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Properties of monovalent nickel complexes with tetraaza-macrocyclic ligands in aqueous solutions ☆

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Abstract

The effects of N-alkylation on the redox potential of the couples $NiL^{i\,2+}/NiL^{i\,+}$, L = tetraaza-14-membered-macrocyclic ligands, and on the properties of the monovalent nickel complexes in aqueous solutions are reported for 14 complexes. The spectra and lifetimes of the $NiL^{i\,+}$ complexes are reported. The self-exchange rates for the couples $NiL^{i\,2+}/NiL^{i\,+}$ were determined. Two of the ligands were synthesized for the first time for this study. Cyclic voltammetry and pulse radiolysis were used. The results point out that: (i) N-alkylation always shifts the redox potential to a less cathodic one; this effect stems to a large degree from the decrease in the solvation energy of the complex caused by the N-alkylation of the ligand. (ii) The lifetime of the monovalent complexes is not linearly related to the redox potential of the $NiL^{i\,2+}/NiL^{i\,+}$ couples. (iii) The $NiL^{i\,+}$ complexes exist in several isomeric forms; the rate of the isomerization depends on the structure of the ligand. (iv) Different isomers of $NiL^{i\,+}$ may be formed when the complex $NiL^{i\,2+}$ is reduced by different reagents; therefore, the pulse-radiolytically formed $NiL^{i\,+}$ complexes might have different properties than those formed electrochemically.

Keywords: Nickel complexes; Aza-macrocyclic ligand complexes

1. Introduction

The discovery that tetraaza-macrocyclic ligands stabilize monovalent and tervalent nickel complexes in aprotic solvents [1] induced a variety of studies on the role of these complexes in catalytic [2], photocatalytic [3] and electrocatalytic [4] processes. Some of the latter studies were performed in aqueous solutions [2b,3a,b,4e–g], though the lifetime of most monovalent and trivalent nickel complexes in aqueous solutions is short [2b,4h,5,6]. Further interest in the chemistry of monovalent and trivalent nickel complexes with tetraaza-macrocyclic ligands in aqueous solutions stems from the recent discovery of a variety of nickel-containing enzymes, the mechanism of reaction of some of those involves monovalent [7] and trivalent [7b,g,8] nickel in the reaction centre.

Trivalent nickel complexes with tetraaza-macrocyclic ligands can be stabilized in aqueous solutions mainly via one of the following methods:

(i) Use of anionic and hydrophilic macrocyclic ligands, e.g. 5,7-dioxo-1,4,8,11-tetraaza-cyclotetradecane [9].

(ii) Availability of axial ligands, usually anionic ones, in the solution. These ligands might be bound to the macrocyclic ligand [10] or can be added as independent ligands into the solution [6e,f,11].

Monovalent nickel complexes with tetraaza-macrocyclic ligands can be stabilized in aqueous solutions mainly via N-alkylation of the macrocyclic ligand [2h,f,6b,12]. Several explanations were offered as the source of the thermodynamic stabilization of monovalent nickel complexes by N-alkylation of the macrocyclic ligands:

(i) N-alkylation of the macrocyclic ligand causes an increase of the cavity of the ligand due to the steric hindrance caused by the N-alkylation [13]. On the other hand, it was shown that an increase in the number of atoms of the macrocyclic ligand does not stabilize monovalent nickel complexes [6a]. However, it was argued that this observation is not conclusive as the increase in the number of atoms of the macrocyclic ligand also causes a change in the preferred binding angles to the central cation and the effect on the redox potential might be affected by this.

(ii) Tertiary amines are poorer σ donors than secondary amines and thus stabilize low valent transition metal complexes [6a,b]. The question why the tertiary amines are poor σ donors while alkyls are electron-donating substituents was not discussed in detail, although this observation was partially

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☆ This paper is dedicated to Professor F. Basolo.

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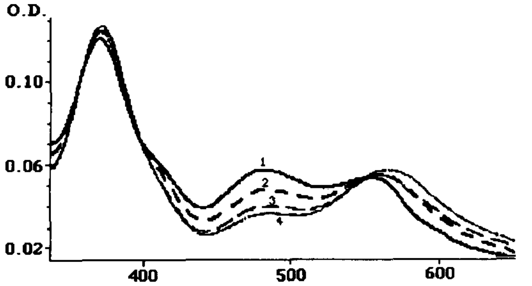


Fig. 1. Spectrum of $NiL^{10}(ClO_4)_2$ in aqueous solution: 1, immediately after dissolution (dissolution at 40 °C); 2, after 1 day; 3, after 2 days; 4, after 3 days.

attributed to the effect of the substituent on the binding angle to the central cation.

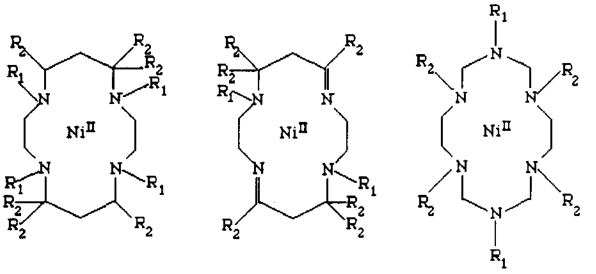
(iii) N-alkylation of the macrocyclic ligand increases the hydrophobicity of the complex, thus stabilizing low valent transition metal complexes [6b,14]. The effect is dual:

(a) As a result of N-alkylation no hydrogen bonds with the solvent are possible; thus charge delocalization is inhibited [6b,15]. This is also a plausible explanation of the observation that tertiary amine ligands are poor σ donors [14].

(b) N-alkylation increases the radius of the complex, thus decreasing its solvation energy [14,15].

In order to clarify which of these factors contributes most to the stabilization of monovalent nickel complexes in aqueous solutions it was decided to study the following points:

(i) The redox potential of the couples $NiL^{i\,2+}/NiL^{i\,+}$ for $i=5$ and 6 and compare them with those for $i=1$ and 3 [6b]. The steric hindrance in NiL^5 and NiL^6 is clearly significantly larger than in NiL^3; however, NiL^5 and NiL^6 are less hydrophobic than NiL^3.



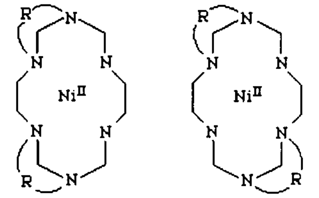
$L^1: R_1 = R_2 = H$
$L^2: R_1 = H ; R_2 = CH_3$ (meso)
$L^3: R_1 = CH_3 ; R_2 = H$ (trans3)
$L^4: R_1 = R_2 = CH_3$
$L^5: R_1 = CH_2CH_2OH ; R_2 = H$
$L^6: R_1 = CH_2COOH ; R_2 = H$

$L^7: R_1 = H ; R_2 = CH_3$
$L^8: R_1 = R_2 = CH_3$

$L^9: R_1 = CH_3 ; R_2 = H$
$L^{10}: R_1 = R_2 = CH_3$

(ii) Compare ΔS° for the reduction of $NiL^{i\,2+}$ for $i=1$–4. These experiments cannot be carried out for $i=5$ and 6 as the electrochemical waves are irreversible for these couples (see below). It is reasonable to assume that the major differences in ΔS° for these complexes will stem from the different reorganization of the outer sphere of solvation, as the macrocyclic ligands are similar and relatively rigid. If indeed $NiL^{i\,2+}$, $i=3$ and 4, are considerably less solvated than $NiL^{i\,2+}$, $i=1$ and 2, then ΔS° should be considerably smaller for the former [16].

(iii) Study the chemical properties of $NiL^{i\,+}$, $i=7$–14, in aqueous solutions applying the cyclic voltammetry and pulse radiolysis techniques. Some of the properties of the monovalent nickel complexes of L^i, $i=7$ [17a,b], 9 [18], 11–14 [1k,19], in aprotic media were studied previously by electrochemical techniques. The complexes $NiL^{i\,+}$, $i=8$ and 10, were not synthesized previously.



$L^{11}: R = (CH_2)_2$
$L^{12}: R = (CH_2)_3$

$L^{13}: R = (CH_2)_2$
$L^{14}: R = (CH_2)_3$

The aim in the study of the properties of the latter complexes was:

(i) To obtain more information on the factors determining the redox potentials of the couples $NiL^{i\,2+}/NiL^{i\,+}$. Thus, for example, it seemed of interest to compare the properties of L^i, $i=7$ and 8, with those of L^i, $i=2$ and 4, respectively, as the imine group is both hydrophobic and a π-acceptor. Similarly, it is of interest to compare the effect of the aliphatic chain and that of the geometry of the complex for L^i, $i=11$–14.

(ii) To analyse the factors affecting the kinetic stability of the monovalent nickel complexes.

(iii) To develop new single and two-electron reducing reagents, which might also act as electro-catalysts or photocatalysts, with a variety of redox potentials.

It should be pointed out that two-electron reducing agents for the desired processes, e.g., the reduction of water and carbon dioxide, should have less positive redox potentials for the couples $NiL^{i\,3+}/NiL^{i\,2+}$, than those of $NiL^{i\,2+}$, $i=3$ and 4, and it is reasonable to expect that this will be the case for $NiL^{i\,2+}$, $i=11$–14.

2. Experimental

2.1. Materials

All the chemicals used were of AR grade and were used without further treatment. The solutions were prepared with heat-distilled water that was then passed through a Millipore setup, the final resistance being above 10 MΩ.

The complexes $Ni^{II}L^i(ClO_4)_2$, $i=1$–7 [6b,10a,b,20], 9 [18] and 11–14 [1i,k], were prepared according to literature procedures. The complexes were characterized using C, H, N elemental analysis and UV–Vis and IR spectroscopy. Elemental analysis was performed at the Micro-analysis Laboratory, The Hebrew University, Jerusalem. The results for all the complexes were in excellent agreement with the expected formula and the literature data.

2.2. *Synthesis of NiL^8(ClO$_4$)$_2$*

To 2 g of NiL^7(ClO$_4$)$_2$ dissolved in 30 ml of DMSO, 4 g of powdered KOH(s) were added and the solution was then stirred for approximately 2 h. Methyl iodide (4 ml) was then dropwise added and the excess of KOH was removed by filtration. A saturated solution of NaClO$_4$ was added to the filtrate and the precipitate was filtered out and washed with ethanol and diethyl ether. The product was recrystallized from CH$_3$CN and precipitated by addition of diethyl ether. The PF$_6^-$ salt was obtained by dissolving the perchlorate salt in H$_2$O and addition of HPF$_6$. The complex precipitates as the dihydrate (see below) or another similar hydrate. *Anal.* Calc. for $NiC_{18}H_{40}N_4P_2F_{12}O_2$: C, 31.19; H, 5.77; N, 8.08; C/N, 3.86. Found: C, 32.07; H, 4.86; N, 8.28; C/N, 3.87. IR analysis, in KBr, showed no N–H stretch, about 3200 cm^{-1}, the C–N stretch at about 1670 cm^{-1} remained, as well as a broad wave at 3250–3700 cm^{-1} which is typical for O–H stretch.

Notice: Perchlorate salts are explosives and have to be handled with care.

2.3. *Synthesis of NiL^{10}(ClO$_4$)$_2$*

Methyl iodide (6 ml) was dropwise added to 2 g of NiL^9(ClO$_4$)$_2$ dissolved in 30 ml of DMSO. Immediately afterwards, 4–6 g of powdered KOH(s) were slowly added to the stirred solution. The methylation reaction was left to proceed while the temperature was kept in the range of 22–25 °C. The solution was stirred until a dark green colour persisted. Residual solids were removed by filtration. The violet filtrate thus obtained was treated with a concentrated solution of NaClO$_4$ until an orange precipitate formed. (Note: If the filtrate obtained is not violet, dilute HClO$_4$ is added until a violet colour persists in the solution.) The orange crystals formed were filtered out and recrystallized from hot ethanol. *Anal.* Calc. for $NiC_{14}H_{34}N_6P_2F_{12}$: C, 26.5; H, 5.4; N, 13.2; C/N, 2.0. Found: C, 25.0; H, 4.9; N, 11.7; C/N, 2.1. IR analysis, in KBr, showed no N–H stretch, about 3200 cm^{-1}. The PF$_6^-$ salt was obtained by dissolving the perchlorate salt in DMSO and addition of HPF$_6$.

Notice: Perchlorate salts are explosives and have to be handled with care.

2.4. *Electrochemical measurements*

A three-electrode cell was used. The working electrode for the cyclic voltammetry (CV) measurements was a Metrohm E-410 hanging mercury drop electrode (HMDE). The auxiliary electrode was a Pt wire and a SCE was used as the reference electrode. The auxiliary and reference electrodes were placed in separate compartments of the cell. All potentials are given versus SCE.

CV measurements were performed using a CV-1B-240 BAS cyclic voltammograph, a Fluke-8000 A digital multimeter and a YEW-3086 XY recorder.

Note that the cyclic voltammograms herein presented always show one-electron redox processes as compared to CV measurements obtained for the NiL$^{3\,2+/+}$ couple which was shown to be a single electron redox process [2h,6b].

2.5. *ΔS^o measurements*

The difference in entropy ($\Delta S^o = \Delta S^o_{red} - \Delta S^o_{ox}$) was calculated from the temperature dependence of the redox potentials of the nickel complexes. The temperature range employed was 5–70 °C. The redox potentials were measured by CV in an arrangement of non-isothermic cells as described elsewhere [21].

2.6. *Pulse radiolysis*

The solutions were handled by the syringe technique. Deaeration was performed by bubbling He 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 1000–3000 rad/pulse. The experimental setup and the techniques used for evaluating the results have been described elsewhere in detail [22,23].

2.7. *Spectroscopic measurements and slow kinetics*

The spectra and the kinetics of the relatively long-lived species ($t_{1/2} \geq 20$ s), as well as the pK_a of the axially bound water, 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.

3. Results and discussion

3.1. *Characterization of NiL^8(ClO$_4$)$_2$*

The elemental analysis as well as the IR data indicate that the complex obtained, both in the precipitate and in solution, is [NiL^8(H$_2$O)$_2$](ClO$_4$)$_2$, i.e. the nickel is in its high spin configuration. The NMR spectrum of the complex in aqueous solutions, or in a variety of organic solvents, consists of a broad band with no fine structure, which could not be analysed with the available apparatus. This result points out that the N-methylation of L^7 decreases the ligand field induced by the ligand in accord with expectations.

The UV–Vis spectra, at pH 6.0, of the complexes are for NiL^7(ClO$_4$)$_2$: λ_1 216 ($\epsilon = 14\,000$ M^{-1} cm^{-1}); λ_2 (shoulder) 230 ($\epsilon \sim 12\,000$ M^{-1} cm^{-1}); λ_3 282 ($\epsilon = 4600$ M^{-1}

cm^{-1}); λ_4 436 ($\epsilon=82$ M^{-1} cm^{-1}); and for $[NiL^8(H_2O)_2](ClO_4)_2$: λ_1 194 ($\epsilon=13\,800$ M^{-1} cm^{-1}); λ_2 224 ($\epsilon=15\,500$ M^{-1} cm^{-1}); λ_3 284 ($\epsilon=4900$ M^{-1} cm^{-1}); λ_4 (non-symmetrical band) about 450 ($\epsilon\sim1200$ M^{-1} cm^{-1}). Clearly the band of $[NiL^8(H_2O)_2]^{2+}$ in the visible region cannot be attributed to a pure d–d transition as the extinction coefficient is too high.

3.2. Characterization of $NiL^{10}(ClO_4)_2$

No NMR spectra of solutions of $NiL^{10}(ClO_4)_2$ dissolved in water, DMSO or acetonitrile are obtained; a result which suggests that the complex has a high spin configuration in these solutions. When the complex is dissolved in nitromethane (the solubility is very low) ^1H NMR spectra are obtained but, due to the low solubility, their quality is poor. This result suggests that in this solvent the complex has a low spin configuration.

The UV–Vis spectrum of $NiL^{10}(ClO_4)_2$ in nitromethane shows one absorption band in the visible region with $\lambda_{max}=480$ nm ($\epsilon\sim86$ M^{-1} cm^{-1}) which is red shifted relative to that of $NiL^9(ClO_4)_2$ for which $\lambda_{max}=449$ nm ($\epsilon=56$ M^{-1} cm^{-1}) [18]. The red shift is in accord with the expected effect of N-methylation on the ligand field splitting [1g,6b,14,15].

When $NiL^{10}(ClO_4)_2$ is dissolved in water its spectrum is time dependent (Fig. 1). The rate of change depends on the temperature. The final spectrum has five absorption bands as follows: λ_1 196 ($\epsilon=6200$ M^{-1} cm^{-1}); λ_2 224 ($\epsilon=7900$ M^{-1} cm^{-1}); λ_3 372 ($\epsilon=31$ M^{-1} cm^{-1}); λ_4 580 ($\epsilon=19$ M^{-1} cm^{-1}); $\lambda_5\sim810$ ($\epsilon=5$ M^{-1} cm^{-1}). This spectrum clearly indicates that the stable form of this complex in aqueous solutions has a high spin configuration. As the rate of equilibration is very slow, much slower than the octahedral (high spin)–square planar (low spin), blue–yellow [12] equilibration, it has to be concluded that the complex rearranges itself into its *cis* isomer in aqueous solutions. As the complex is only slightly soluble in its *trans* form and dissolves slowly some heating is required in order to obtain a solution. Thus we were unable to get a solution of the pure *trans* isomer in aqueous solutions.

3.3. Binding constants of hydroxides to $Ni(II)L^{9;\,10}{}_{aq}$

In alkaline solutions the high spin forms of the tetraazamacrocyclic complexes are transformed into the corresponding hydroxo complexes:

$$NiL^i(H_2O)_2^{2+} \leftrightharpoons NiL^i(OH)(H_2O)^+ + H_3O^+ \text{ (or } NiL^i(OH)_2 + 2H_3O^+) \quad (1)$$

The hydroxo complex may also appear as a penta-coordinated high spin complex [6b,d,e]. It was shown that N-alkylation of ligands, open chain and macrocyclic ones, lowers the pK_a values of their complexes [6b,16]. This effect is attributed to the decreased charge delocalization in the complexes with the N-methylated ligands [14,15]. It was decided therefore to measure the pK_a of $NiL^{9;\,10}(H_2O)_2^{2+}$ by spectrophotometric titrations. The corresponding measurements are impossible for $NiL^8(H_2O)_2^{2+}$ as the aqua and hydroxo complexes have very similar spectra. The results are summed up in Table 1. The results are in accord with expectations, i.e. the pK_a of $NiL^{10}(H_2O)_2^{2+}$ is considerably lower than that of $NiL^9(H_2O)_2^{2+}$. It is of interest to note that, whereas the pK_a values of $NiL^3(H_2O)_2^{2+}$ and of $NiL^{10}(H_2O)_2^{2+}$ are similar as expected, those of $NiL^1(H_2O)_2^{2+}$ and $NiL^9(H_2O)_2^{2+}$ differ considerably though the ligand field splittings of the latter complexes are very similar, as can be deduced from the location of their absorption bands in the visible (445 nm [1g] and 446 nm [18], respectively). The source of this discrepancy is not clear at present.

Table 1
Binding constants of hydroxide ions to $NiL^{i\,2+}{}_{aq}$ complexes

L^i	$pK_a([NiL^i(H_2O)_2^{2+}]/[NiL^i(H_2O)(OH)^+][H_3O^+])$
L^1	13.67 [b]
L^2	> 14.5 [a]
L^3	11.94 [b]
L^4	13.6 [a]
L^9	12.7 [c]
L^{10}	11.7 [c]

[a] From Ref. [21].
[b] From Ref. [32].
[c] This work.

3.4. Electrochemical studies

The redox potentials of the couples $NiL^{i\,2+}/NiL^{i\,+}$ ($i=5$–14) in aqueous solutions were determined using the CV technique, with a HMDE as the working electrode, unless otherwise stated, versus SCE. The complexes were reduced in neutral and/or slightly alkaline aqueous solutions and the reduction potentials are independent of the supporting electrolyte used: NaCl, $NaClO_4$, Na_2SO_4, K_2SO_4, unless otherwise stated below. The choice of the supporting electrolyte used often depended on its effect on the solubility of the complex. The results are summed up in Table 2.

Cyclic voltammograms of $NiL^{5\,2+}$ (Fig. 2) indicate that the reduction is a single electron process but not an electrochemical reversible process; the reduction peak occurs at −1.31 V, whereas the oxidation peak occurs at −1.03 V. However, a shoulder on the oxidation peak is observed at −1.25 V, where the oxidation peak should appear if the process is reversible. The results suggest that NiL^{5+} isomerizes in a fast process on the time scale of the CV experiment. The redox potential in the absence of the isomerization is estimated to be −1.28 V which is the value used in Table 2.

Cyclic voltammograms of $NiL^{6\,2+}$ are irreversible; a reduction peak appears at −1.46 V and no oxidation peak is

Table 2
Properties of the $Ni^{I}L^{i+}{}_{aq}$ complexes

L	λ_{max} (ϵ) [a] (nm (M^{-1} cm^{-1}))	$E^{o}{}_{1/2}(Ni^{II}L^{i}{}_{aq})/(Ni^{I}L^{i}{}_{aq})$ [b] (V vs. SCE)	k_{12} [c] (M^{-1} s^{-1})	k_{11} [c] (M^{-1} s^{-1})	$t_{1/2}$ [c] (min)
L^1 [d]	375(4500)	−1.58	6.4×10^8	0.00034	several s
L^2 [d]	380(5150)	−1.42	3.8×10^8	0.0035	~1
L^3 [d]	355(3150)	−1.15	4.9×10^7	0.021	~30
L^4 [d]	335(3600)	−0.98	3.0×10^7	0.75	several h
L^5		~ −1.28			
L^6		~ −1.40			
L^7		−1.35 [h]			
L^8	440(5250); 480(4400); 600(3200)	−1.14 [h]			~40 ms [j]
L^9	385(7440) 248(4270); 302(1050); 350(870) [e]	< −1.45 [i]	1.6×10^8	0.0001	<0.5 5.8 [e]
L^{10}	350(2500) 304; 438 [e]	−1.13 [f]; 1.32 [g]			<0.5 35 [e]
L^{11}	358(5280); 582(170)	−1.37	2.0×10^8	0.0024	2.3
L^{12}	374(5560)	−1.25	1.8×10^8	0.039	35
L^{13}	356(5190) 298(850); 356(1230) [e]	−1.38	1.1×10^8	0.00034	1.4 23 [e]
L^{14}	368(5750)	−1.27	9.6×10^7	0.0044	23

[a] Error limits for λ are ±10 nm and for ϵ ±20%.

[b] Error limits are ±0.01 V; except for $L^5$and L^6 for which the error limits are ±0.02 V.

[c] Error limits are ±10%.

[d] Data from Ref. [6b].

[e] Results for the long-lived isomer.

[f] Redox potential of the *trans* isomer.

[g] Redox potential of the *cis* isomer.

[h] Working electrode: graphite, see text.

[i] See text.

[j] Lifetime from pulse-radiolysis studies, the electrochemical lifetime is significantly longer, see discussion.

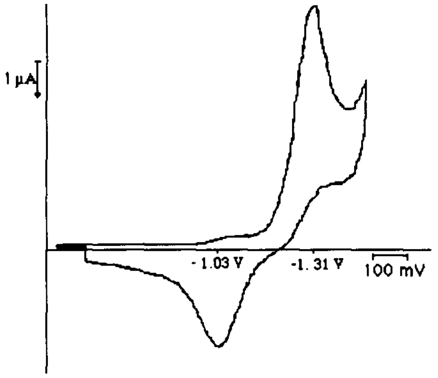


Fig. 2. Cyclic voltammograms at pH 6.5 of 0.002 M $NiL^{5\,2+}$; supporting electrolyte 0.5 M Na_2SO_4; v = 50 mV/s; working electrode HMDE; reference electrode SCE.

observed in the back-scan even at scan rates of 100 mV/s. Clearly the monovalent nickel complex NiL^{6+} is very short lived, an observation which is not surprising in view of the redox potential of the couple $NiL^{6\,3+}/NiL^{6\,2+}$. The redox potential of the couple $NiL^{6\,2+}/NiL^{6+}$ is estimated as about −1.40±0.03 V as the peak-to-peak separation is not larger than 120 mV in any of the systems studied.

Cyclic voltammograms of $NiL^{8\,2+}$ on HMDE show a very broad and asymmetrical reduction wave from which a redox potential of −1.30 V is estimated (Fig. 3(A)). Cyclic voltammograms of $NiL^{7\,2+}$ under the same conditions have a more conventional shape and indicate a redox potential of −1.50 V. A detailed analysis indicates that these divalent complexes are adsorbed to the mercury. Therefore, cyclic voltammograms of $NiL^{8\,2+}$ were performed on a graphite electrode (Fig. 3(B)) on which reversible, single electron waves were obtained. Furthermore, on this electrode the

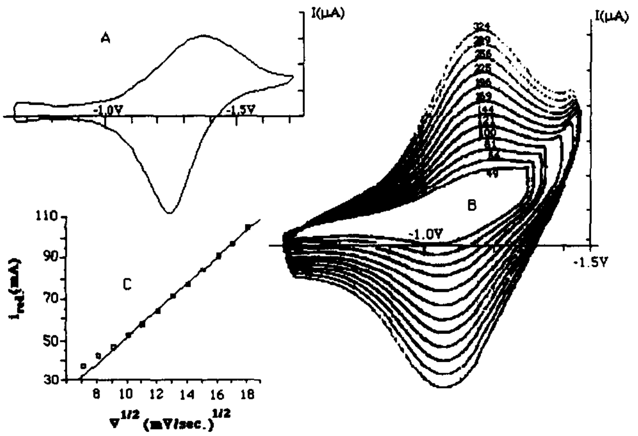


Fig. 3. Cyclic voltammograms at pH 6.5 of 0.0005 M $NiL^{8\,2+}$; supporting electrolyte 0.5 M NaCl + 0.03 M $NaClO_4$: (A) working electrode HMDE, scan rate 100 mV/s, *Y* scale 0.25 mA/division; (B) working electrode graphite, *Y* scale 12.5 mA/division, scan rate on each scan. (C) Dependence of the reduction wave on scan rate.

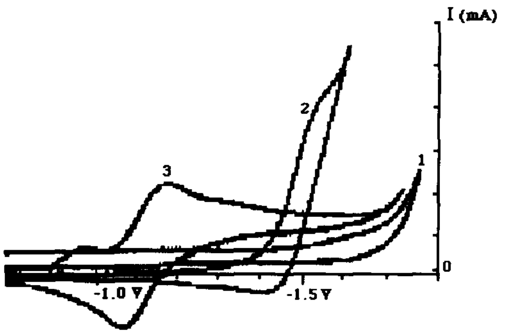


Fig. 4. Cyclic voltammograms at pH 6.5 of 0.001 M $NiL^{9;\,10}(ClO_4)_2$; supporting electrolyte 0.5 M NaCl; $v = 100$ mV/s; Y scale 1.25 mA/division; working electrode HMDE; reference electrode SCE: 1, supporting electrolyte only; 2, $NiL^9(ClO_4)_2$; 3, $NiL^{10}(ClO_4)_2$, fresh solution dissolved at 40 °C.

dependence of the current on the scan rate (Fig. 3(C)) indicates that the current is diffusion controlled. On this electrode the redox potentials are -1.14 and -1.35 V, respectively; these values are attributed to the true redox potentials of the complexes and are quoted in Table 2. On mercury clearly the divalent complexes are adsorbed more strongly than the monovalent complexes. This adsorption causes the shift of the half-wave potentials of the complexes to more cathodic values.

The cyclic voltammograms of $NiL^{10\,2+}$ depend on the way the solution is prepared due to the isomerization of this complex with time (see above). Cyclic voltammograms of freshly prepared solutions, dissolved at 40 °C, of $NiL^{10\,2+}$ on HMDE consist of a pre-wave attributed to adsorption and a quasi-reversible single electron wave (Fig. 4). When the solution is allowed to stand for a few days, or heated for a few minutes, until all the complex is in its *cis* configuration the reduction wave becomes very broad and irreversible, i.e., $\Delta E_p \sim 350$ mV. The estimated redox potential of the *cis* isomer is -1.32 V, whereas that of the *trans* isomer, obtained from the freshly prepared solutions, is -1.13 V. Cyclic voltammograms of $NiL^{9\,2+}$ on HMDE show only a shoulder on the water reduction wave, which is shifted to less cathodic potentials than in the absence of the complex (Fig. 4). From the results, the redox potential of the complex is estimated as less than -1.45 V and it is concluded that this complex is an electrocatalyst for the reduction of water on mercury. Analogous observations were reported for other nickel complexes with tetraazamacrocyclic ligands [4f,g].

Cyclic voltammograms of $NiL^{i\,2+}$, $i = 11$–14, indicate that these complexes are reduced via one-electron quasi-reversible electrochemical processes, $\Delta E_p \sim 80$ mV (Fig. 5). The results clearly indicate that the monovalent complexes of these ligands are relatively long lived.

The results of the electrochemical studies are summed up in Table 2. The results of the CV studies lead to the following conclusions:

(i) N-alkylation of the macrocyclic ligands shifts in all cases the redox potential of the $NiL^{i\,2+}$ to less cathodic potentials. This finding corroborates the earlier conclusions on this point [6b,14].

(ii) The effect of N-methylation of L^1 and L^9 on the redox potential of their complexes is similar.

(iii) It is of interest to note that the redox potential of $NiL^{7\,2+}$ is similar to those of $NiL^{11\,2+}$ and $NiL^{13\,2+}$. In the latter two complexes, two of the four nitrogen-donating atoms are secondary ones and two are tertiary ones. Whereas, in the former, two of the nitrogen atoms are secondary ones and two are imines. The effect of imine groups on the redox potential of such complexes was attributed to their π acidity [12,17a]. However, one should note that imine groups also inhibit charge delocalization via hydrogen bonding of the type M^n–N–H···O. Thus, part of the stabilization by imine groups is probably due to their hydrophobic nature. This idea is corroborated by the similar redox potentials of $NiL^{8\,2+}$, $NiL^{3\,2+}$ and $NiL^{10\,2+}$, which all have four tertiary donating nitrogen atoms (Table 2).

(iv) The redox potentials of $NiL^{12\,2+}$ and $NiL^{14\,2+}$ are less cathodic than those of $NiL^{11\,2+}$ and $NiL^{13\,2+}$. The difference between these two couples is only in the length of the $(CH_2)_n$ bridging groups. Clearly, the longer chain induces a more hydrophobic nature to the complexes and shifts the redox potentials to less cathodic ones.

(v) The observation that the redox potentials of $NiL^{5\,2+}$ and $NiL^{6\,2+}$ are considerably more cathodic than that of $NiL^{3\,2+}$, although the substituents on L^5 and L^6 are considerably bulkier than the methyls on L^3, clearly points out that steric hindrance is not the major contribution to the effect of N-alkylation on the redox potentials of these complexes. These observations are attributed to the more hydrophilic nature of the substituents on L^5 and L^6.

(vi) Many of the cyclic voltammograms indicate that the redox processes are only quasi reversible, i.e., suggest that the electron transfer process is accompanied with some chem-

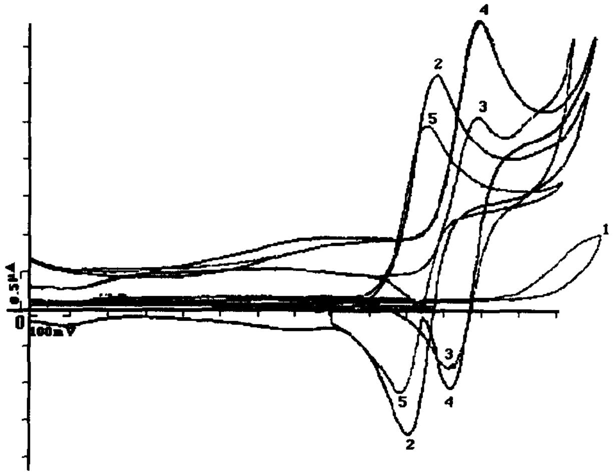


Fig. 5. Cyclic voltammograms at pH 9.3 of 0.002 M $NiL^{i\,2+}$; supporting electrolyte 0.15 M NaCl; $v = 15$ mV/s; working electrode HMDE; reference electrode SCE: 1, supporting electrolyte only; 2, $NiL^{14\,2+}$; 3, $NiL^{11\,2+}$; 4, $NiL^{13\,2+}$; 5, $NiL^{12\,2+}$.

Table 3
$\Delta S°$ for the reduction of the $\mathrm{NiL}^{i\,2+}_{\mathrm{aq}}$ complexes

L	$E°$ (V)	$\Delta S°$ (cal mol^{-1} deg^{-1})
L^1	−1.58	20.3
L^2	−1.42	22.3
L^3	−1.15	25.0
L^4	−0.98	3.0

ical process, most probably isomerization processes (see below).

3.5. ΔS^o measurements

If indeed a large part of the stabilization of the monovalent nickel complexes by N-alkylation is due to the hydrophobic nature of the complexes with tertiary-amine ligands, then the solvation of the latter is considerably smaller than that of the complexes with secondary-amine ligands. It was shown that a decrease in the solvation of the high valent complex decreases the $\Delta S°$ of the reduction process, i.e. $\Delta S°_{\mathrm{red}} - \Delta S°_{\mathrm{oxid}}$ [14,16]. Indeed, it was shown that $\Delta S°$ for the reduction of $\mathrm{CrL}^{3\,3+}$ is considerably smaller than that for the reduction of $\mathrm{CrL}^{1\,3+}$ [24] and that the single electron reduction of several Cu(II) complexes with open chain tertiary-amine ligands has a very small $\Delta S°$ [15]. In order to determine the contribution of hydrophobicity of the nickel complexes as a stabilization factor of the monovalent nickel complexes, it was decided to measure $\Delta S°$ for the reduction of $\mathrm{NiL}^{i\,2+}$, $i = 1$–4. These complexes were chosen as they are extreme examples of the effect studied. The results are summed up in Table 3.

The results indeed indicate that $\Delta S°$ for the reduction of $\mathrm{NiL}^{4\,2+}$ is considerably smaller, i.e. by about 20 cal mol^{-1} deg^{-1}, than for the reduction of $\mathrm{NiL}^{2\,2+}$. The contribution of this change in $\Delta S°$ can be calculated. The $\Delta E°$ between the complexes corresponds to $\Delta\Delta G°$ as follows:

$$\Delta\Delta G^o = nF\Delta E° = 1 \times 96\,500 \times (1.42 - 0.98)/4.18 = 10\,158 \text{ cal mol}^{-1}$$

while the change in entropy is

$$\Delta\Delta S^o = 295(22.3 - 3.0) = 5693 \text{ cal mol}^{-1}$$

The results thus point out that at least in this case more than 50% of the change in $E°$ caused by N-methylation is due to the entropy change in the reduction process. This finding corroborates the conclusion that a large part of the stabilization of monovalent nickel complexes by N-alkylation is due to the hydrophobic nature of the N-alkylated complexes. It should be pointed out that the decrease in solvation is also expected to contribute to $\Delta H°$.

Surprisingly the $\Delta S°$ values for the reductions of $\mathrm{NiL}^{3\,2+}$ and of $\mathrm{NiL}^{1\,2+}$ are similar. A plausible explanation for this observation is as follows. The electrochemical reduction of $\mathrm{NiL}^{4\,2+}$ on the HMDE is reversible only if the solution is left to stand for a prolonged period over a mercury pool [6b]. This observation was attributed to some kind of isomerization of the $\mathrm{NiL}^{4\,2+}$ complex in contact with mercury [6b]. Therefore, the measurements of $\Delta S°$ for $\mathrm{NiL}^{4\,2+}$ were carried out after such an equilibration. It is proposed that probably the reduction of $\mathrm{NiL}^{3\,2+}$ also involves some kind of isomerization and that this isomerization is the source of the large $\Delta S°$ observed in this case. Further evidence that the reduction of the $\mathrm{NiL}^{i\,2+}$ complexes is often accompanied by significant isomerization processes is given below.

3.6. Pulse-radiolysis studies

As the electrochemical results suggested that the monovalent nickel complexes might prefer a different ligand configuration than the divalent ones, it was decided to study this point by applying the pulse-radiolysis technique. He saturated aqueous solutions containing 2×10^{-4} M $\mathrm{NiL}^{i}(\mathrm{ClO_4})_2$, 0.05 M HCOONa, pH 3–11, were irradiated. Under these conditions the $\mathrm{NiL}^{i\,+}$ complexes are formed via the following reaction sequence [25]:

$$\mathrm{H_2O} \xrightarrow{e^-;\ \gamma} e^-_{\mathrm{aq}}(2.65);\ \mathrm{H^{\bullet}}(0.60);\ {}^{\bullet}\mathrm{OH}(2.65);\ \mathrm{H_2}(0.45);\ \mathrm{H_2O_2}(0.75) \qquad (2)$$

where the values in parentheses give the relative yields of the primary products [26].

$$\mathrm{HCOO^-} + \mathrm{H^{\bullet}}/{}^{\bullet}\mathrm{OH} \rightarrow {}^{\bullet}\mathrm{COO^-} + \mathrm{H_2}/\mathrm{H_2O}$$
$$\mathrm{k}_H = 2.1 \times 10^8\ \mathrm{M^{-1}\,s^{-1}} \qquad (3)$$
$$\mathrm{k_{OH}} = 3.2 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{NiL}^{i\,2+}_{\mathrm{aq}} + e^-_{\mathrm{aq}} \rightarrow \mathrm{NiL}^{i\,+}_{\mathrm{aq}} \qquad (4)$$

$$\mathrm{NiL}^{i\,2+}_{\mathrm{aq}} + {}^{\bullet}\mathrm{COO^-} \rightarrow \mathrm{NiL}^{i\,+}_{\mathrm{aq}} + \mathrm{CO_2} \qquad (5)$$

The hydrated electron, e^-_{aq}, is a powerful single electron reducing agent, $E° = -2.87$ V versus NHE [27] and accordingly reduces all the $\mathrm{NiL}^{i\,2+}_{\mathrm{aq}}$ complexes, $k_4 > 10^{10}\ \mathrm{M^{-1}\,s^{-1}}$ was obtained.

3.7. Reductions by $CO_2^{\bullet -}$ and comments on the properties of $NiL^{i\,2+}_{aq}$ as catalysts for the reduction of CO_2

$\mathrm{CO_2^{\bullet -}}$ is a powerful single electron reducing agent, $E° = -1.90$ V versus NHE [27b]. It is however an inner-sphere reducing agent, due to the fact that it is bent and the product $\mathrm{CO_2}$ is linear. The measured specific rates of reaction (5) are $1 \times 10^9 < k_5 < 2 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$, with one exception, the rate of reduction of $\mathrm{NiL}^{4\,2+}_{\mathrm{aq}}$ is only $k_5 = 4 \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$ due to the steric hindrance in this case.

As it was shown that $\mathrm{CO_2}$ forms complexes with $\mathrm{NiL}^{i\,+}_{\mathrm{aq}}$ complexes [4g,29] and as reaction (5) proceeds via the inner-sphere mechanism, it is reasonable to suggest that it is better described by

$$\mathrm{NiL}^{i\,2+}{}_{\mathrm{aq}}+{}^{\bullet}\mathrm{COO}^- \rightarrow \mathrm{L}^i\mathrm{Ni}^+\cdot\mathrm{CO}_2 \rightleftharpoons \mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}+\mathrm{CO}_2 \qquad (5a)$$

However, the rate of CO_2 loss from the transient complex is expected to be extremely high due to the Jahn–Teller distortion of monovalent nickel complexes and due to the very low stability constants of these complexes [4g,29].

$\mathrm{NiL}^{1\,2+}$ and some analogous complexes were shown to be electrocatalysts [4], photo-electrocatalysts [3b] and photocatalysts [3] for the reduction of CO_2. Such a catalysis can proceed in principle via one of the following routes:

(i) Via reaction (−5) followed by the reaction of $\mathrm{CO}_2^{\bullet -}$ with a second $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$. However, as the redox potential of the couple $\mathrm{NiL}^{1\,2+}{}_{\mathrm{aq}}/\mathrm{NiL}^{1\,+}{}_{\mathrm{aq}}$ is −1.34 V versus NHE, one calculates $K_5(\mathrm{NiL}^1) \sim 10^{9.5}$ and $k_{-5}(\mathrm{NiL}^1) \sim 3\ \mathrm{s}^{-1}$. The latter rate seems considerably too low to explain the observed electrocatalytic currents.

(ii) Via a two-electron redox reaction, i.e. via

$$\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}+\mathrm{CO}_2+2\mathrm{H}_3\mathrm{O}^+ \rightarrow \mathrm{NiL}^{i\,3+}+\mathrm{CO}+3\mathrm{H}_2\mathrm{O} \qquad (6)$$

However, from the redox potentials of the couples $E^{\circ}(\mathrm{NiL}^{1\,2+}{}_{\mathrm{aq}}/\mathrm{NiL}^{1\,+}{}_{\mathrm{aq}}) = -1.34$ V and $E^{\circ}(\mathrm{NiL}^{1\,3+}{}_{\mathrm{aq}}/\mathrm{NiL}^{1\,2+}{}_{\mathrm{aq}}) = 1.00$ V [12], one calculates $E^{\circ}(\mathrm{NiL}^{1\,3+}{}_{\mathrm{aq}}/\mathrm{NiL}^{1\,+}{}_{\mathrm{aq}}) = -0.17$ V and, as $E^{\circ}(\mathrm{CO}_2+2\mathrm{H}_3\mathrm{O}^+/\mathrm{CO}+3\mathrm{H}_2\mathrm{O}) = -0.103$ V [28], it is clear that reaction (6) is exothermic only at $\mathrm{pH} < 1$. However, the efficiency of the electrocatalytic current is pH independent at $\mathrm{pH} < 5$ [4g].

Thus, this mechanism also cannot account for the observed catalytic processes. This conclusion is also in accord with the observation that the electrocatalysis occurs for adsorbed $\mathrm{NiL}^{1\,+}{}_{\mathrm{aq}}$ to the mercury electrode [4e,f,g] and to the extremely low efficiency of the photocatalytic processes [4g,3].

(iii) Two $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ complexes reducing one CO_2 molecule coherently. This could in principle occur via one of two routes:

(a) Two $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ complexes disproportionating:

$$2\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}} \rightarrow \mathrm{NiL}^i+\mathrm{NiL}^{i\,2+} \qquad (7)$$

followed by

$$\mathrm{NiL}^i+\mathrm{CO}_2+2\mathrm{H}_3\mathrm{O}^+ \rightarrow \mathrm{NiL}^{i\,2+}+\mathrm{CO}+3\mathrm{H}_2\mathrm{O} \qquad (8)$$

This mechanism does not fit the observations as reaction (7) is clearly very slow, and the $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ are relatively long-lived species (see below). Furthermore, the decomposition of the $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ complexes seems to require a substantial isomerization of these complexes prior to decomposition, which might involve disproportionation (see below) and it is difficult to envisage that reaction (8) with the ‘isomer complex’ will yield back $\mathrm{NiL}^{i\,2+}$ in its stable conformation.

(b) $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ forming a complex with CO_2:

$$\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}+\mathrm{CO}_2 \rightleftharpoons \mathrm{L}^i\mathrm{Ni}^+\cdot\mathrm{CO}_2 \qquad (9)$$

followed by the reduction of this complex by the electrode:

$$\mathrm{L}^i\mathrm{Ni}^+\cdot\mathrm{CO}_2+2\mathrm{H}_3\mathrm{O}^+ + e^- \rightarrow \mathrm{NiL}^{i\,2+}+\mathrm{CO}+3\mathrm{H}_2\mathrm{O} \qquad (10)$$

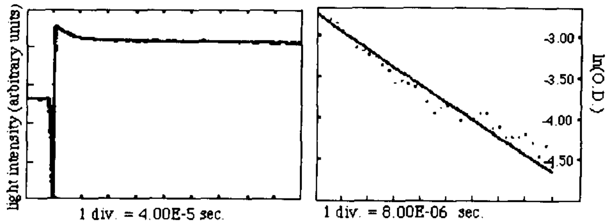


Fig. 6. Isomerization reaction of NiL^{10+}. Solution composition: 2.5×10^{-4} M $\mathrm{NiL}^{10}(\mathrm{ClO}_4)_2$; 0.05 M HCOONa; He saturated; pH 7.5. Wavelength of observation 300 nm. Observed rate $2.6\times10^4\ \mathrm{s}^{-1}$.

Or, alternatively, by a second $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ complex:

$$\mathrm{L}^i\mathrm{Ni}^+\cdot\mathrm{CO}_2+\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}+2\mathrm{H}_3\mathrm{O}^+ \rightarrow 2\mathrm{NiL}^{i\,2+}+\mathrm{CO}+3\mathrm{H}_2\mathrm{O} \qquad (11)$$

Reaction (10) seems to be in accord with all the results reported on the electrocatalytic studies and reaction (11), taking into account the low value of K_9, explains the low yields [3] of the photocatalytic processes.

3.8. Decomposition kinetics of the $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ complexes

The kinetics of decomposition of the $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$, $i = 8$–14, were studied. As the results for $\mathrm{NiL}^{8+}{}_{\mathrm{aq}}$ differ considerably from the rest they will be described separately.

Decomposition of $\mathrm{NiL}^{8+}{}_{\mathrm{aq}}$ in aqueous solutions

The decomposition of this complex in neutral aqueous solutions is rather complex and consists of at least three consecutive processes which are not well separated in time. Therefore, it was not possible to analyse the mechanism of this process in detail. The last process is over after about 0.2 s, i.e. much faster than the electrochemical results indicate. The only explanation for this observation is that the electrochemical reduction yields another isomer of $\mathrm{NiL}^{8+}{}_{\mathrm{aq}}$ than the pulse-radiolytic reduction; this point in general will be discussed in detail below.

The final product has a lower absorption in the near UV than the starting material. It seems that the decomposition involves the partial reduction of the imine bonds of the ligand. This conclusion also explains the difference in the kinetics observed for the decomposition of $\mathrm{NiL}^{8+}{}_{\mathrm{aq}}$ and the other $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$ complexes studied.

Decomposition of $\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}}$, $i = 9$–14, in aqueous solutions

The reduction reaction, reaction (5), was always followed by a process obeying a first-order rate law (see, for example, Fig. 6). The rate of this reaction is $(1\text{–}5)\times10^3\ \mathrm{s}^{-1}$ for $i = 11$–14, and somewhat faster for the sterically less hindered complexes, $i = 9$, 10. This reaction involves significant spectral changes for $i = 9$, 10 and 13 (Table 2 and Figs. 7 and 8) and only minor spectral changes for the other complexes. The process observed is attributed to an isomerization reaction:

$$\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}} \rightarrow (\mathrm{NiL}^{i\,+}{}_{\mathrm{aq}})_{\mathrm{r}} \qquad (12)$$

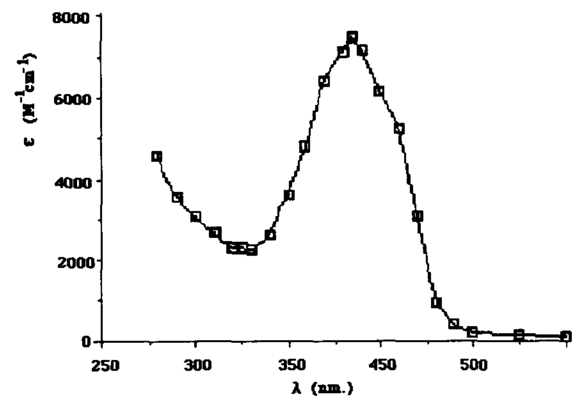


Fig. 7. Spectrum of the first isomer of NiL^{9+}. Solution composition: 2.5×10^{-4} M $NiL^9(ClO_4)_2$; 0.05 M HCOONa; He saturated; pH 9.5. Measured 100 μs after the pulse.

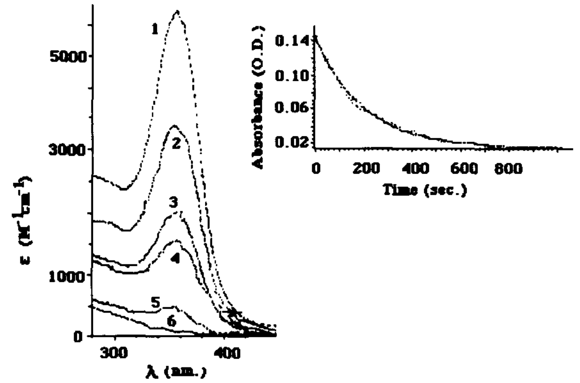


Fig. 8. Spectrum of the second isomer of NiL^{9+}. Solution composition: 2.5×10^{-4} M $NiL^9(ClO_4)_2$; 0.05 M HCOONa; He saturated; pH 9.5. Measured: 1, ~30 s; 2, ~105 s; 3, ~180 s; 4, ~280 s after the pulse. Inset: kinetic first-order fit of the decomposition of this isomer, measured at 290 nm.

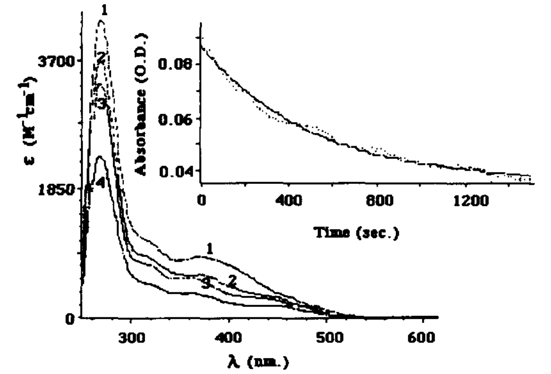


Fig. 9. Spectrum of the second isomer of NiL^{11+}. Solution composition: 2.5×10^{-4} M $NiL^{11}(ClO_4)_2$; 0.05 M HCOONa; He saturated; pH 9.3. Measured: 1, ~30 s; 2, ~130 s; 3, ~230 s; 4, ~330 s; 5, ~530 s; 6, ~1030 s after the pulse. Inset: kinetic first-order fit of the decomposition of this isomer, measured at 350 nm.

where the 'r' denotes an isomerized configuration of the complex.

This process is followed by a considerably slower process which was studied spectrophotometrically by irradiating the sample in an optical cell by several pulses from a linear accelerator and placing the cell within 30 s in the spectrophotometer (see, for example, Figs. 8 and 9). This process obeys a first-order rate law (Figs. 8 and 9); however, the fit is not optimal. The deviation from the pure first-order rate law suggests that the decomposition involves a rate determining process obeying a first-order rate law, followed by a somewhat faster process which might obey a second-order rate law. It should be noticed that as the complexes are too weak to act as reducing agents for the reduction of water by a single electron process, a second-order process has to be part of the decomposition mechanism. Therefore, the decomposition process is attributed to the following reactions:

$$(NiL^{i\,+}{}_{aq})_r \xrightarrow{\text{r.d.}} (NiL^{i\,+}{}_{aq})_{r'} \qquad (13)$$

followed by

$$(NiL^{i\,+}{}_{aq})_{r'} + (NiL^{i\,+}{}_{aq})_r \xrightarrow{\text{fast}} (NiL^{i}{}_{aq})_r + (NiL^{i\,2+}{}_{aq})_r \qquad (14)$$

The complex $(NiL^{i}{}_{aq})_r$, where 'r' denotes only that the configuration of the ligand might differ from that of $NiL^{i\,2+}{}_{aq}$, reduces either the solvent or a solute via a two-electron process. The overall rates of these processes are summed up in Table 2. It should be noted that these rates are not correlated to the redox potentials of these complexes, an observation which corroborates the conclusion that the rate determining step is not a redox process.

pH effect on the properties of $(NiL^{11\,+}{}_{aq})_r$

The pH effect on the properties of this complex were studied in the pH range $2.5 < pH < 9.3$. Neither the spectra nor the kinetics of decomposition are affected by the pH at $pH > 3$. At lower pH values, the formation of a nickel mirror is observed.

Spectra of the $(NiL^{i\,+}{}_{aq})$ complexes

The spectra of the $(NiL^{i\,+}{}_{aq})$ complexes are summed up in Table 2 and typical spectra are shown in Figs. 7–9. The spectra of the complexes with unsaturated ligands, $i = 7$ and 8, cannot be compared with the rest as $d \rightarrow \pi$ transitions are clearly involved.

The $d \rightarrow d$ transitions of the other complexes are all too weak to be observed under our experimental conditions, with the exception of $NiL^{11\,+}{}_{aq}$. These observations are in accord with recently reported spectra of a variety of monovalent nickel complexes in CH_3CN [30]. However, the spectra of $NiL^{i\,+}$, $i = 11$–14, in CH_3CN have considerably larger molar absorption coefficients which were attributed to 'an intensity increasing mechanism' such as a tetrahedral distortion [1k]. Clearly this mechanism does not operate in aqueous solutions. However, this again points out the relative lability towards isomerization of these complexes.

The near-UV absorption bands of these complexes are commonly attributed to charge transfer transitions [30,31]. The observation that λ_{max} of these absorption bands is shifted to the red when the redox potentials of the $NiL^{i\,2+}{}_{aq}/NiL^{i\,+}{}_{aq}$

couples are shifted to less cathodic potentials, for $i=1$–4, suggested that these absorption bands are due to charge transfer to the solvent transitions [6b]. However, a trial to plot λ_{max} versus E^0 for all the known $NiL^{i+}{}_{aq}$ complexes (Table 2) and the *cis* isomers of $NiL^{2+}{}_{aq}$ and $NiL^{4+}{}_{aq}$ [31] and of Ni(1,4,8,12-tetraazacyclopentadecane)$^+{}_{aq}$ [6a], indicates that no such relation exists and the points are scattered all around. Thus, the results do not corroborate the suggestion that the observed absorption bands are due to charge transfer to the solvent transitions; as the ligands are saturated the only alternative seems to be L → M charge transfer bands. Though Ni^0 is not expected to be stabilized by these ligands the high energy of these bands enables such transitions.

3.9. *Self-exchange rates of the NiL^i complexes*

In order of obtaining more information on the potential use of the NiL^{i+} complexes as kinetically active reducing agents, it was decided to measure their self-exchange rates:

$$*NiL^{i+} + NiL^{i2+} \xrightarrow{k_{11}} *NiL^{i2+} + NiL^{i+} \qquad (15)$$

Therefore, the rates of reaction of the NiL^{i+} complexes with $Ru(NH_3)_6^{3+}$ were studied:

$$NiL^{i+} + Ru(NH_3)_6^{3+} \xrightarrow{k_{12}} NiL^{i2+} + Ru(NH_3)_6^{2+} \qquad (16)$$

The results are summed up in Table 2. Reaction (16) clearly proceeds via the outer-sphere mechanism. Therefore the self-exchange rates k_{11} can be calculated using the Marcus cross relation [32a] from the values k_{12}; the redox potentials of the NiL^{i2+}/ NiL^{i+} couples (Table 2); the redox potential of the $Ru(NH_3)_6{}^{3+}/Ru(NH_3)_6{}^{2+}$ couple [32b] and the specific rate of the self-exchange rate of the latter couple [32b]. The results are summed up in Table 2.

The results clearly indicate that N-alkylation of the macrocyclic ligands increases the rate of the self-exchange reactions. For the complexes NiL^i, $i=11$–14, which have only two tertiary amines the effect is significantly smaller than for NiL^4, which is considerably more hydrophobic. The effect is also larger for NiL^i, $i=12$ and 14, than for NiL^i, $i=11$ and 13, i.e., the length of the aliphatic chain affects the self-exchange rate. Also the configuration of the complex affects significantly the rate of the self-exchange reaction, i.e., the rate is considerably higher for the *cis* isomers, $i=11$ and 12, than for the corresponding *trans* isomers. The effect of N-alkylation of the macrocyclic ligand on the rate of the self-exchange rate was attributed to the decrease in the outer-sphere solvation of these complexes which decreases the required activation energy of the electron transfer reactions [6b]. This conclusion is based on the reasonable assumption that N-alkylation of the macrocyclic ligand does not decrease the inner-sphere rearrangement energy of the complex during the redox process.

It is of interest to note that C-alkylation was shown to increase k_{11} for the NiL^{i3+}/NiL^{i2+} couples [12,33]. The results indicated that, when the alkylation introduces a barrier to the approach of axial ligands to the central cation, k_{11} decreases. This effect overrides the effect of C-alkylation on the outer-sphere solvation of these complexes [33]. N-alkylation clearly introduces a considerably larger barrier to the approach of axial ligands to the central nickel but this does not slow down the rate of the self-exchange process as this bond is long in the monovalent nickel complexes [6b,16].

It is of interest to note that the self-exchange rate for the couple $Ni^{2+}{}_{aq}/Ni^+{}_{aq}$ was recently estimated as 3.8 $M^{-1}\,s^{-1}$ [14]. Thus, the self-exchange rates for all the macrocyclic complexes are slower than that of the aquo complex, a quite surprising observation. This result suggests that the redox process of the NiL^{i2+}/NiL^{i+} couples requires considerable rearrangement of the macrocyclic ligands, a quite unexpected conclusion.

4. Concluding remarks

The results obtained in this study lead to the following general conclusions.

4.1. *Comparison of pulse-radiolysis and electrochemical results*

These two techniques are commonly used as complimentary techniques for the study of the chemical properties of transition metal complexes with uncommon oxidation states. The results described above point out that sometimes different isomers of the desired complex are obtained by the two techniques. Thus, for example, the lifetime of NiL^{8+} obtained by pulse radiolysis is considerably shorter than that obtained electrochemically. On the other hand, the complex NiL^{9+} obtained by pulse radiolysis is considerably longer lived than that obtained electrochemically.

The source of these apparent discrepancies is the different redox potential used by the two techniques. Thus, the reducing reagents $e^-{}_{aq}$ and $CO_2^{\bullet-}$ are powerful reducing agents [27b] and reduce therefore the NiL^{i2+} complexes in the configuration in which they are present in the solution, even if the monovalent complexes prefer another configuration. On the other hand, in the electrochemical reductions, at least in those which are quasi-reversible, the divalent complex has to rearrange to a configuration similar to that required by the monovalent complex, otherwise large overpotentials would be required. Thus, it is reasonable that sometimes different isomers of the complexes are obtained by the two techniques.

4.2. *Isomerizations of the NiL^{i+} complexes*

The results clearly indicate that the reduction of the divalent nickel complexes is often accompanied, or followed, by isomerization processes. This conclusion is based on the following observations.

(a) The pulse-radiolysis experiments which include such a step for many of the complexes described, including the systems for which considerable shifts in the absorption spectra were observed, i.e. for $\mathrm{NiL}^{i\,+}$, $i=9$, 10 and 13.

(b) The differences in the lifetimes of the $\mathrm{NiL}^{i\,+}$, $i=8$ and 9, complexes obtained via pulse radiolysis or electrochemically.

(c) The large ΔS° for the reduction of $\mathrm{NiL}^{3\,2+}$, as discussed above.

(d) The dependence of the ESR spectrum of $\mathrm{NiL}^{3\,+}$ on the reducing agent [6b].

(e) The kinetics of decomposition of the $\mathrm{NiL}^{i\,+}$ complexes, which all obey first-order rate laws though they clearly involve second-order processes, as discussed above.

(f) The observation that the electrochemical reductions are always only quasi-reversible, i.e., that $\Delta E_{\mathrm{peak}} > 60$ mV.

(g) The observation that k_{11} is larger for the $\mathrm{NiL}^{2+}{}_{\mathrm{aq}}/\mathrm{NiL}^{+}{}_{\mathrm{aq}}$ couple than for the $\mathrm{NiL}^{i\,2+}/\mathrm{NiL}^{i\,+}$ couples.

Thus, although the macrocyclic frame of the ligand is relatively rigid, the results clearly point out that redox processes of these complexes are accompanied by considerable isomerization processes. This conclusion is in accord with recent X-ray crystal structure determinations of several monovalent nickel complexes with tetraaza-macrocyclic ligands [1k,30].

4.3. N-alkylation of the tetraaza-macrocyclic ligands stabilizes thermodynamically the monovalent nickel complexes

The results corroborate earlier observations [6b,14–16] that N-alkylation of the ligands stabilizes low valent transition metal complexes. The results are in accord with the proposal that this stabilization is due mainly to the effect of the N-alkylation on the solvation energy of the complexes. This conclusion is based on the following observations.

(a) The difference in the redox potentials of $\mathrm{NiL}^{3\,2+}/\mathrm{NiL}^{3+}$ and $\mathrm{NiL}^{5\,2+}/\mathrm{NiL}^{5+}$ and $\mathrm{NiL}^{6\,2+}/\mathrm{NiL}^{6+}$ couples.

(b) The effect of N-alkylation on ΔS° for the reduction of $\mathrm{NiL}^{4\,2+}$.

(c) The effect of N-alkylation on k_{11} for the $\mathrm{NiL}^{i\,2+}/\mathrm{NiL}^{i\,+}$ couples.

It is of interest to note that the lifetimes of the monovalent nickel complex are not regularly dependent on their redox potentials.

Finally, it is of interest to note that for NiL^{i}, $i=9$–14, also the trivalent nickel complexes are relatively stable in aqueous solutions [34]. Though the redox potentials of these couples are not suited for the two-electron reduction of CO_2 and H_2O, it is reasonable to expect that such redox couples might be designed.

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