DALTON
COMMUNICATION

Kinetic stabilization of trivalent nickel complexes with tertiary tetraaza macrocyclic ligands in aqueous solution

Israel Zilbermann,[a,b] **Gilad Golub,**[b] **Haim Cohen**[a,b] **and Dan Meyerstein** *[b,c]

[a] *Nuclear Research Centre Negev, Beer-Sheva, Israel*
[b] *Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel*
[c] *The College of Judea and Samaria, Ariel, Israel*

The nickel(II) complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane and *meso*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane gave trivalent nickel complexes upon electrochemical oxidation, the properties of these new, powerful single-electron oxidizing trivalent species have been investigated.

The thermodynamic and kinetic stability imparted by tetraaza macrocyclic ligands to transition-metal ions in uncommon oxidation states has led to extensive studies of their properties in the past two decades.[1–4] This unique property was first recognized for nickel complexes and many recent studies have dealt with their redox chemistry both in aqueous and in organic solvents.[5] The complex with 1,4,8,11-tetraazacyclotetradecane, cyclam (L^1) was shown to stabilize best nickel(III).[1,6,7] The redox properties of nickel complexed with L^2 are very similar to those with L^1.[8,9] Substituents on the macrocyclic backbone affect the redox characteristics by restricting axial ligand binding which usually stabilizes the trivalent oxidation state of nickel complexes,[5,10–13] and by inductive effects.[5,10–13]

N-Methylation of the macrocyclic frame was shown to stabilize the monovalent nickel complexes both kinetically, by slowing down the rate of ligand loss and by inhibiting the reduction of water,[14] and thermodynamically, by increasing the cavity formed by the macrocyclic ligand;[15] by decreasing the ligand-field strength imparted by the nitrogen donor atoms[16–22] and by increasing the hydrophobic nature of the ligand thus decreasing the solvation energy.[16,17,23–26] Indeed $[NiL^3]^+$ and $[NiL^4]^+$ are surprisingly stable in aqueous solution.[16]

It is thus not surprising that various efforts to oxidize $[NiL^3]^{2+}$ and $[NiL^4]^{2+}$ in aqueous solution failed. These attempts included (1) cyclic voltammetry (CV) which indicated that these complexes cannot be oxidized at potentials below that of the water oxidation on a variety of electrodes. These experiments are in accord with the reported redox potential of the couple $[NiL^3]^{3+/2+}$ in MeCN of + 1.25 V *vs.* ferrocenium–ferrocene.[20] (2) By oxidation of the corresponding monovalent complexes with N_2O, equation (1). This reaction occurs for $[NiL^i]^+$ when $i = 1$ or

$$[NiL^i]^+ + N_2O + 2H_3O^+ \longrightarrow [NiL^i]^{3+} + N_2 + 3H_2O \quad (1)$$

2,[16] but is not observed for $[NiL^3]^+$ nor $[NiL^4]^+$,[16] probably due to the fact that reaction (2) is considerably faster than reaction

$$[NiL^i]^+ + [NiL^i]^{3+} \longrightarrow 2[NiL^i]^{2+} \quad (2)$$

(1).[14] (3) By oxidation with $Br_2^{\bullet-}$ as in equation (3). Although

$$[NiL^i]^{2+} + Br_2^{\bullet-} \longrightarrow [NiL^i]^{3+} + 2Br^- \quad (3)$$

this reaction occurs for $[NiL^i]^{2+}$ when $i = 1$ or 2,[25] it is not observed for $[NiL^3]^{2+}$ nor $[NiL^4]^{2+}$ (ref. 25), probably due to steric hindrance towards attack along the *z* axis caused by the N-methyl groups.[16]

However it was noted, in a 'wrongly' planned experiment, that during a slow scan rate CV experiment of $[NiL^3]^{2+}$ to potentials well above the 'water wave' the colour of the solution around the working electrode turns temporarily to slightly red. Therefore aqueous solutions containing 1×10^{-3} mol dm^{-3} of $[NiL^i]^{2+}$, $i = 3$ or 4 (the complexes, in their *trans*-III configuration, were synthesized according to published methods[21,22]) and 0.05 mol dm^{-3} Na_2SO_4 at pH 3.0 were electrolysed using a platinum net ($S = 34$ cm^2) as a working electrode at +1.5 V *vs.* the saturated calomel electrode (SCE). After a period of 15 min for L^4 and 3 min for L^3 deep orange-red solutions were obtained in both cases.

As it seemed plausible that the deep colour is due to the formation of the corresponding trivalent complexes the ESR

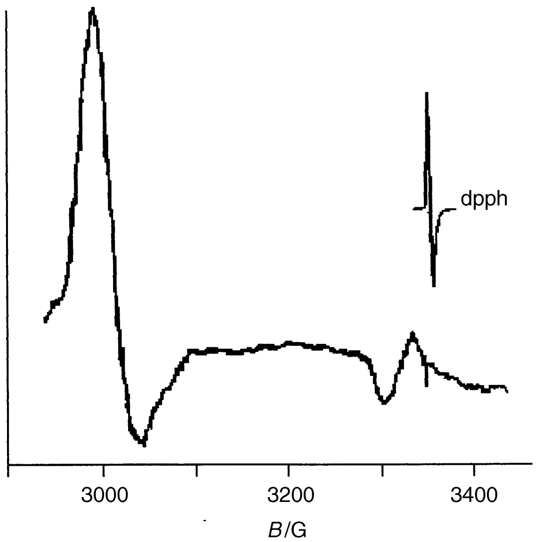
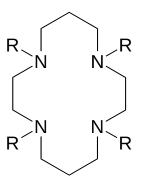
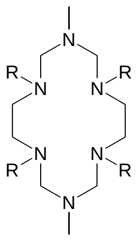


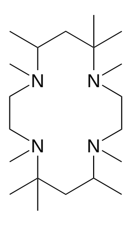
Fig. 1 ESR spectrum of ≈5 × 10^{-5} mol dm^{-3} $[NiL^4]^{3+}$, 0.05 mol dm^{-3} Na_2SO_4, pH 3.0, frozen at 117 K



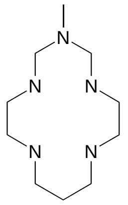
L^1 R = H
L^3 R = Me



L^2 R = H
L^5 R = Me



L^4



L^6

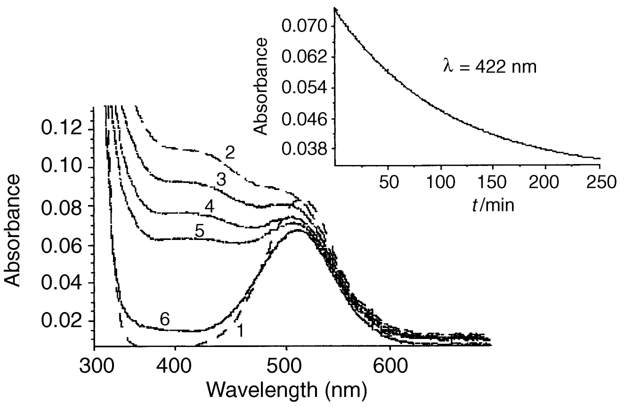
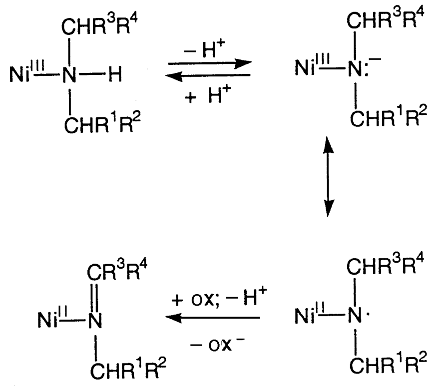


Fig. 2 Absorbance spectra of 0.001 mol dm^{-3} $[\mathrm{NiL}^4]^{2+}$ at $t = 0$ (1), 1 (2), 8 (3), 15 (4), 21 (5) and 1200 min (6) after electrolysis



Scheme 1 ox = oxidizing agent

spectra of the two solutions obtained were measured at 117 K, the results are summarized in Fig. 1 and Table 1.The results clearly show that the trivalent nickel complexes, $[\mathrm{NiL}^3]^{3+}$ and $[\mathrm{NiL}^4]^{3+}$, have been formed under these experimental conditions. Naturally the electrochemical yield of these oxidations is low as most of the current is due to water oxidation.

The UV/VIS spectra and the kinetics of decomposition of the trivalent nickel complexes were measured, the results are summarized in Table 1 and Fig. 2. The kinetics of decomposition obey a first-order rate law and the rate of reaction is pH independent in the range pH 2.5–10.5. The observation that these reactions obey a first-order rate law though the oxidation of both the ligands or the water are two-electron processes indicates that the rate-determining step involves some type of rearrangement, isomerization, of the trivalent complex followed by a fast reaction with a second trivalent complex.

The observation that the rates of decomposition of $[\mathrm{NiL}^3]^{3+}$ and $[\mathrm{NiL}^4]^{3+}$ are considerably lower than those of the corresponding complexes in which secondary nitrogen atoms are the donor groups, at least in solutions with pH > 7, though the redox potential of the latter are considerably lower, is not surprising. The mechanism of decomposition of the trivalent nickel complexes with ligands with secondary nitrogen atom donors is believed to be that depicted in Scheme 1.[26] Clearly $[\mathrm{NiL}^3]^{3+}$ and $[\mathrm{NiL}^4]^{3+}$ cannot decompose *via* this mechanism.

In order to check the potential use of the trivalent complexes as oxidizing agents they were treated with I^-, Br^-, SCN^- and $\mathrm{N_3}^-$. Both complexes oxidize, *via* fast reactions, I^- to yield $\mathrm{I_3}^-$. This reaction was used for the determination of the molar absorption coefficients of the trivalent complexes. The ion $[\mathrm{NiL}^4]^{3+}$ oxidizes both SCN^- and $\mathrm{N_3}^-$ but not Br^-, while $[\mathrm{NiL}^3]^{3+}$ does not oxidize $\mathrm{N_3}^-$ nor Br^- and is precipitated when SCN^- is added to the solution.

As the trivalent nickel complexes are single-electron oxidizing agents the mechanisms of these oxidations are expected to be those shown in equations (4) and (5), or alternatively as shown

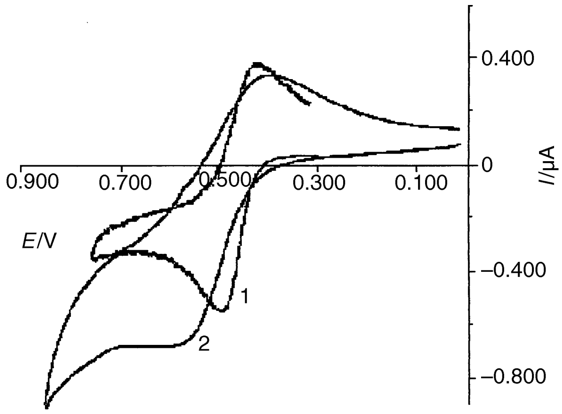


Fig. 3 (1) 5 × 10^{-4} mol dm^{-3} $[\mathrm{NiL}^5]^{2+}$ and (2) 5 × 10^{-4} mol dm^{-3} $[\mathrm{NiL}^2]^{2+}$ with 0.15 mol dm^{-3} $\mathrm{NaClO_4}$, pH 3.5, gold working electrode *vs.* SCE

Table 1 Physical properties of $[\mathrm{NiL}^i]^+$

L	$t_{\frac{1}{2}}$/min[a]	$\lambda_{\max}$/nm (ε dm^3 mol^{-1} cm^{-1})[b]	$g_{\parallel}$[c]	$g_{\perp}$[c]
L^1			2.0386[d]	2.2138[d]
L^3	6.7	320 (5400[e]); 402 (2400[e])	2.039	2.245
L^4	23.5	220 (3840[e]); 334 (520[e]); 422 (400[e])	2.036	2.234

[a] $\Delta t_{\frac{1}{2}} = \pm 5\%$. [b] $\Delta\lambda = \pm 2$ nm, $\Delta\varepsilon = \pm 10\%$. [c] $\Delta g = \pm 0.001$ in this study. [d] From ref. 24. [e] Apparent molecular absorption coefficient as some other oxidizing agents (*i.e.* hydrogen peroxide) might be involved during the bulk electrolysis at +1.5 V *vs.* SCE.

$$[\mathrm{Nil}^i]^{3+}{}_{\mathrm{aq}} + \mathrm{X}^- \rightleftharpoons [\mathrm{NiL}^i]^{2+}{}_{\mathrm{aq}} + \mathrm{X}^{\bullet} \tag{4}$$

$$\mathrm{X}^{\bullet} + \mathrm{X}^- \longrightarrow \mathrm{X_2}^{\bullet -} \tag{5}$$

in equation (4a) followed by (4b) followed by equation (6a), (6b)

$$[\mathrm{NiL}^i]^{3+}{}_{\mathrm{aq}} + \mathrm{X}^- \rightleftharpoons [\mathrm{Ni^{III}XL}^i]^{2+}{}_{\mathrm{aq}} \tag{4a}$$

$$[\mathrm{Ni^{III}XL}^i]^{2+}{}_{\mathrm{aq}} + \mathrm{X}^- \rightleftharpoons [\mathrm{NiL}^i]^{2+}{}_{\mathrm{aq}} + \mathrm{X_2}^{\bullet -} \tag{4b}$$

$$2\mathrm{X}^{\bullet} \longrightarrow \text{products} \tag{6a}$$

$$2\mathrm{X_2}^{\bullet -} \longrightarrow \text{products} \tag{6b}$$

or equation (7).

$$[\mathrm{NiL}^i]^{3+}{}_{\mathrm{aq}} + \mathrm{X_2}^{\bullet -} \longrightarrow [\mathrm{NiL}^i]^{2+}{}_{\mathrm{aq}} + \mathrm{X_2} \tag{7}$$

Although reactions (6) and (7) shift the equilibria (4) to the right oxidations of X^- are not expected to be fast for systems where the redox potential of the couple $\mathrm{X_2}^{\bullet -}$–$2\mathrm{X}^-$ or the couple $\mathrm{X}^{\bullet}$–X^- is considerably more anodic than that for $[\mathrm{NiL}^i]^{3+}{}_{\mathrm{aq}}$–$[\mathrm{NiL}^i]^{2+}{}_{\mathrm{aq}}$. The redox potentials for the couples $\mathrm{Br_2}^{\bullet -}$–$2\mathrm{Br}^-$, $(\mathrm{NCS})_2{}^{\bullet -}$–$2\mathrm{NCS}^-$, $\mathrm{N_3}^{\bullet}$–$\mathrm{N_3}^-$ and $\mathrm{I_2}^{\bullet -}$–$2\mathrm{I}^-$ are 1.63, 1.31, 1.30 and 1.03 V *vs.* the normal hydrogen electrode (NHE) respectively.[27] Thus the results indicate that the trivalent nickel complexes are indeed powerful oxidizing agents and that $[\mathrm{NiL}^4]^{3+}{}_{\mathrm{aq}}$, although it is sterically more hindered, is a stronger oxidizing agent than $[\mathrm{NiL}^3]^{3+}{}_{\mathrm{aq}}$.

The complex $[\mathrm{NiL}^5][\mathrm{ClO_4}]_2$ exists in the solid state in its *trans* III isomeric form but in aqueous solution it isomerizes slowly to its *cis* isomeric form.[23] The redox properties of the couple $[\mathrm{NiL}^5]^{2+/+}$ were shown to be very similar to those of the couple $[\mathrm{NiL}^3]^{2+/+}$.[23] Surprisingly enough (Fig. 3) the redox potential for the couple $[\mathrm{NiL}^5]^{3+/2+}$ is considerably lower, 450 mV *vs.* SCE, and is even somewhat lower than that of the couple $[\mathrm{NiL}^2]^{3+/2+}$.

This result is very surprising as the ligand field induced by L^5 is relatively low.[23]

The complex $[NiL^5]^{3+}$ oxidized I^- and ascorbate. The oxidation of I^- was used to determine the molar absorption coefficients of $[NiL^5]^{3+}_{aq}$, $\lambda_{max} = 282$ ($\varepsilon^* = 500$), 414 nm (150 $dm^3\ mol^{-1}\ cm^{-1}$). Surprisingly enough the product of reduction of $[NiL^5]^{3+}_{aq}$ by ascorbate is $[NiL^5]^{2+}_{aq}$ in its planar *trans* III isomeric form. At present we have no detailed explanations for the surprising properties of $[NiL^5]^{3+}_{aq}$, one tentative explanation is that this complex is stabilized *via* hydrogen bonding of the aqua ligands to the 1,8-nitrogens, similar arguments were recently suggested to explain the effect of the nature of substituents R on the redox potential of the couples $[NiL^6]^{3+/2+}$ where L^6 = 1-R-1,3,5,8,12-pentaazacyclotetradecane.[28]

Finally it should be re-emphasized that the complexes $[NiL^3]^{3+}_{aq}$ and $[NiL^4]^{3+}_{aq}$ are new, relatively stable, single-electron oxidizing agents, the preparation of which is relatively simple.

Acknowledgements

This study was supported in part by grants from the Israel Academy of Sciences and from the Israel Atomic Energy Committee. D. M. expresses his thanks to Mrs. Irene Evens for her continuous interest and support.

---

* Apparent molecular absorption coefficient as some other oxidizing agents (*i.e.* H_2O_2) might be involved during the bulk electrolysis at +1.5 V *vs.* SCE.

References

1 F. V. Lo Vecchio, E. S. Gore and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3110.
2 *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum Press, New York, 1979.
3 M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517.
4 *The Chemistry of Macrocyclic Ligand Compounds*, ed. L. F. Lindoy, Cambridge University Press, Cambridge, 1989.
5 A. G. Lappin and A. McAuley, *Adv. Inorg. Chem.*, 1988, **32**, 241.
6 A. Bencini, L. Fabrizzi and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.
7 M. G. Fairbank, A. McAuley, P. R. Norman and O. Olubuyide, *Can. J. Chem.*, 1985, **63**, 2982.
8 M. P. Suh and S. G. Kang, *Inorg. Chem.*, 1988, **27**, 2544.
9 I. Zilbermann, A. Meshulam, H. Cohen and D. Meyerstein, *Inorg. Chim. Acta*, 1993, **206**, 127.
10 H. Cohen, L. J. Kirschenbaum, E. Zeigerson, M. Jaacobi, E. Fuchs, G. Ginzburg and D. Meyerstein, *Inorg. Chem.*, 1979, **18**, 2763.
11 E. Zeigerson, G. Ginzburg, N. Schwartz, Z. Luz and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1979, 241.
12 E. Zeigerson, G. Ginzburg, J. Y. Becker, L. J. Kirschenbaum, H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1981, **20**, 3918.
13 E. Zeigerson, I. Bar, J. Bernstein, L. J. Kirschenbaum and D. Meyerstein, *Inorg. Chem.*, 1982, **21**, 73.
14 D. Meyerstein, *Current Topics in Macrocyclic Chemistry*, ed. E. Kimura, Hiroshima University, 1987.
15 N. Jubran, H. Cohen and D. Meyerstein, *Isr. J. Chem.*, 1985, **25**, 118.
16 N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh and D. Meyerstein, *Inorg. Chem.*, 1985, **24**, 251.
17 N. Jubran, H. Cohen and D. Meyerstein, *Inorg. Chim. Acta*, 1986, **117**, 129.
18 C. Che, K. J. Wong and C. K. Poon, *Inorg. Chem.*, 1986, **25**, 1809.
19 E. K. Barefield, G. M. Freeman and D. G. Van der Veer, *Inorg. Chem.*, 1986, **25**, 552.
20 A. J. Blake, R. O. Gould, T. I. Hyde and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1987, 431.
21 F. Wagner, M. T. Morella, M. Y. D'Annello, A. H. Wang and E. K. Barefield, *J. Am. Chem. Soc.*, 1974, **96**, 2625.
22 F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1976, **15**, 408.
23 I. Zilbermann, M. Winnik, D. Sagiv, A. Rotman, H. Cohen and D. Meyerstein, *Inorg. Chim. Acta*, 1995, **240**, 503.
24 R. I. Haines and A. McAuley, *Inorg. Chem.*, 1980, **19**, 719.
25 I. Zilbermann, H. Cohen and D. Meyerstein, unpublished work.
26 G. Golub, I. Zilbermann, H. Cohen and D. Meyerstein, *Supramol. Chem.*, 1996, **6**, 275.
27 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data Suppl.*, 1988, **17**, 513.
28 F. Abba, G. De Santis, L. Fabrizzi, M. Licchelli, A. M. Manotti, P. Lanfredi, P. Pallavacini, A. Poggi and F. Ugozolli, *Inorg. Chem.*, 1994, **33**, 1366.

Received 10*th September* 1996; *Communication* 6/06260A