(1)	106.1(3)
C(1)−C(2)−C(3)	112.9(4)	C(4)−N(2)−C(3)	109.2(4)
N(2)−C(3)−C(2)	111.8(4)	C(4)−N(2)−Ni(1)	109.8(3)
C(5)−C(4)−N(2)	106.7(4)	C(3)−N(2)−Ni(1)	119.5(3)
C(4)−C(5)−N(1)′	109.2(4)	O(1)−Cl(1)−O(3)	109.6(3)
C(7)−C(6)−N(1)	116.2(4)	O(1)−Cl(1)−O(4)	109.6(4)
C(8)−C(7)−C(6)	123.4(5)	O(3)−Cl(1)−O(4)	109.3(3)
C(5)′−N(1)−C(1)	107.0(4)	O(1)−Cl(1)−O(2)	112.7(4)
C(5)′−N(1)−C(6)	109.9(4)	O(3)−Cl(1)−O(2)	108.1(3)
C(1)−N(1)−C(6)	111.9(4)	O(4)−Cl(1)−O(2)	107.4(3)

Electrochemical Properties. The redox properties of $(NiL^1)^{2+}$ in aqueous solutions were determined electrochemically by cyclic voltammetry. The anodic shifts for the two redox couples $[NiL^1]^{2+/+}$ and $[NiL^1]^{3+/2+}$ relative to the corresponding redox couples of $[NiL^2]$[15] are shown in Figure 2 and Figure 3. The redox potentials of the $[NiL^i]^{3+/2+}$ couples are affected by $[SO_4^{2-}]$ due to the formation of the $[L^iNi^{III}(SO_4)_2]^-$ complexes.[15c,16] If the binding constant of SO_4^{2-} to $[Ni^{III}L^1]^{3+}$ is lower than that to $[Ni^{III}L^2]^{3+}$, then the observed anodic shift might be partially due to this effect.[17] The results are summed up in Table 3.

It should be noted that the redox wave of the $[NiL^2]^{2+/+}$ couple is not well observed on the glassy carbon electrode

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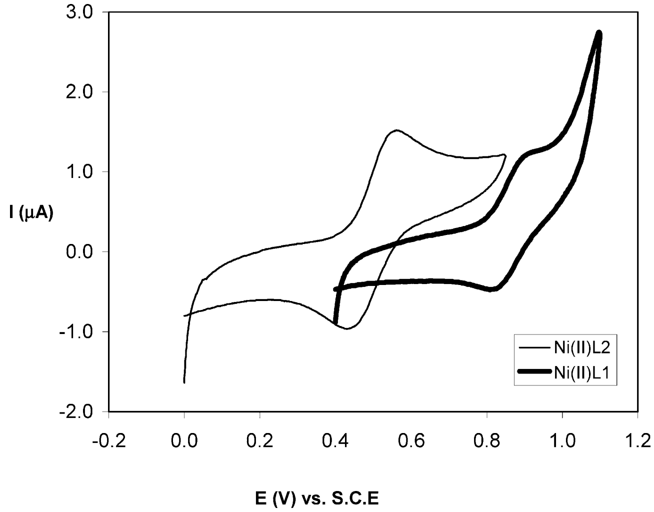


Figure 2. Oxidation voltammetry of aqueous solution of $[\mathrm{Ni(II)L}^i]^{2+} = 2 \times 10^{-4}$ M, $[\mathrm{SO_4}^{2-}] = 0.5$ M, pH = 2.8, scan rate = 50 mV/s.

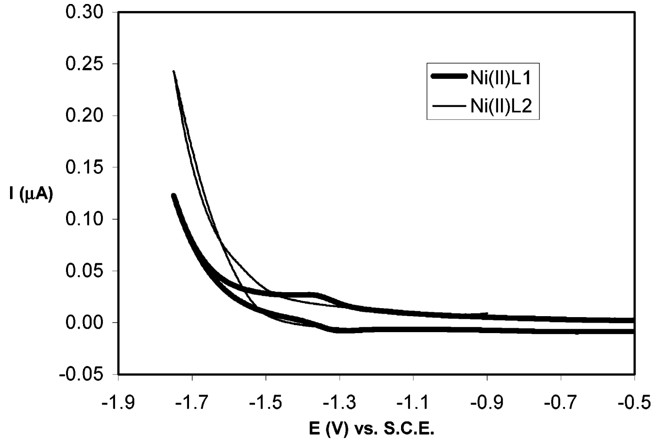


Figure 3. Reduction voltammetry of aqueous solution of $[\mathrm{Ni(II)L}^i]^{2+}=2 \times 10^{-4}$ M, $[\mathrm{NaClO_4}] = 0.1$ M, pH = 6.8, scan rate = 250 mV/s.

Table 3. Redox Potential Values versus NHE[a]

Ni(II)(1,8-di-2-propenyl-1,4,8,11-tetraazacyclotetradecane), $\mathrm{Ni^{II}L^1}$		Ni(II)(1,4,8,11-tetraazacyclotetradecane), $\mathrm{Ni^{II}L^2}$	
$\mathrm{NiL}^{2+/+}$	$\mathrm{NiL}^{3+/2+}$	$\mathrm{NiL}^{2+/+}$	$\mathrm{NiL}^{3+/2+}$
−1.33 V[c] quasireversible	∼ +1.10 V[c] quasireversible	∼ −1.58 V[b] nonreversible	+0.72 V[c] reversible

[a] Experimental conditions as in Figure 2 and Figure 3. [b] Literature value.[1] [c] Measured value.

while it is clearly reversible on HMDE.[14,15] However, the electrochemical data for $[\mathrm{NiL^1}]^{2+}$ are measured on the glassy carbon electrode due to the adsorption of the complex to the mercury electrode.

Although the reduction wave of $[\mathrm{NiL^1}]^{2+}$ is quasireversible, the current at the oxidation wave is lower than that in the reduction wave. This means that some of the monovalent nickel complex disappears during the estimated 3 s period for completing the cycle. Therefore, the stability of $[\mathrm{NiL^1}]^{+}$ was studied using the pulse-radiolytic technique.

NMR Studies. Before the pulse-radiolysis experiments, it was decided to try to determine the nature of the final products. For this purpose, He saturated solutions containing 2.5×10^{-4} M $[\mathrm{Ni(II)L^1}]^{2+}$, 0.3 M $\mathrm{HCO_2Na}$, and 0.1 M phosphate buffer at pH 6.0 were irradiated by a dose of 3×10^3 Gy in the ^{60}Co γ-source. Assuming $G = 4.5$ for the reduction, this dose supplies 5 electrons per each complex. The irradiated solution was dried, the remaining salts were dissolved in $\mathrm{D_2O}$, and the ^{13}C NMR was recorded, see Figure 4. A comparison of Figure 4a,b clearly demonstrates that the reduction caused the disappearance of the allylic peaks at 125−128 ppm, and the appearance of new aliphatic peaks in the 10−30 ppm region. (Due to the large dose, secondary products are also expected.) This result clearly demonstrates that the radiation induces saturation of the allylic substituents by the monovalent central nickel ion.

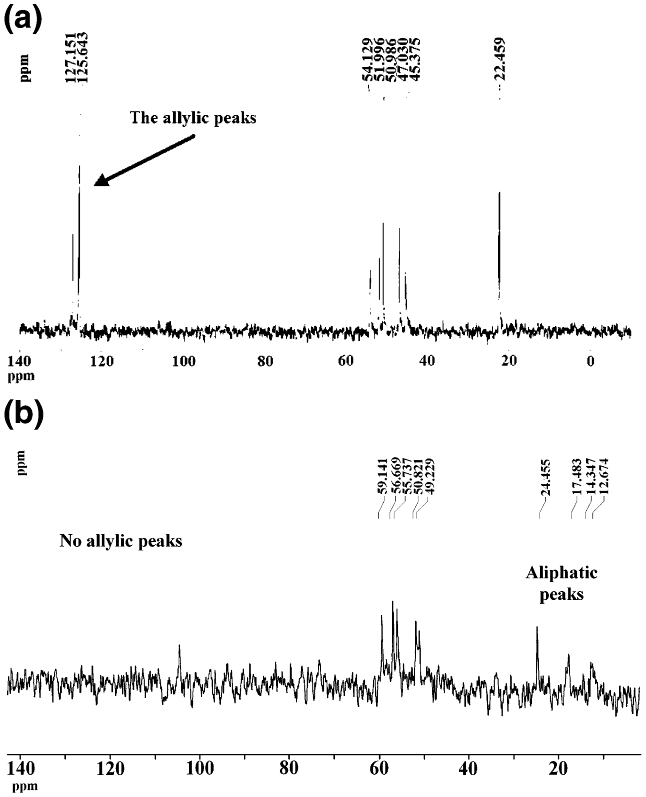


Figure 4. (a) ^{13}C NMR record of the solution before the irradiation of 2.5×10^{-4} M $[\mathrm{NiL^1}]^{2+}$, 0.3 M $\mathrm{HCOO^-}$, 0.1 M phosphate, He saturated in $\mathrm{D_2O}$. (b) ^{13}C NMR record of the solution after irradiation with 3 Mrad.

Pulse-Radiolysis Studies. $[\mathrm{NiL^1}]^{+}$, **I**, can be prepared by irradiating He saturated solutions containing $\mathrm{HCO_2Na}$.[1] The radiation forms in these solutions two strong reducing radicals: $\mathrm{e^-_{aq}}$ and $\mathrm{CO_2}^{\bullet -}$ (see Experimental Section). These radicals are expected to react with $[\mathrm{NiL^1}]^{2+}$ as follows:[1,12a]

$$[\mathrm{NiL^1}]^{2+} + \mathrm{e^-_{aq}} \rightarrow [\mathrm{NiL^1}]^{+} \quad (2)$$

$$[\mathrm{NiL^1}]^{2+} + \mathrm{CO_2}^{\bullet -} \rightarrow [\mathrm{NiL^1}]^{+} + \mathrm{CO_2} \quad (3)$$

Analogous reactions were reported for $[\mathrm{NiL^2}]^{2+}$ and other Ni(II) complexes.[1,12a] Therefore, all the primary radicals are transformed into the desired $[\mathrm{NiL^1}]^{+}$ complex. The yield of $[\mathrm{NiL^1}]^{+}$ is thus expected to be $G([\mathrm{NiL^1}]^{+}) = 6.0$. However, $[\mathrm{NiL^1}]^{+}$ is expected to react with the $\mathrm{H_2O_2}$ formed by the radiation, a reaction which will decrease the yield to $G([\mathrm{NiL^1}]^{+}) = 4.5$.

Pulse-radiolysis of He saturated solutions results in the very fast formation of a short-lived intermediate. A typical

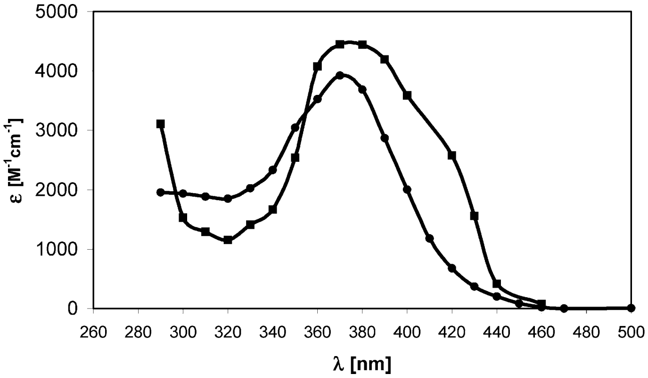


Figure 5. Spectra of $[\mathrm{Ni(I)L^i}]^+$ complexes. $[\mathrm{NiL_1}]^+$ (●) solution composition: $[\mathrm{NiL^1}]^{2+} = 2 \times 10^{-4}$ M, $[\mathrm{HCOO^-}] = 0.1$ M, pH 6.0, Ar saturated solution, measured 20 μs after the pulse. $[\mathrm{NiL^2}]^+$ (■) solution composition: $[\mathrm{NiL^2}]^{2+} = 2 \times 10^{-4}$ M, $[\mathrm{HCOO^-}] = 0.3$ M, [phosphate] = 0.1 M, pH 6.2, He saturated solution, measured 20 μs after the pulse.

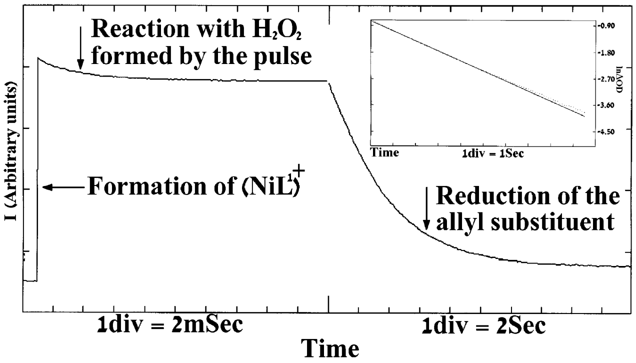


Figure 6. Decomposition kinetics of $(\mathrm{NiL^1})^+$ solution composition: $[\mathrm{NiL^1}]^{2+} = 2 \times 10^{-4}$ M, $[\mathrm{HCOO^-}] = 0.05$ M, [phosphate] = 0.05 M, pH 6.2, He saturated, $\lambda = 370$ nm.

spectrum of this intermediate is shown in Figure 5. Since this spectrum is similar to the spectrum of $[\mathrm{NiL^2}]^+$, it is concluded that indeed $[\mathrm{NiL^1}]^+$, **I**, is formed via reactions 2 and 3 as expected.

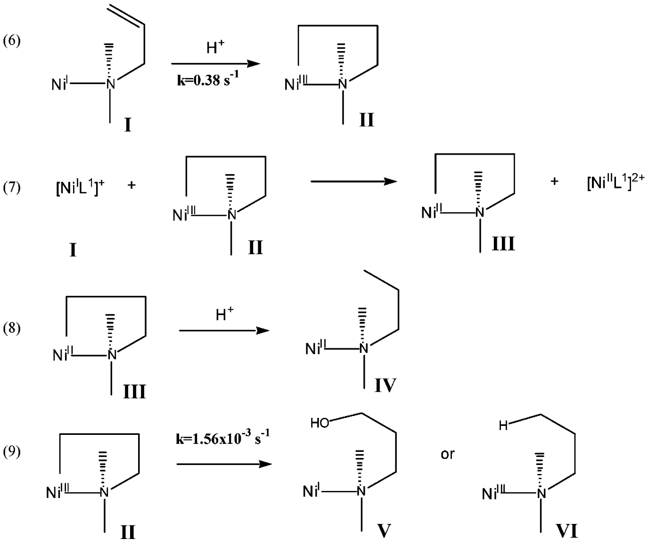
The formation of the intermediate is followed by three further, time separated processes, of which the first two are shown in Figure 6. The first of them does not cause a significant change in the spectrum of the intermediate; it causes only a decrease in the intensity of the absorption bands. This process is attributed to the reaction of $[\mathrm{NiL^1}]^+$ with the H_2O_2 formed by the pulse. The kinetics of this reaction is independent of the solution composition and pH.

The rate of the second process observed increases upon delivering repeated pulses to the solution. This is clearly due to the formation of one of the final products of the process. Two products seemed reasonable. The first is formation of CO via the following reactions:

$$(\mathrm{Ni(II)L^1})^{2+} + \mathrm{CO_2}^{\bullet -} \rightarrow (\mathrm{Ni(I)L^1})^+ + \mathrm{CO_2} \qquad (3)$$

$$2\mathrm{H^+} + 2(\mathrm{Ni(I)L^1})^+ + \mathrm{CO_2} \rightleftarrows \mathrm{CO} + 2(\mathrm{Ni(II)L^1})^{2+} + \mathrm{H_2O} \qquad (4)$$

Scheme 2. Schematic Reduction Mechanism of $[\mathrm{Ni(I)L^2}]^+$



CO is expected to act as a ligand to the monovalent nickel complex[18] as it does to many low valent transition metal complexes, e.g., Cu(I) and Ni(I).[19] However, the results pointed out that the reaction rate does not change upon addition of CO(g) to the solution. Thus, one has to conclude that the effect of repetitive pulsing on the observed rate is not due to the formation of CO(g).

The second product is the formation of bicarbonate via reactions 3 and 5, which might also affect the observed rate. The results indeed point out that the addition of bicarbonate increases the rate of the second observed process, though the rate is not affected when the bicarbonate concentration is increased from 0.001 to 0.01 M. The effect of bicarbonate is attributed to its action as a general acid catalyst. Indeed, the addition of phosphate buffer to the solution has a similar effect on the rate, and the spectrum of the product of the second process is independent of the nature of the buffer present in the solution.

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

The observed rate of the second process at pH 6.2 in the presence of 0.1 M phosphate is 0.38 ± 0.07 $\mathrm{s^{-1}}$. It is proposed that this process is that suggested in reaction 6 in Scheme 2, i.e., the transformation of intermediate **I** into intermediate **II**.

The third process, which is too slow for measuring in the pulse-radiolysis setup, was measured using the spectrophotometer. Figure 7 shows the time dependence of the spectrum of the third process. One can clearly notice the disappearance of the characteristic absorption of the second intermediate after 6 min.

This reaction also obeys a first-order rate law with a rate constant of $(1.56 \pm 0.3) \times 10^{-3}\ \mathrm{s^{-1}}$. It is suggested that this process is reaction 9 in Scheme 2. Upon repetitive pulses, or under continuous irradiation, reaction 9 might be replaced, or partially replaced, by reaction 7, which is followed by reaction 8.

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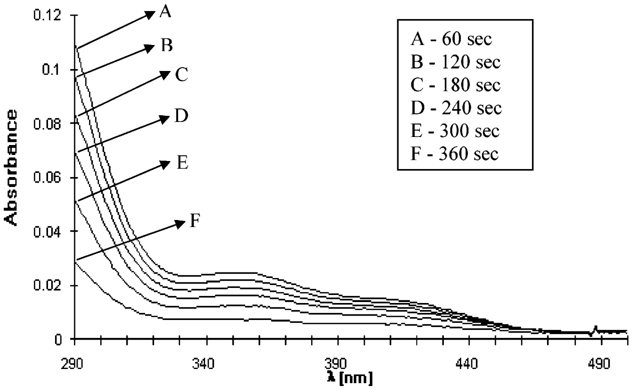

Figure 7. Time dependence of the spectrum of the third process. Solution composition: 2×10^{-4} M $(NiL^1)^{2+}$, 0.3 M $HCOO^-$, 0.1 M phosphate, pH 6.2, He saturated.

Conclusions

The study shows that the allylic substituents thermodynamically stabilize the monovalent nickel cation of the complex $[Ni(I)L^1]^+$. However, kinetically they shorten the lifetime of the monovalent complex. The decomposition of the monovalent complex is a two-step process, the first of which is general acid catalyzed. The complete proposed mechanism is outlined in Scheme 2.

It is proposed that the second intermediate formed, **II**, is a Ni(III) complex with a Ni−C bond, analogous to the $[L^2Ni^{III}-CH_3]^{2+}$ complex.[20] This intermediate might decompose via reaction 7 followed by reaction 8. This is probably the major mechanism in the ^{60}Co low dose rate irradiated samples, or via reaction 9, which might be of importance in the linear accelerator experiments as the spectrum of the second intermediate resembles that of $[L^2Ni^{III}-CH_3]^{2+}$.[20] Clearly, a mixture of final products after several pulses or a prolonged irradiation is expected, in accord with the NMR of the final products, Figure 4. Preliminary experiments point out that $(Ni^IL^2)^+$ reduces a variety of alkenes, e.g., ethylene and maleic acid.

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