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Mechanism of Isomerization of Ni(cyclam) in Aqueous Solutions

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Nickel complexes of cyclam and cyclam derivatives isomerize in aqueous solutions via two different mechanisms: i. deprotonation of one of the coordinated amino groups followed by inversion and ii. cleavage of the Ni–N bond followed by inversion. While the first mechanism is relevant for the di- and tri-valent nickel complexes, the second one occurs for the mono-valent complexes, and for complexes with tertiary amines as ligands.

Introduction

Qualitative studies based on molecular models first performed by Bosnich et al.[1,2] described the five possible conformational isomers (*trans-I-trans-V*, Figure 1, a) of planar complexes of the "classic" macrocyclic ligand system, cyclam. Of the five possible configurational isomers of $[Ni(cyclam)]^{2+}$, $(NiL^1)^{2+}$, it has long been supposed that the *trans-III* configuration is the most stable one.[1,3]

Molecular mechanics (MM) theoretical studies predicted that when four-coordinate low-spin species are involved, the *trans-I* isomer is favoured over the *trans-III* one, while if six-coordinate species are present, the stabilities are reversed.[4] Later theoretical studies applying MM techniques[5–8] and local density functional theory analysis[9] that compare the calculated data to the already published X-ray structures of *trans-III* and *trans-V*,[5,11–13] indicated that the *trans-I* and *trans-III* isomers of $[Ni(cyclam)]^{2+}$ (Figure 1, c), are energetically most stable, and that the energy difference between them is insignificant.

Solution ^{1}H-NMR studies[10a,10b] indicate that both $[Ni(cyclam)]^{2+}$ *trans-I* and *trans-III* forms coexist in aqueous solutions, the *trans-I* isomer comprising ca. 15% of the total complex at room temperature. The rate of equilibration (1) is rapid at high pH, but extremely slow at acidic pH. On the other hand, the equilibrium is shifted to produce more of the *trans-I* isomer at higher temperatures. Based on the latter and on the fact that *trans-I*-$[Ni(cyclam)]^{2+}$ has an extremely small tendency to add axial ligands, the latter complex could be isolated.[10b]

$$trans\text{-}I\text{-}[Ni(cyclam)]^{2+} \rightleftarrows trans\text{-}III\text{-}[Ni(cyclam)]^{2+} \qquad (1)$$

Studies performed on the low-spin *N*-alkylated derivative (tmc)-$(NiL^3)^{2+}$ of $[Ni(cyclam)]^{2+}$ (tmc = *N*,*N*′,*N*′′,*N*′′′-Me_4-cyclam) led to the conclusion that the *trans-III* configuration is the lowest energy structure and the *trans-I* configuration is kinetically favored.[12–14] The two isomers are not interconvertable unless strong coordinating solvents are present[12] and then the *trans-I* species is favoured.

Solution ^{13}C-NMR studies[15] showed that the published methods[16] for the preparation of *trans-I*-$[Ni(tmc)]^{2+}$ also produce some amounts of the *trans-II* isomer in the crude product. If triflate is used instead of perchlorate as the precipitation agent, a markedly higher proportion of the *trans-II* isomer is obtained. Recrystallization of these products in CH_3NO_2 converts the *trans-II* isomer almost entirely to the *trans-I* isomer. A strong donor solvent such as DMF enhances the rate of isomerization from *trans-II* to *trans-I*. The authors[15] propose that the isomerization mechanism involves the inversion about a nitrogen, which probably requires the inverting nitrogen to detach from the divalent metal centre rendering the previously tetradentate tmc temporarily to become a tridentate chelate.

A very similar mechanism is proposed for the isomerization of the Ni^{II} complex with an alkylated derivative of diazacyclam,[17] L^9 [see reaction (2) and Figure 1, b].

$$trans\text{-}I\text{-}[Ni(L^9)]^{2+} \rightleftarrows trans\text{-}III\text{-}[Ni(L^9)]^{2+} \qquad (2)$$

The authors suggest an inversion of one tertiary and one secondary nitrogen donor in the six-membered chelate ring. The coordination of a water molecule to the metal centre following the detachment of a coordinated nitrogen in the transition state is also proposed. The authors also propose

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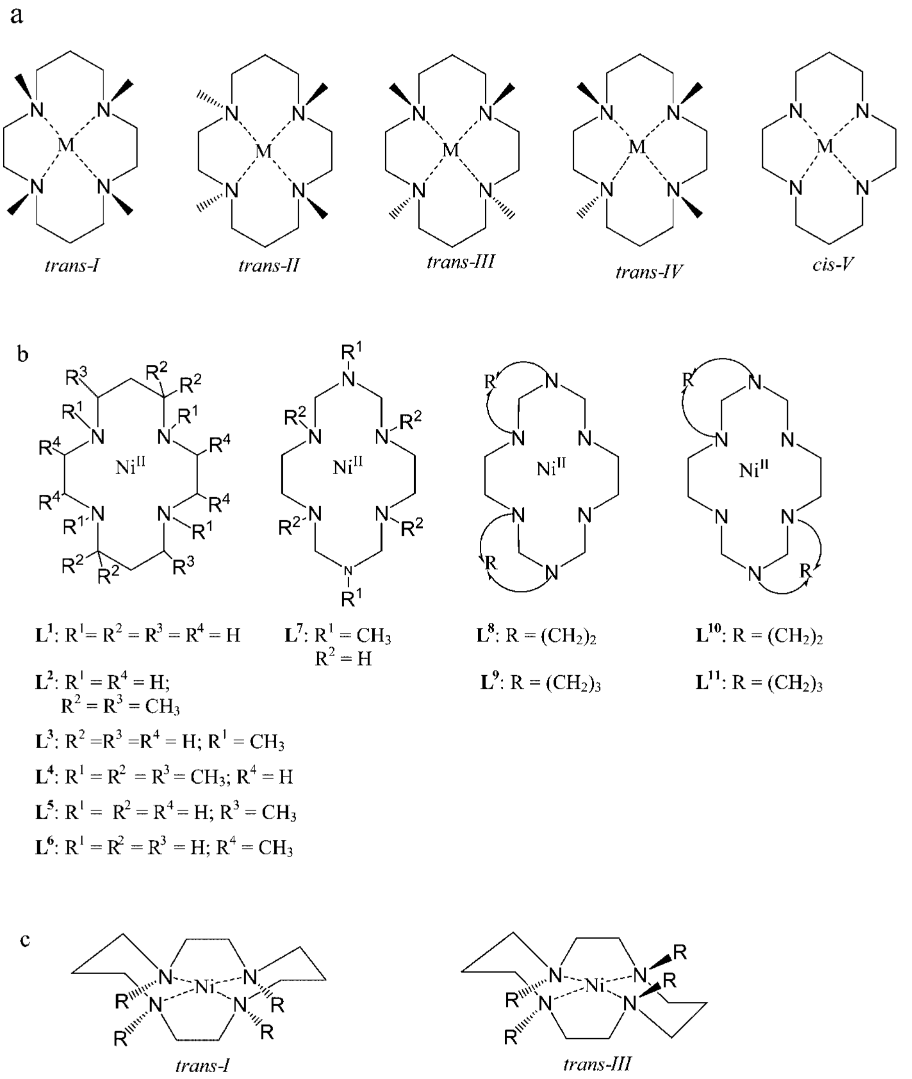


Figure 1. **a**: The five known isomers of metal complexes of cyclam. **b**: The nickel complexes of cyclam and alkylated derivatives. **c**: The most stable isomers of cyclam and derivatives (in this study R = H or CH_3).

the formation of the *trans-II* isomer as one of the intermediates in the mechanistic cycle.

The isomerization of the macrocyclic frame bound to the nickel ion both in the +1 and +3 oxidation states of the metal was also reported. Isomerization according to (3) leads to an equilibrated mixture of a ca. 1:3 ratio, respectively, has been reported to occur in aqueous solutions over a period of several hours.[18a,18b]

$$trans\text{-}I\text{-}[\mathrm{Ni^I(tmc)}]^+ \rightleftarrows trans\text{-}III\text{-}[\mathrm{Ni^I(tmc)}]^+ \quad (3)$$

It is of interest to note that the very fast reduction of $[\mathrm{Ni(cyclam)}]^{2+}$ and analogous complexes by e^-_{aq} or by $CO_2^{\cdot -}$,[19] is followed by reactions obeying first order kinetics with rate constants in the range $(0.1–2.6) \times 10^3\ s^{-1}$, which were attributed to isomerization processes.

Kelly et al.[20] showed that the fast addition of CO to $[\mathrm{Ni^I(cyclam)}]^+$ in aqueous solutions is followed by a slower first-order reaction with a rate constant of $1.8\ s^{-1}$, which was tentatively attributed to the isomerization process (4).

$$trans\text{-}III\text{-}[\mathrm{Ni^I(cyclam)CO}]^+ \rightleftarrows trans\text{-}I\text{-}[\mathrm{Ni^I(cyclam)CO}]^+ \quad (4)$$

Such a reaction channel was not observed for $[\mathrm{Ni^I(L^6)CO}]^+$ perhaps due to steric constrains, but it does operate for $[\mathrm{Ni^I(L^5)CO}]^+$, which is less sterically restrained.[21]

Electrochemical studies[10b] demonstrated the rapid conversion (5) on a time scale of 400 ms.

$$trans\text{-}I\text{-}[\mathrm{Ni^{III}(cyclam)}]^{3+} \rightleftarrows trans\text{-}III\text{-}[\mathrm{Ni^{III}(cyclam)}]^{3+} \quad (5)$$

Isomerization processes of $[\mathrm{Ni^{III}(cyclam)}]^{3+}$[22] or cyclam and diazacyclam derivatives were observed following the oxidation of the divalent nickel by strong single electron oxidizing agents.[23–27] Furthermore, the decomposition processes of $[\mathrm{Ni^{III}(cyclam)}]^{3+}$ or diazacyclam (L^{7-11})[27–29] complexes were shown to obey first order kinetics even though the common decomposition mechanism requires second order kinetics. It was proposed that the rate-determining step in the decomposition process is presumably an isomerization reaction.

Clearly the suggestion that $[Ni^{III}(L^1)(H_2O)_2]^{3+}$ isomerizes faster than $[Ni^{II}(L^1)]^{2+}$[10b] and the effect of pH on the rate of isomerization of $[Ni^{II}(L^1)]^{2+}$[10b] do not fit a mechanism requiring the detachment of a nitrogen atom from the central nickel ion. The availibility of *trans-I*-$[Ni^{II}(L^1)]^{2+}$ and *trans-III*-$[Ni^{II}(L^1)]^{2+}$ suggested that the homogeneous isomerization of the corresponding $[Ni^{I}(L^1)]^{+}$ and $[Ni^{III}(L^1)(H_2O)_n]^{3+}$ could be studied in order to elucidate the isomerization mechanisms and the factors that affect them.

Results and Discussion

The Case of $[Ni^{III}(L^1)]$

As already mentioned, the *trans-III*-$[Ni^{II}(L^1)]^{2+}$ and *trans-I*-$[Ni^{II}(L^1)]^{2+}$ isomers were separated[10a] and their oxidatively induced interconversion was studied using electrochemical techniques.[10b] Since the time scale of the isomerization process is 400 ms, which is close to the detection limit of the electrochemical techniques used, and as it occurs near the electrode and might therefore be a heterogeneous process, it was decided to study this process in homogeneous solutions using the pulse radiolysis technique.

N_2O saturated aqueous solutions containing 5×10^{-4} M *trans-III*-$[Ni^{II}(L^1)]^{2+}$ or *trans-I*-$[Ni^{II}(L^1)]^{2+}$ at pH 3.4–4.2, were irradiated by fast 5 MeV electrons at a dose rate of 2.5–25 Gy/pulse. Under these experimental conditions over 90% of the primary radicals formed by the radiation, reaction (6), are transformed into $^{\cdot}OH$ radicals via reaction (7).

$$H_2O \xrightarrow{e^-,\ \gamma} e^-_{aq}\ (2.65);\ H^{\cdot}\ (0.60);\ ^{\cdot}OH\ (2.65);\ H_2\ (0.45);\ H_2O_2\ (0.75);\ H^+\ (2.65) \qquad (6)$$

where the values in parentheses give the relative yields of the primary products.[36a]

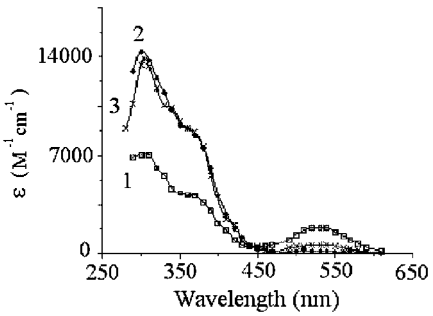
$$N_2O + e^-_{aq} + H_2O \rightarrow N_2 + {}^{\cdot}OH + OH^-$$
$$k_7 = 8.7\times10^9\ M^{-1}\ s^{-1[31]} \qquad (7)$$

The $^{\cdot}OH$ radicals then oxidize $[Ni^{II}(L)]^{2+}$ according to equation (8), presumably with conservation of the isomeric composition.

$$^{\cdot}OH + [Ni^{II}(L)]^{2+} \rightarrow OH^- + [Ni^{III}(L)]^{3+}$$
$$k_8 > 2\times10^9\ M^{-1}s^{-1[27]} \qquad (8)$$

The spectra of *trans-III*-$[Ni^{III}(L^1)_{aq}]^{3+}$ and *trans-I*-$[Ni^{III}(L^1)_{aq}]^{3+}$ thus formed differ considerably, Figure 2. *trans-III*-$[Ni^{III}(L^1)_{aq}]^{3+}$ is long-lived, whereas the spectrum of *trans-I*-$[Ni^{III}(L^1)_{aq}]^{3+}$ changes in a process which obeys first order kinetics, Figure 3, to form a species with a spectrum which is identical to that of *trans-III*-$[Ni^{III}(L^1)_{aq}]^{3+}$. Therefore the observed process is attributed to the isomerization reaction (5).

$$trans\text{-}I\text{-}[Ni^{III}(L^1)_{aq}]^{3+} \rightarrow trans\text{-}III\text{-}[Ni^{III}(L^1)_{aq}]^{3+}$$
$$k_5 = (3.3\pm0.7)\times10^3\ s^{-1}\ \text{at pH}\,3.2 \qquad (5)$$



1) 14 µs after the pulse → $5\cdot10^{-4}$ M *trans-I*-($Ni^{II}L$); N_2O saturated; pH 3.2; 8 Gy/pulse

2) 40 ms after the pulse → $5\cdot10^{-4}$ M *trans-I*-($Ni^{II}L$); N_2O saturated; pH 3.2; 8 Gy/pulse

3) 40 ms after the pulse → $5\cdot10^{-4}$ M *trans-III*-($Ni^{II}L$); N_2O saturated; pH 3.2; 8 Gy/pulse

Figure 2. Spectra of the tervalent nickel complexes of the *trans-I* and *trans-III* complexes formed by the oxidation of $[Ni^{II}(L^1)]^{2+}$.

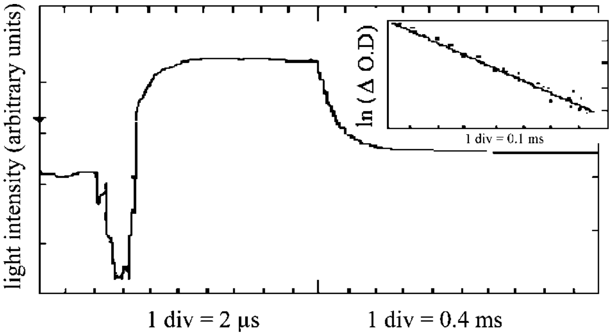


Figure 3. The formation and isomerization of *trans-I*-$[Ni^{III}(L^1)_{aq}]^{3+}$ 5×10^{-4} M *trans-III*-$[Ni^{II}(L^1)]^{2+}$, N_2O-saturated solution, pH 3.2, irradiation at λ = 550 nm, 18 Gy.

The observed rate constant, k_5, decreases by a factor of 10 when the pH of the solutions is raised from 3.2 to 4.2. The experiments could not be performed either at more alkaline pH values since *trans-I*-$[Ni^{II}(cyclam)]^{2+}$ isomerizes fast at higher pH,[10b] or at a more acidic pH since at pH < 3 the production of $^{\cdot}OH$ radicals is not quantitative.[23] The pH effect may be explained by the formation of *trans-I*-$[Ni^{III}(L^1)(OH)]^{2+}$[22] which might slow down the isomerization process by allowing a more energetically appropriate pentacoordinate geometry for the latter and by raising the pK_a of the Ni–N–H group, see below.

The product *trans-III*-$[Ni^{III}(L^1)_{aq}]^{3+}$ is stable on a time scale of hours at pH 3.2. At this point it must be mentioned that the specific rate constant for the isomerization process measured here differs by three orders of magnitude from that reported by Billo et al.[10b] for the same pH. This apparent discrepancy might be explained in terms of different conditions in the electrochemical experiments i.e probably the involvement of heterogeneous factors (viz. the electrode surface) in the latter study.

The isomerization process in reaction (5) might in principle proceed via one of the following mechanisms:
a) deprotonation of one of the coordinated amino groups followed by inversion
b) cleavage of the Ni–N bond followed by inversion, though it is difficult to envisage why this should be faster for $[Ni^{III}(L^1)_{aq}]^{3+}$ than for $[Ni^{II}(L^1)_{aq}]^{2+}$.

In order to differentiate between these mechanisms, it was decided to see whether the isomerization is accompanied by proton exchange of the N–H groups with the solvent. For this purpose ^{1}H-NMR experiments were carried out in order to see whether the N–H groups are transformed into N–D groups when the oxidation reaction is carried out in D_2O. The following experiments were performed.

^{1}H-NMR measurements were performed using D_2O solutions of $(2–5)\times10^{-3}$ M of *trans-I*-$[Ni^{II}(L^1)_{aq}]^{2+}$ at pH 2.0 (Figure 4, a). The broad singlet at 3.5 ppm is attributed to N–H. The quartet at 3.1 ppm is interpreted as an overlapped double triplet and is attributed to H–C–H (Figure 4, a, $-H_C$), i.e. it is a result of the splitting of the genuine triplet by coupling to the N–*H* proton. Due to overlaps the detailed signals of H_d, H_e and H_f could not be separated. When solutions containing *trans-I*-$[Ni^{II}(L^1)_{aq}]^{2+}$ were made alkaline by the addition of NaOD, the singlet disappeared and the quartet was transformed into a triplet, indicating that the amine proton exchanged with deuterium (Figure 4, b). The same solution at pH 2.0 was reacted with an equivalent amount of $Na_2S_2O_8$ to oxidize the metal centre and then immediately reduced by an equivalent amount of $NaHSO_3$. The ^{1}H-NMR spectrum of the product was then recorded. The broad known spectrum[11a] of the paramagnetic "blue" *trans-III*-$[Ni^{II}(L^1)(H_2O)_2]^{2+}$ was shifted by raising the temperature to 75 °C, where the "yellow" diamagnetic species is the prevailing one.[10b] Under these conditions the ^{1}H-NMR spectrum could be resolved. The spectrum showed no singlet at 3.5 ppm and a triplet at 3.1 ppm (Figure 4, c), indicating that isomerization proceeds via deprotonation, i.e. via route (a) above.

As sulfate was shown to stabilize $[Ni^{III}(L^i)]^{3+}$ (i = 1, 2, 7),[22,23,27,28] it seemed of interest to investigate the difference in behaviour of the two $[Ni^{III}(cyclam)]^{3+}$ isomers. CV and square-wave experiments showed that the *trans-III*-$[Ni^{III}(cyclam)]^{3+}$ isomer as expected for the relative symmetrical octahedral environment, binds two sulfate anions (Figure 5) with $K = 2\times10^6$ M^{-2}, the CVs are reversible. While the *trans-I*-$[Ni^{III}(cyclam)]^{3+}$ isomer prefers to be pentacoordinate binding only one sulfate anion with $K = 8.2\times10^5$ M^{-1}, in this case the CVs are quasi-reversible. The latter result indicates that the rate of isomerization of *trans-I*-$[Ni^{III}L]_{aq}$ is slowed down at least by several orders of magnitude by the complexation with sulfate.

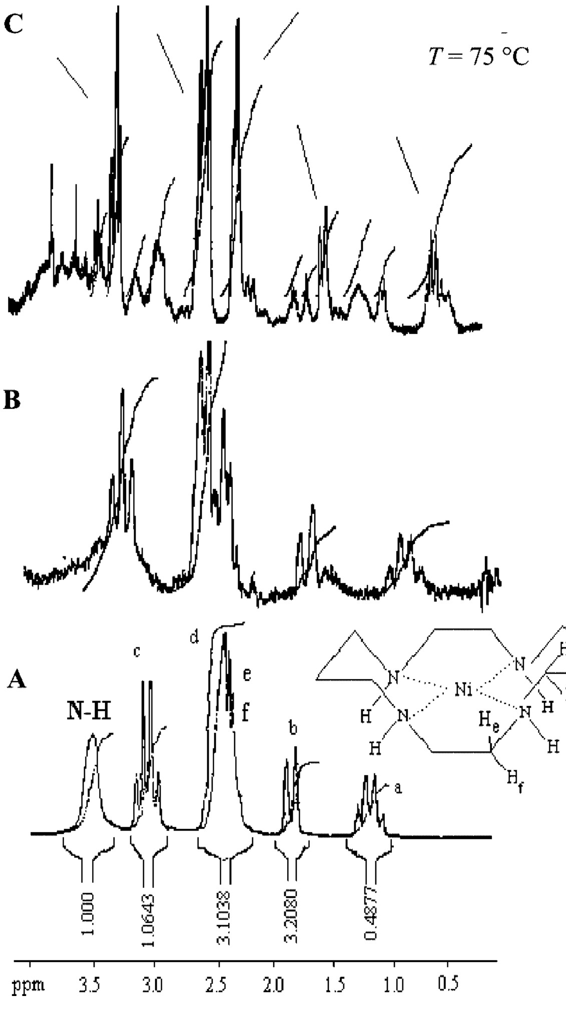


Figure 4. ^{1}H-NMR measurements performed for *trans*-I-$[Ni^{II}(L^1)]^{2+}$. **A**: *trans-I*-$[Ni^{II}(L^1)]$, pH 2.0, D_2O, room temperature. **B**: *trans*-I-$[Ni^{II}(L^1)]$, pH 8.0, D_2O, room temperature. **C**: $[Ni^{II}(L^1)]$, pH 2.0, D_2O, obtained by oxidation of the *trans-I* isomer to give the *trans-III* isomer and then reduction.

The Case of $[Ni^I(L^i)]$

Ni^{II} complexes of saturated tetraazamacrocycles undergo an one-electron reduction to produce Ni^I species, both in organic solvents[30a,30b] and in aqueous solutions.[31] The reduced species react with CO and were studied in water,[32–34] dimethylformamide[32] and in acetonitrile[21,35] as solvents.

As already mentioned, Kelly et al.[20] reported the chemistry of $[Ni^I(L^1)]^+$ in the presence of CO in aqueous solutions. When *trans-III*-$[Ni^{II}(L^1)]^{2+}$ was reduced in the presence of CO, two consecutive reactions were observed.
i. The formation of the complex *trans-III*-$[Ni^I(L^1)(CO)]^+$, in a process approaching the diffusion-controlled limit, which has an absorption band with λ_{max} = 470 nm.
ii. Followed by a unimolecular rearrangement to yield a more stable product with λ_{max} = 350 nm. The $\Delta S^{\#}$ of the latter reaction was determined to be –14.4 cal K^{-1} mol^{-1}. The observed reaction is assumed to proceed according to reaction (9).

$$trans\text{-}III\text{-}[Ni^I(L^1)(CO)]^+ \rightarrow trans\text{-}I\text{-}[Ni^I(L^1)(CO)]^+ \qquad (9)$$

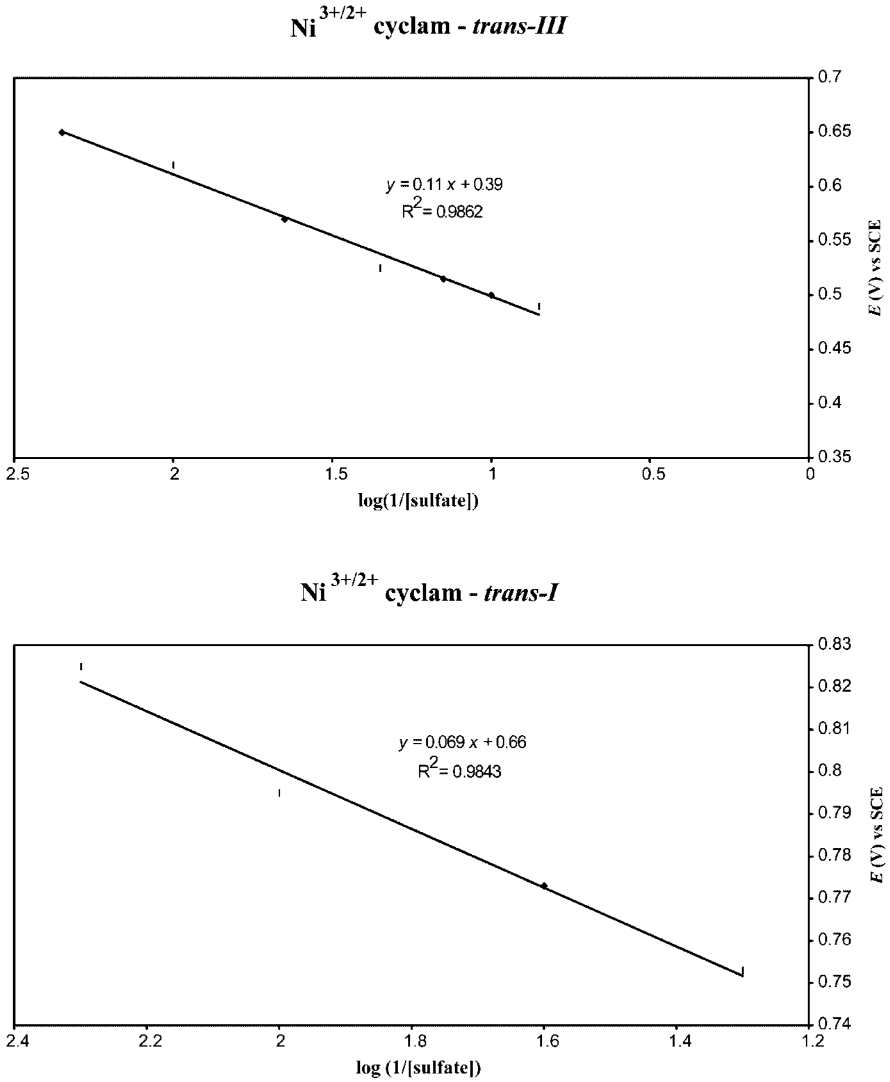


Figure 5. The dependence of $E^{1/2}$ $[Ni(L^1)]^{3+/2+}$ of the two isomers on [sulfate] 5×10^{-4} M $[Ni^{II}(L^1)]^{2+}$, 0.005–0.14 M Na_2SO_4, pH 3.2, ionic strength kept constant by addition of $NaClO_4$, working electrode: glassy carbon, 80 mV/s.

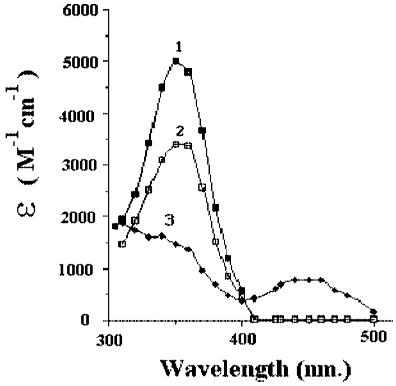
It seemed of interest to verify this assignment and to determine the source of the negative $\Delta S^{\#}$ value. For this purpose *trans-III*-$[Ni^I(L^3)]^+$ (L^3 = 1*R*,4*R*,8*S*,11*S*-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ≡ *trans-III*-tmc) and *trans-I*-$[Ni^I(L^3)]^+$ (L^3 = 1*R*,4*S*,8*R*,11*S*-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ≡ *trans-I*-tmc) were prepared in the presence of CO and their reactions with CO were studied. These experiments are of interest as it is known that the interconversion between *trans-I*- and *trans-III*-$[Ni^I(L^3)]^+$ is very slow.[18a,18b] Furthermore, we also determined $\Delta V^{\#}$ for reaction (9).

Indeed the formation of *trans-I*-$[Ni^I(L^3)]^+$ in the presence of CO is followed by a fast reaction. The rate of this process is proportional to [CO] and is attributed to reaction (13).

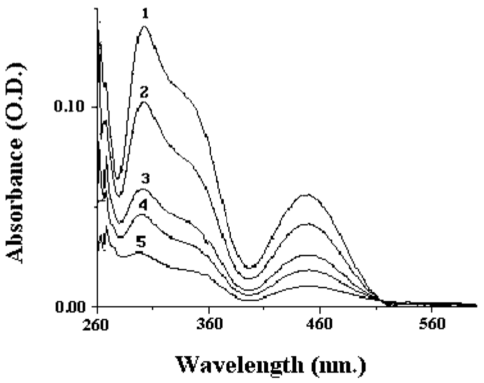
$$trans\text{-}I\text{-}[Ni^I(L^3)]^+ + CO \rightleftarrows trans\text{-}I\text{-}[Ni^I(L^3)(CO)]^+$$
$$k_{13} = 3.7\times10^8\ \mathrm{M^{-1}\,s^{-1}},\ K_{13} = 4.3\times10^3\ \mathrm{M^{-1}} \quad (13)$$

The product does not isomerize and decomposes on a time scale of several minutes. The spectra of *trans-I*-$[Ni^I(L^3)]^+$ and *trans-I*-$[Ni^I(L^3)(CO)]^+$ were measured, see Figure 6. The spectrum and the kinetics of decomposition of *trans-I*-$[Ni^I(L^3)(CO)]^+$ at pH 10.5 were also measured, Figure 7, and no isomerization was observed during the decomposition process.

No complexation of *trans-III*-$[Ni^I(L^3)]^+$ by CO was observed at pH 10.5 and a slow isomerization process was observed, which has a life time of several minutes, Figure 8. The *trans-I*-$[Ni^I(L^3)]^+$ formed in the isomerization process naturally forms the *trans-I*-$[Ni^I(L^3)(CO)]^+$ complex. Neither *trans-I*-$[Ni^I(L^3)(CO)]^+$ nor *trans-III*-$[Ni^I(L^3)]^+$ isomerizes in the presence of CO, on the time scale on which $[Ni^I(L^1)(CO)]^+$ isomerizes. This finding is in agreement with expectations due to the known rigidity of complexes of the L^3 ligand. Thus our observations corroborate the sugges-



1. Spectrum measured 8 μs after the pulse no CO
2. Spectrum measured 8 μs after the pulse 0.0002 M CO
3. Spectrum measured 36 μs after the pulse 0.0002 M CO



1. 30 s after irradiation
2. 180 s after irradiation
3. 480 s after irradiation
4. 1380 s after irradiation
5. 2670 s after irradiation

Figure 6. UV/Vis spectra of *trans-I*-$[Ni^I(L^3)_{aq}]^+$ and *trans-I*-$[Ni^I(L^3)(CO)]^+$: 5×10^{-4} M *trans-I*-$[Ni^{II}(L^3)]^{2+}$, 0.1 M HCOONa, 2×10^{-4} M CO, pH 7.4, He saturated solution. The second plot shows the spectra obtained after the solution was irradiated with 200 Gy in a 1-cm quartz cell (blank: non-irradiated solution).

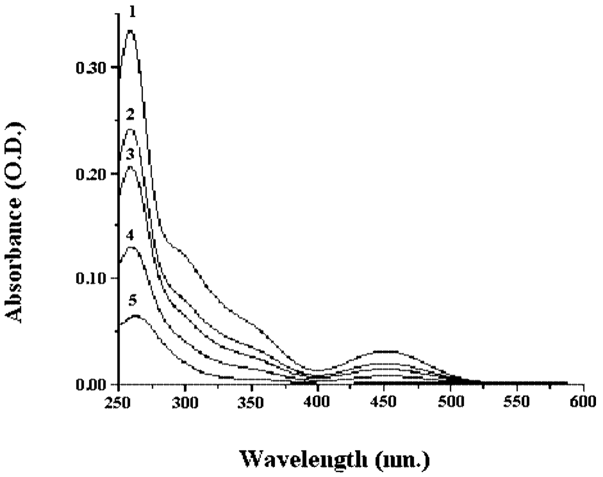
tion by Kelly et al.[20] that the fast isomerization observed is described by reaction (9).

The volume of activation of reaction (9) was found to be $\Delta V^{\#} = 0\pm1$ cm^3 mol^{-1}. This result points out that the reported $\Delta S^{\#}$ is due to a transition state in which the macrocyclic ligand is less flexible which does not involve a significant volume change during the isomerization process.

Concluding Remarks

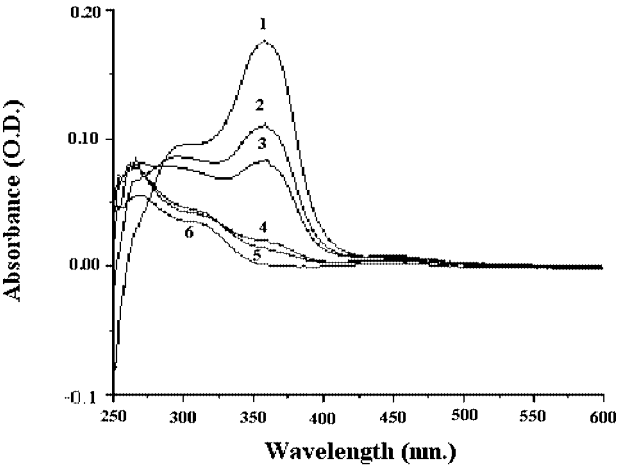
The results obtained in this study indicate that two different mechanisms are involved in the isomerization processes of nickel complexes with cyclam and cyclam derivatives as chelates.

i. Detachment of the Ni–N bond and inversion presumably via the *cis-V* isomer. This mechanism is relevant to low valent complexes and seems to occur in general for tmc complexes as was also observed for copper.[37]



1. 30 s after irradiation
2. 270 s after irradiation
3. 840 s after irradiation
4. 1620 s after irradiation
5. 2550 s after irradiation

Figure 7. UV/Vis spectra of *trans-I*-$[Ni^I(L^3)(CO)]^+$ at pH 10.5: 5×10^{-4} M *trans-I*-$[Ni^{II}(L^3)]^{2+}$, 0.1 M HCOONa, 2×10^{-4} M CO, He saturated solution. The solution was irradiated with 200 Gy in a 1-cm quartz cell (blank: non-irradiated solution).



1. 30 s after irradiation
2. 210 s after irradiation
3. 330 s after irradiation
4. 600 s after irradiation
5. 780 s after irradiation
6. 2160 s after irradiation

Figure 8. UV/Vis spectra of *trans-III*-$[Ni^I(L^3)]^+$ in the presence of CO. 5×10^{-4} M *trans-III*-$[Ni^{II}(L^3)]^{2+}$, 0.1 M HCOONa, 2×10^{-4} M CO, pH 10.5, He saturated solution. The solution was irradiated with 200 Gy in a 1-cm quartz cell (blank: non-irradiated solution).

ii. Deprotonation of coordinated N–H and inversion, presumably also via the *cis-V* isomer. This mechanism seems to be relevant to high oxidation state complexes. This mechanism explains the reason for a faster isomerization step in the case of nickel for the tervalent complex vs. the divalent complex. This mechanism corroborates also the pH effect in the case of the $[Ni^{II}(L^1)]^{2+}$ complex. A similar effect was observed also for $[Cd^{II}(L^1)]^{2+}$ and $[Zn^{II}(L^1)]^{2+}$.[38a,38b]

Experimental Section

Materials: All the chemicals used were of AR grade and were used without further purification. The solutions were prepared with heat-distilled water that was then passed through a Millipore set-up, the final resistance being greater than 10 MΩ

The complexes $[Ni^{II}(cyclam)](ClO_4)_2$, *trans-III*-$[Ni^{II}(cyclam)](ClO_4)_2$, *trans-I*-$[Ni^{II}(cyclam)](ClO_4)_2$, *trans-III*-$[Ni^{II}(tmc)](ClO_4)_2$, *trans-I*-$[Ni^{II}(tmc)](ClO_4)_2$ were prepared according to literature procedures.[10a,11,39] The complexes were characterized by C,H,N elemental analysis and UV/Vis and IR spectroscopy. The results for all the complexes were in excellent agreement with the expected formula and the literature data.

NMR Measurements: ^{1}H-NMR measurements were run at 200 MHz on a Bruker-WP-200-SY spectrometer using a 5-mm broadband probe. Spectra were acquired in the double precision mode at ambient (20 °C) and at higher (75 °C) temperatures.

A typical sample consisted of 1–2 mg of complex dissolved in 1 mL of D_2O. Homonuclear decoupling experiments were carried out using the lowest decoupling power which saturated the desired resonance. Chemical shifts were referenced by computer to the TMS frequency.

Electrochemical Measurements: A three-electrode cell was used. The working electrode for the CV measurements was a Metrohm teflon-shrouded glassy carbon electrode (0.07 cm^2). The auxiliary electrode was a Pt wire and a SCE was used as the reference electrode. The auxiliary and the reference electrodes were placed in separate compartments of the cell. All potentials are reported vs. SCE CV measurements were performed using a EG&G Princeton Applied Research potentiostat/galvanostat, Model 263, operated by a Research Electrochemistry Software EG&G PARC. Potentials were determined by square wave voltammetry. Measurements were performed at 80 mv/s.

Pulse Radiolysis: The solutions were handled by the syringe technique. Deaeration was performed by bubbling He or N_2O (when oxidizing conditions were required) through the solutions. The experiments were carried out at the linear accelerator facility of the Hebrew University of Jerusalem: 0.5–1.5 µs, 5 MeV and 200-mA pulses were used. The dose per pulse was in the range of 2.5–25 Gy/pulse. The experimental set up and the techniques used for evaluating the results have been described elsewhere in detail.[40] The high-pressure experiments were performed using an instrument which has been described in detail elsewhere.[41,42]

Preparation of *trans-I*- and *trans-III*-$[Ni^IL^3]^+$ Complexes: *trans-I*-$[Ni^I(L^3)(CO)]^+$ was prepared via the reduction of the corresponding Ni^{II} complex in the presence of CO. Aqueous He-saturated solutions containing 5×10^{-4} M *trans-I*-$[Ni^{II}(L^3)]^{2+}$, 0.1 M HCOONa, and $(0.1–1)\times10^{-3}$ M CO at pH 7.4, were irradiated by a pulse of 5 MeV electrons. Under these conditions reactions (10)–(12) have to be considered.

$$HCOO^- + H^{\cdot}/^{\cdot}OH \rightarrow COO^{\cdot-} + H_2/H_2O \quad k_{10\ H/OH} = 2.1\times10^8/3.2\times10^9\ M^{-1}\ s^{-1[36b]} \tag{10}$$

$$trans\text{-}I\text{-}[Ni^{II}(L^3)]^{2+} + e^-_{aq} \rightarrow trans\text{-}I\text{-}[Ni^I(L^3)]^+ \quad k_{11} > 1\times10^{10}\ M^{-1}\ s^{-1} \tag{11}$$

$$trans\text{-}I\text{-}[Ni^{II}(L^3)]^{2+} + COO^{\cdot-} \rightarrow trans\text{-}I\text{-}[Ni^I(L^3)]^+ + CO_2 \quad k_{12} \approx 1\times10^9\ M^{-1}s^{-1} \tag{12}$$

trans-III-$[Ni^I(L^3)]^+$ was prepared by using an analogous experimental approach.

Spectrophotometric Measurements and Slow Kinetics: The spectra and the kinetics of the relatively long lived species ($t_{1/2} \geq 20$ s) were recorded using a HP 8452 A diode-array spectrophotometer. The long lived monovalent nickel species were produced by irradiating He-saturated solutions in a 1-cm quartz spectrophotometric cell.

IR Spectra: Were recorded using KBr pellets on a NICOLET 5ZDX FT-IR spectrometer.

Elementary Analyses: Were performed at the micro-analysis laboratory at the Hebrew University in Jerusalem.

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