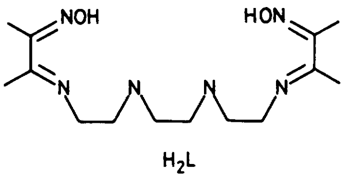
J. CHEM. SOC. DALTON TRANS. 1982 1861

Kinetics and Mechanism of Reduction of a Nickel(IV) Complex by Tris(1,10-phenanthroline)cobalt(II); Spectrophotometric Detection of a Nickel(III) Intermediate

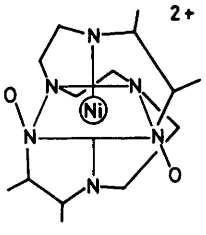
A. Graham Lappin * **and Mauro C. M. Laranjeira**
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

The kinetics of reduction of a nickel(IV) di(oxime–imine) complex, $[Ni^{IV}L]^{2+}$ (H_2L = 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime), by $[Co(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) are reported. The reaction is biphasic. An initial, rapid, pH-independent reaction between $[Ni^{IV}L]^{2+}$ and $[Co(phen)_3]^{2+}$ has a second-order rate constant of 3.2×10^5 dm^3 mol^{-1} s^{-1} at 25.0 °C and I = 0.10 mol dm^{-3} (Na[NO$_3$]) and leads to formation of a nickel(III) intermediate, $[Ni^{III}L]^+$. Subsequent reductions of this intermediate and its protonated form $[Ni^{III}LH]^{2+}$ by $[Co(phen)_3]^{2+}$ with second-order rate constants 8.3×10^2 and 4.1×10^4 dm^3 mol^{-1} s^{-1} respectively give the nickel(II) product. Both nickel(IV) and nickel(III) reactions proceed by outer-sphere electron-transfer mechanisms. The nickel(III) intermediates are generated electrochemically and both forms are characterised. Data previously published for the ascorbate reduction of the nickel(IV) complex are reinterpreted.

A number of complexes containing nickel, formally in its tetravalent state, have been reported,[1] but many of these are best described as complexes of the divalent ion with oxidised forms of the ligands. However, complexes with oxime–imine-containing ligands allow oxidation at the metal centre, certainly as far as the trivalent level,[2,3] and have reasonable lifetimes in aqueous solution. The compound with the sexidentate ligand 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime, H_2L, has pseudo-octahedral co-ordination (see below) and forms with the loss of two oxime protons.[4] It is substitution inert even in strongly acidic media and can be optically resolved [5] consistent with the low-spin d^6 electronic configuration of nickel(IV).



H_2L



$[Ni^{IV}L]^{2+}$

The low substitution lability and high reduction potential of the nickel(IV) complex, $[Ni^{IV}L]^{2+}$, are likely to result in outer-sphere electron-transfer mechanisms. Molecular structure data of related complexes [6,7] indicate no major geometry changes in reduction of nickel(IV) to nickel(II) although there is some Ni–N bond lengthening. An outer-sphere two-electron transfer mechanism was thought to be a possibility with this reagent but reduction by the two-electron reductant, ascorbate ion, proceeds by two consecutive one-electron steps.[2]

In this paper the kinetics and mechanism of reduction of $[Ni^{IV}L]^{2+}$ by the one-electron reagent $[Co(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) are reported together with cyclic voltammetry studies of the Ni^{IV}, Ni^{III}, and Ni^{II} couples in nitrate media. The results allow some reinterpretation of the mechanistic details of the ascorbate reduction.[2]

Experimental

The nickel(II) and nickel(IV) complexes with H_2L were obtained as the perchlorate salts by methods outlined previously.[2,3] Solutions of nickel(IV) were standardised spectrophotometrically using literature [3] absorption coefficients: λ/nm (ε/dm^3 mol^{-1} cm^{-1}), 500 (6 300), 430 (5 960). The nickel(III) complexes with H_2L were generated electrochemically by oxidation of $[Ni^{II}LH_2]^{2+}$ using a flow system [8] with a graphite powder working electrode packed in a porous glass column and wrapped externally with a Pt wire electrode. The absorption coefficient was determined by addition of aliquots of standardised ascorbic acid solution. Solutions of tris(1,10-phenanthroline)cobalt(II) were prepared from cobalt nitrate (B.D.H., AnalaR) with sufficient phen (B.D.H., AnalaR) to ensure >98% formation of the tris complex (*e.g.* 4.0×10^{-3} mol dm^{-3} at pH 3.26). All other reagents were of AnalaR quality.

Cyclic voltammetry measurements were made in 2.50×10^{-2} mol dm^{-3} acetate, phosphate, or borate buffer solutions at an ionic strength of 0.10 mol dm^{-3} (Na[NO$_3$]) and at 25.0 ± 0.1 °C with either the nickel(II) or nickel(IV) complex at 5×10^{-4} mol dm^{-3}. A three-electrode system consisting of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl (NaCl) reference electrode was used. Voltammograms were generated using a Bioanalytical Systems Inc. CV-1A instrument and recorded on a PL 51 X-Y recorder (J. J. Lloyd Ltd.). Some experiments were duplicated

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* *Present address:* Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

using a carbon paste working electrode. All potentials are quoted *versus* a normal hydrogen electrode (n.h.e.).

Kinetic measurements were made in 1.0×10^{-2} mol dm^{-3} acetate, phosphate, or borate buffer at an ionic strength of 0.10 mol dm^{-3} (Na[NO$_3$]). Experiments were run under pseudo-first-order conditions with an excess of $[\mathrm{Co(phen)_3}]^{2+}$. The pH was varied from 3.5 to 9.0 and was determined immediately after reaction using an E.I.L. 7055 pH meter. A saturated calomel (NaCl) reference electrode was used and hydrogen-ion concentrations were evaluated using the relationship $-\log[\mathrm{H^+}] = \mathrm{pH} - 0.02$, correcting for both hydrogen ion activity and liquid-junction potential.

Reactions were monitored at the absorption maximum of the nickel(IV) complex at 500 nm or at 319 nm using an Applied Photophysics stopped-flow spectrophotometer thermostatted at 25.0 ± 0.1 °C. The absorbance changes, recorded on a Tektronix 5111 storage-oscilloscope, were biphasic, showing two well separated exponential decays. Observed rate constants, $k_{\mathrm{obs.}}$, were evaluated by least-squares analysis using a Data General Nova 2 minicomputer. At least three rate determinations were made for each experiment. Linear regression techniques, weighting $k_{\mathrm{obs.}}^{-1}$ where appropriate, were employed for data analysis.

The reaction stoicheiometry was determined by the addition of aliquots of $[\mathrm{Co(phen)_3}]^{2+}$ solution to a standard nickel(IV) solution which was then restandardised.

U.v.–visible spectra were run on a Beckman 5270 spectrophotometer. E.p.r. spectra were obtained at 125 K in aqueous glasses using a JEOL JES-FE1X *X*-band instrument.

Results

Over the pH range 1—10 reversible or pseudo-reversible cyclic voltammetric behaviour is observed for the nickel(IV)–nickel(II) change. The behaviour is independent of the initial oxidation state of the nickel complex except under conditions of high acidity where the nickel(II) complex is subject to hydrolysis. Most experiments were performed using nickel(IV) as the starting state.

The nature of the voltammograms is very dependent on pH. At pH <4, a single reversible voltammetric response was noted for reduction of $[\mathrm{NiL}]^{2+}$. The peak-to-peak separation was approximately 30 mV at scan rates less than 20 mV s^{-1} and increased with increasing scan rate. The midpoint potential (the average of the anodic and cathodic peak potentials, E_a and E_c respectively) decreased 60 mV with each unit of pH increase, Table 1.

Above pH 4, the peak-to-peak separation was greater than 30 mV even at low scan rates until, around pH 5, two separate voltammetric responses could be discerned. Both responses show a peak-to-peak separation of 60 mV. The higher potential response is independent of pH while the lower response shows a strong (greater than 60 mV per decade) dependence between pH 5 and 6, a 60 mV per pH unit dependence between pH 6 and 7.5, and pH independence above pH 7.5. This behaviour is illustrated in Figure 1.

Controlled potential electrolysis of the nickel(II) complex (pH 6.0) at 0.57 V (*versus* n.h.e.) produced a red solution exhibiting the spectrum shown in Figure 2(*a*). This spectrum differs from that of $[\mathrm{Ni^{IV}L}]^{2+}$ with absorption maxima at 505 (2 890) and 398 nm (ε 3 000 dm^3 mol^{-1} cm^{-1}) comparable with nickel(III) oxime-imine complexes.[9] The complex is stable for greater than 24 h in neutral solution. In 0.05 mol dm^{-3} acid solution, the band at 398 nm disappears and a single broad band at 490 nm (ε 2 980 dm^3 mol^{-1} cm^{-1}) is noted, Figure 2(*b*). This species disproportionates slowly ($t_{\frac{1}{2}}$ *ca.* 5 min) to yield the spectrum of nickel(IV).

Electron paramagnetic resonance spectra of the nickel(III) complex in neutral solution are axial with $g_{\perp} = 2.155$ and $g_{\parallel} = 2.033$. Spectra of the acid quenched sample are approximately axial with $g_{\perp} = 2.09$ and $g_{\parallel} = 2.04$.

Table 1. Cyclic voltammetric data for the nickel(IV)/(III)/(II) system at 25.0 °C and $I = 0.10$ mol dm^{-3} (Na[NO$_3$])

$-\log[\mathrm{H^+}]$	$\frac{1}{2}(E_a + E_c)$[a]/ V *versus* n.h.e.	$E_a - E_c$/V
0.98	0.877	0.030
1.18	0.865	0.030
1.48	0.852	0.045
1.99[b]	0.820	0.035
2.46[b]	0.792	0.040
2.98[b]	0.755	0.045
3.36[b]	0.731	0.035
3.98[b]	0.705	0.030
4.48[b]	0.676	0.040
4.98[b]	0.645	0.040
5.58[c]	0.654	peaks
	0.560	overlap
5.98[c]	0.647	0.060
	0.520	0.060
6.48[c]	0.655	0.060
	0.475	0.060
6.98[c]	0.655	0.060
	0.445	0.080[d]
7.48[c]	0.650	0.060
	0.422	0.100[d]
7.98[e]	0.657	0.060
	0.420	0.110[d]
8.48[e]	0.657	0.060
	0.420	0.110[d]
8.98[e]	0.657	0.065
	0.420	0.100[d]
9.98[e]	0.655	0.080
	0.420	0.110[d]

[a] Scan rate 5—20 mV s^{-1}; ±0.005 V. [b] Acetate buffer (2.50×10^{-2} mol dm^{-3}). [c] Phosphate buffer (2.50×10^{-2} mol dm^{-3}). [d] Peak is pseudo-reversible even at low scan rates. [e] Borate buffer (2.50×10^{-2} mol dm^{-3}).

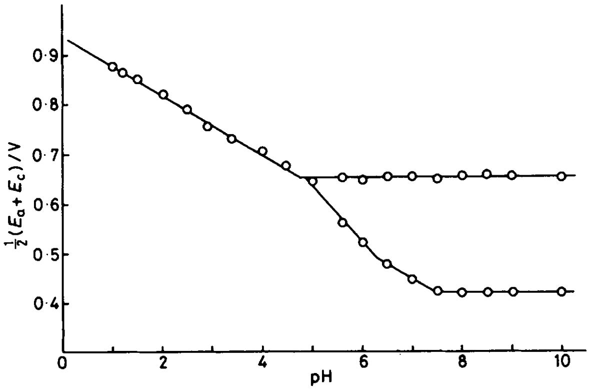

Figure 1. Dependence of the reduction potential of $[\mathrm{Ni^{IV}L}]^{2+}$ on pH at 25.0 °C in 0.10 mol dm^{-3} Na[NO$_3$]

In Table 2, the stoicheiometry of reduction of $[\mathrm{Ni^{IV}L}]^{2+}$ by $[\mathrm{Co(phen)_3}]^{2+}$ is shown to be 1 : 2, consistent with equation (1) and formation of $[\mathrm{Co(phen)_3}]^{3+}$ in the reaction.

$$[\mathrm{Ni^{IV}L}]^{2+} + 2\,[\mathrm{Co(phen)_3}]^{2+} \longrightarrow [\mathrm{Ni^{II}L}] + 2\,[\mathrm{Co(phen)_3}]^{3+} \quad (1)$$

Absorbance changes for the reduction of $[\mathrm{Ni^{IV}L}]^{2+}$ by $[\mathrm{Co(phen)_3}]^{2+}$ are biphasic in nature. The first step is very

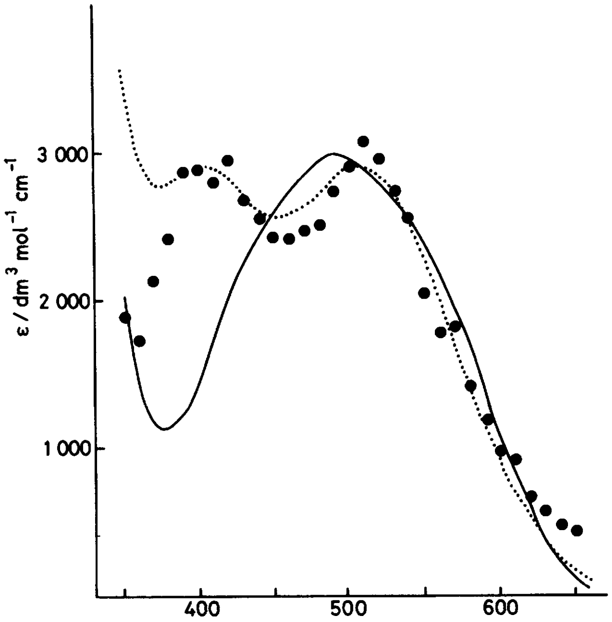

Figure 2. (*a*) (· · · ·) Spectrum of $[Ni^{III}L]^+$ generated electrochemically (0.575 V *versus* n.h.e.) at pH 6.0, 25.0 °C, and $I = 0.10$ mol dm^{-3} ($Na[NO_3]$); (*b*) (——) spectrum of $[Ni^{III}LH]^{2+}$ in 0.05 mol dm^{-3} HNO_3 at 25.0 °C and $I = 0.10$ mol dm^{-3} ($Na[NO_3]$); (*c*) (●) spectrum of the intermediate detected in the $[Co(phen)_3]^{2+}$ reduction of $[Ni^{IV}L]^{2+}$ {$[Co(phen)_3{}^{2+}] = 2.50 \times 10^{-4}$ mol dm^{-3}, $[Ni^{IV}L^{2+}] = 8.7 \times 10^{-6}$ mol dm^{-3}, pH 6.11, 25.0 °C, and $I = 0.10$ mol dm^{-3} ($Na[NO_3]$)}

Table 2. Stoicheiometry of the reaction [a] between $[Ni^{IV}L]^{2+}$ and $[Co(phen)_3]^{2+}$

Amount of reagent/mmol		Amount $[Ni^{IV}L]^{2+}$ remaining/ mmol	$[Co(phen)_3]^{2+}$/ $[Ni^{IV}L]^{2+}$ [b]
$[Ni^{IV}L]^{2+}$	$[Co(phen)_3]^{2+}$		
2.90	4.00	0.99	2.09
3.87	4.00	1.90	2.03
5.81	4.00	3.55	1.77
7.74	4.00	5.63	1.89
			Average 1.95 ± 0.14

[a] At pH 6.0, 25.0 °C, and $I = 0.10$ mol dm^{-3} ($Na[NO_3]$). [b] Molar ratio of reagents consumed in the reaction.

rapid and is first order in both $[Ni^{IV}L^{2+}]$ and $[Co(phen)_3{}^{2+}]$, Figure 3. The reaction rate is independent of pH. A point-by-point spectrum of the absorbance of the solution when this reaction is complete is shown in Figure 2(*c*). The absorbance at 500 nm is approximately half of the original nickel(IV) absorbance.

The second, slower phase is well separated from the first especially at high pH, allowing separate treatment of the absorbance data. These give good first-order plots and the pseudo-first-order rate constants, Table 3, show a linear dependence on $[Co(phen)_3{}^{2+}]$. A strong pH dependence for the second-order rate constant, k_2 (Figure 4), was analysed according to expression (2) using an iterative least-squares

$$k_2 = (K_h k_{2b} + k_{2a}[H^+])/(K_h + [H^+]) \qquad (2)$$

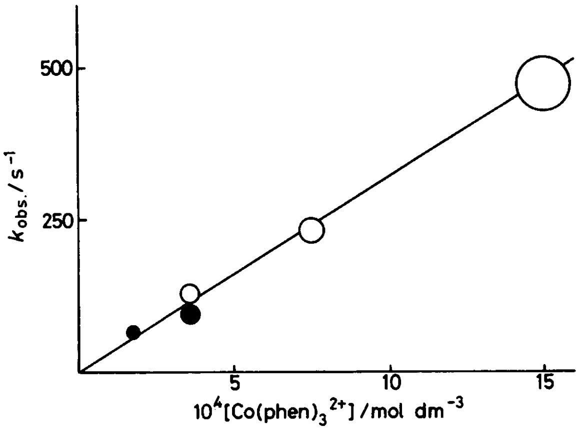

Figure 3. Plot of $k_{obs.}$ against $[Co(phen)_3{}^{2+}]$ for the reduction of $[Ni^{IV}L]^{2+}$ at 25.0 °C and $I = 0.10$ mol dm^{-3} ($Na[NO_3]$); (○) pH 6.10, (●) pH 4.04. Size of spheres indicates relative uncertainty

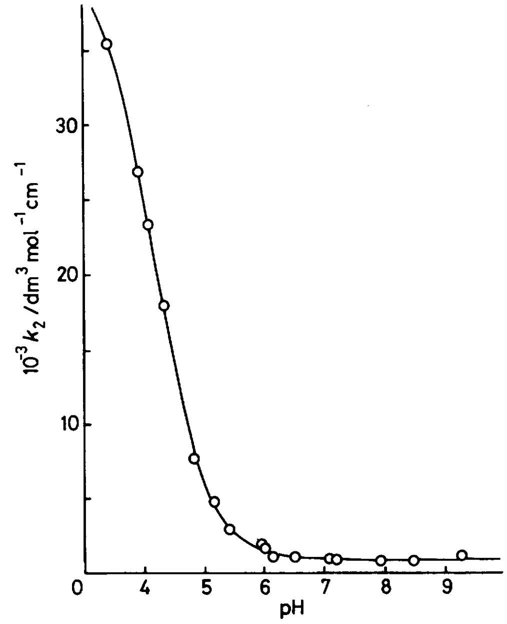

Figure 4. The dependence of the second-order rate constant k_2 on pH for the reduction of nickel(III) by $[Co(phen)_3]^{2+}$ at 25.0 °C and $I = 0.10$ mol dm^{-3} ($Na[NO_3]$)

procedure. Best fit values for $K_h = (8.91 \pm 1.5) \times 10^{-5}$ mol dm^{-3}, $k_{2a} = (4.13 \pm 0.05) \times 10^4$ dm^3 mol^{-1} s^{-1}, and $k_{2b} = (8.3 \pm 1.1) \times 10^2$ dm^3 mol^{-1} s^{-1} yield the calculated curve shown in Figure 4.

Discussion

The reduction potential, $\bar{E}$, of a complex $[ML]^{n+}$ involving *n* electrons and *m* protons, equation (3), depends on pH according to equation (4) (E° = standard potential). The

$$[ML]^{n+} + n\,e^- + m\,H^+ \rightleftharpoons [MLH_m] \qquad (3)$$

$$\bar{E} = E^\circ - 0.059\,\frac{m}{n}\,pH \qquad (4)$$

number of electrons, n, can be established from the peak-to-peak separation in a cyclic voltammetry experiment. For a reversible couple, the peak-to-peak separation is $59/n$ mV.

The cyclic voltammetry data at low pH [4] can be readily explained by a one-step, two-electron transfer accompanied by one proton per electron and consistent with equation (5).

$$[\mathrm{Ni^{IV}L}]^{2+} + 2\,e^- + 2\,\mathrm{H^+} \rightleftharpoons [\mathrm{Ni^{II}LH_2}]^{2+} \qquad E^\ominus = 0.937 \pm 0.0004\ \mathrm{V} \quad (5)$$

Above pH 5, the nickel(III)/(II) potential is smaller than the nickel(IV)/(III) potential and two distinct one-electron processes can be defined. The nickel(IV)/(III) reduction (6) is

$$[\mathrm{Ni^{IV}L}]^{2+} + e^- \rightleftharpoons [\mathrm{Ni^{III}L}]^{+} \qquad E^\ominus = 0.654 \pm 0.0004\ \mathrm{V} \quad (6)$$

independent of pH while protic equilibria involving the nickel(II) complex [4] with pK_h values 5.79 and 7.69 provide an explanation of the pH dependence of the nickel(III)/(II) reduction, equations (7)—(9). The form of these results and

$$[\mathrm{Ni^{III}L}]^{+} + e^- + 2\,\mathrm{H^+} \rightleftharpoons [\mathrm{Ni^{II}LH_2}]^{2+} \qquad E^\ominus = 1.23 \pm 0.01\ \mathrm{V} \quad (7)$$

$$[\mathrm{Ni^{III}L}]^{+} + e^- + \mathrm{H^+} \rightleftharpoons [\mathrm{Ni^{II}LH}]^{+} \qquad E^\ominus = 0.86 \pm 0.01\ \mathrm{V} \quad (8)$$

$$[\mathrm{Ni^{III}L}]^{+} + e^- \rightleftharpoons [\mathrm{Ni^{II}L}] \qquad E^\ominus = 0.420 \pm 0.007\ \mathrm{V} \quad (9)$$

the derived potentials are very similar to those obtained by Mohanty and Chakravorty [4] in 0.01 mol dm^{-3} KCl. Protonation of these complexes stabilises the lower oxidation states.

An important observation for the remaining discussion is the absence, over the pH range examined, of evidence for a protic equilibrium involving the nickel(IV) complex, $[\mathrm{Ni^{IV}L}]^{2+}$.

Controlled potential electrolysis of solutions of the nickel(II) complex at pH 7.0 leads to formation of $[\mathrm{Ni^{III}L}]^{+}$ which is relatively long-lived in neutral solution. This complex has a visible spectrum very similar to that of $[\mathrm{Ni^{IV}L}]^{2+}$, Figure 2(*a*), but about half the intensity. The peak around 400 nm for $[\mathrm{Ni^{III}L}]^{+}$ is shifted to higher energy than the corresponding peak for $[\mathrm{Ni^{IV}L}]^{2+}$ (430 nm) and may be indicative of a ligand-to-metal charge transfer. E.s.r. data for $[\mathrm{Ni^{III}L}]^{+}$ suggest that the complex is best described as a true nickel(III) species with the unpaired electron in a d_{z^2} orbital, and not a nickel(II)–ligand radical complex.[10,11] This spectrum is in good agreement with previous reports.[2,4]

On protonation, the nickel(III) peak around 400 nm is lost and the e.s.r. spectrum indicates a much smaller orbital contribution to paramagnetism giving the complex more ligand radical character.[10] As predicted by the redox potential data, the complex slowly disproportionates to nickel(II) and nickel(IV).

The reduction of $[\mathrm{Ni^{IV}L}]^{2+}$ by $[\mathrm{Co(phen)_3}]^{2+}$ has a 1 : 2 stoicheiometry as might be expected since $[\mathrm{Co(phen)_3}]^{2+}$ ($E^\ominus = 0.37$ V) [12] can be oxidised by both nickel(IV) and nickel(III). The reaction as monitored at 500 nm is biphasic, both processes showing a first-order decay in absorbance and both first order in $[\mathrm{Co(phen)_3}]^{2+}$.

In order to identify these processes, the spectrum of the reaction at the end of the first phase, Figure 2(*c*), at pH 6.1 was compared with the spectrum of $[\mathrm{Ni^{III}L}]^{+}$ at the same pH produced by controlled potential electrolysis. The spectra are virtually superimposable over the range where only the metal ion complex absorbs. An isosbestic point for the $[\mathrm{Ni^{IV}L}]^{2+}/[\mathrm{Ni^{III}L}]^{+}$ conversion exists at 390 nm. The final nickel(II) product has comparatively little absorbance in the visible region: 780 (36), 500 nm (ε 78 dm^3 mol^{-1} cm^{-1}).[3]

Table 3. Pseudo-first order rate constants for reduction of nickel(III) by $[\mathrm{Co(phen)_3}]^{2+}$ at 25.0 °C and I = 0.10 mol dm^{-3} (Na[NO$_3$])

$-\log\,[\mathrm{H^+}]$	$10^4[\mathrm{Co(phen)_3}^{2+}]$/ mol dm^{-3}	$10^6[\mathrm{Ni^{III}}]$/ mol dm^{-3}	$k_{\mathrm{obs.}}$/s^{-1}
3.40 [a]	2.50	9.6	8.85 ± 0.04
3.88 [a]	2.50	9.6	6.7 ± 0.3
4.02 [a]	7.45	38.0 [b]	17.5 ± 0.5
4.02 [a]	7.45	17.9	16.0 ± 1.0
4.33 [a]	2.50	9.6	4.5 ± 0.1
4.80 [a]	2.50	9.6	1.91 ± 0.06
5.12 [a]	2.50	9.6	1.16 ± 0.05
5.40 [a]	2.50	9.6	0.71 ± 0.06
5.89 [a]	2.50	4.7	0.49 ± 0.09
5.98 [c]	0.50	5.9	0.10 ± 0.01
5.98 [c]	1.50	5.9	0.24 ± 0.01
5.98 [c]	2.50	5.9	0.42 ± 0.04
5.98 [c]	3.75	5.9	0.53 ± 0.01
5.98 [c]	5.00	5.9	0.75 ± 0.01
6.09 [a]	14.90	38.0 [b]	1.47 ± 0.01
6.09 [a]	14.90	75.2 [d]	1.38 ± 0.08
6.50 [e]	2.50	4.7	0.27 ± 0.02
7.02 [e]	2.50	5.5	0.21 ± 0.01
7.18 [e]	2.50	4.7	0.21 ± 0.01
7.57 [f]	2.50	5.5	0.20 ± 0.02
7.92 [f]	2.50	4.7	0.19 ± 0.01
8.46 [f]	2.50	5.5	0.19 ± 0.01
9.28 [g]	2.50	5.5	0.22 ± 0.01

[a] Acetate buffer (1.0 × 10^{-2} mol dm^{-3}). [b] Electrochemically generated nickel(III). [c] Acetate buffer (2.5 × 10^{-2} mol dm^{-3}). [d] Average of 500 and 390 nm traces. [e] Phosphate buffer (1.0 × 10^{-2} mol dm^{-3}). [f] Mixed phosphate–borate buffer (1.0 × 10^{-2} mol dm^{-3} total). [g] Borate buffer (1.0 × 10^{-2} mol dm^{-3}).

The first, rapid absorbance change which is independent of pH is identified with reduction of $[\mathrm{Ni^{IV}L}]^{2+}$, equation (10).

$$[\mathrm{Ni^{IV}L}]^{2+} + [\mathrm{Co(phen)_3}]^{2+} \xrightarrow{k_1} [\mathrm{Ni^{III}L}]^{+} + [\mathrm{Co(phen)_3}]^{3+} \quad (10)$$

This absorbance change is replaced by a small induction period at 390 nm. Low-spin, d^6 nickel(IV) is substitution inert and the value for $k_1 = (3.27 \pm 0.19) \times 10^5$ dm^3 mol^{-1} s^{-1} at 25 °C in 0.10 mol dm^{-3} Na[NO$_3$] is consistent with an outer-sphere reaction.

The slower reaction which is pH dependent is thus identified with reduction of $[\mathrm{Ni^{III}L}]^{+}$. This was confirmed by using electrogenerated $[\mathrm{Ni^{III}L}]^{+}$ as reactant. Since the complex $[\mathrm{Co(phen)_3}]^{2+}$ exhibits no protic equilibria in the pH range of interest, protonation must occur at the nickel(III) complex, equation (11). Values for $K_h = (8.91 \pm 1.5) \times 10^{-5}$ mol dm^{-3}, $k_{2a} = (4.13 \pm 0.05) \times 10^4$ dm^3 mol^{-1} s^{-1}, and $k_{2b} = (8.28 \pm 1.07) \times 10^2$ dm^3 mol^{-1} s^{-1} are obtained from equation (2) at 25 °C and I = 0.10 mol dm^{-3} (Na[NO$_3$]). There is no information about the lability of these nickel(III) complexes although the axial positions of tetragonal nickel(III) complexes are relatively labile. However, substitution rates [13] are generally less than 10^2 s^{-1} and it is likely that reactions (12) and (13) go by outer-sphere pathways also.

$$[\mathrm{Ni^{III}L}]^{+} + \mathrm{H^+} \overset{K_h}{\rightleftharpoons} [\mathrm{Ni^{III}LH}]^{2+} \quad (11)$$

$$[\mathrm{Ni^{III}L}]^{+} + [\mathrm{Co(phen)_3}]^{2+} \xrightarrow{k_{2b}} [\mathrm{Ni^{II}L}] + [\mathrm{Co(phen)_3}]^{3+} \quad (12)$$

$$[\mathrm{Ni^{III}LH}]^{2+} + [\mathrm{Co(phen)_3}]^{2+} \xrightarrow{k_{2a}} [\mathrm{Ni^{II}LH}]^{+} + [\mathrm{Co(phen)_3}]^{3+} \quad (13)$$

Protonation enhances the reactivity of nickel(III). This is primarily due to the increased reduction potential of the protonated species $[Ni^{III}LH]^{2+}$, equation (14), with a value of

$$[Ni^{III}LH]^{2+} + e^- \rightleftharpoons [Ni^{II}LH]^+ \qquad (14)$$

0.64 V compared with 0.42 V for $[Ni^{III}L]^+$. The trend of increasing difficulty of protonation with increasing oxidation state of the metal ion is clearly illustrated with initial protonation pK_h 7.69,[4] 4.05, and <1 for Ni^{II}, Ni^{III}, and Ni^{IV} respectively. Similar trends are shown by the corresponding iron(II) and iron(III) complexes.[14,15]

The reagent $[Co(phen)_3]^{2+}$ is well characterised and has a self-exchange rate [16] of 45 $dm^3 mol^{-1} s^{-1}$ at 25 °C and $I = 0.10$ mol dm^{-3}. Application of Marcus theory to these outer-sphere reactions leads to estimates for the self-exchange rates of $[Ni^{IV/III}L]^{2+/+}$ of 1×10^5 $dm^3 mol^{-1} s^{-1}$, and for $[Ni^{III/II}L]^{+/0}$ and $[Ni^{III/II}LH]^{2+/+}$ of 2×10^3 and 1×10^3 $dm^3 mol^{-1} s^{-1}$ respectively. All these values are rapid, consistent with little structural barrier to electron transfer. The similarity of the values for the two nickel(III) complexes is of interest since electron paramagnetic resonance data indicate differences in their electronic structure.

Reduction by Ascorbate Ion: a Reinterpretation.—The results of the present study of the reduction of $[Ni^{IV}L]^{2+}$ by $[Co(phen)_3]^{2+}$ and particularly, the characterisation of the nickel(III) intermediate, $[Ni^{III}L]^+$, allow a reinterpretation of a previous report [2] of the reduction by ascorbate ion. In the ascorbate reduction, a single, rapid absorbance change was detected at 500 nm and the reaction spectrum, mistaken as characteristic of nickel(IV), is now shown to be nickel(III). The strong pH dependence of the reaction with pK_h 3.70 ($Na[ClO_4]$) can be equated with protonation of nickel(III) as in the present work. Rate constants for reaction of $[Ni^{III}L]^+$ and $[Ni^{III}LH]^{2+}$ with ascorbate ion are 1.36×10^4 and 3.02×10^5 $dm^3 mol^{-1} s^{-1}$ respectively. Reduction of $[Ni^{IV}L]^{2+}$ proceeds at a rate in excess of 10^7 $dm^3 mol^{-1} s^{-1}$. However, the broad mechanistic outline with two discrete electron-transfer steps rather than a simultaneous two-electron step is confirmed.

Conclusions

At 25 °C in 0.10 mol dm^{-3} $Na[NO_3]$, the reduction potentials for the complexes $[Ni^{IV}L]^{2+}$, $[Ni^{III}L]^+$, and $[Ni^{III}LH]^{2+}$ are 0.65, 0.42, and 0.64 V respectively. The reduction of $[Ni^{IV}L]^{2+}$ by the one-electron reductant $[Co(phen)_3]^{2+}$ and the two-electron reductant ascorbate ion both proceed in discrete one-electron steps and the intermediate $[Ni^{III}L]^+$ has been characterised. The nickel(III) complex undergoes protonation with pK_h 4.05. These redox reactions of nickel(IV) and nickel(III) are outer sphere in nature and self-exchange rates are around 10^5 $dm^3 mol^{-1} s^{-1}$ for the nickel(IV)/(III) change and 10^3 $dm^3 mol^{-1} s^{-1}$ for the nickel(III)/(II) change.

Acknowledgements

We thank the S.E.R.C. for a grant to purchase a stopped-flow spectrophotometer, CAPES (Brazil) for a maintenance grant (to M. C. M. L.), and Dr. E. Smith for the use of e.s.r. facilities.

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Received 8*th March* 1982; *Paper* 2/403