

Kinetic Studies of the Reduction of Nickel Oxime Complexes by Tris(1,10-phenanthroline)cobalt(II) and Hydroquinone in Aqueous Media†

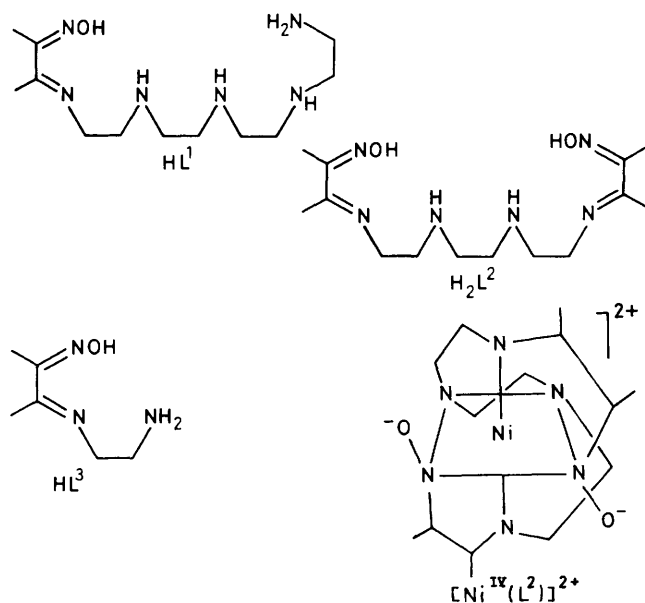
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Rate studies have been made on the reduction of a nickel(IV) bis-oxime, bis(6-amino-3-methyl-4-azahex-3-en-2-one oximate)nickel(IV), $[\text{Ni}(\text{L}^3)_2]^{2+}$, and a nickel(III) mono-oxime (15-amino-3-methyl-4,7,10,13-tetra-azapentadec-3-en-2-one oximate)nickel(III), $[\text{Ni}(\text{L}^1)]^{2+}$, species using $[\text{Co}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) and hydroquinone (H_2quin), and on the oxidation of $[\text{Ni}^{\text{II}}(\text{HL}^1)]^{2+}$ using $[\text{Ni}^{\text{III}}(\text{L}^4)_2]^{3+}$ ($\text{L}^4 = 1,4,7\text{-triazacyclononane}$). Reactions were carried out in the pH range 4–8, and using the lack of proton dependence on the rate associated with the Co^{II} reductions, it is possible to distinguish pathways involving species derived from proton-related equilibria for both the nickel complexes and hydroquinone. Self-exchange rates have been determined using a Marcus correlation. In the case of the monoxime, for the deprotonated couple, $[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+} - [\text{Ni}^{\text{II}}(\text{L}^1)]^+$, $k_{\text{exc.}} = (4 \pm 2) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and for $[\text{Ni}^{\text{III}}(\text{HL}^1)]^{3+} - [\text{Ni}^{\text{II}}(\text{HL}^1)]^{2+}$, $k_{\text{exc.}} \text{ ca. } 6 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. For the deprotonated bis-oxime complexes $[\text{Ni}^{\text{IV}}(\text{L}^3)_2]^{2+} - [\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ and $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+ - [\text{Ni}^{\text{II}}(\text{L}^3)_2]^0$, $k_{\text{exc.}} = (8 \pm 3) \times 10^4$ and $(8 \pm 4) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. For the protonated couple, ($\text{p}K = 4.43 \pm 0.04$), $[\text{Ni}^{\text{III}}(\text{L}^3)(\text{HL}^3)]^{2+} - [\text{Ni}^{\text{II}}(\text{L}^3)(\text{HL}^3)]^+$, $k_{\text{exc.}} \text{ ca. } 5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. However, for the reactions of the nickel(III) species with the quinone and catecholate anions, Hquin^- and Hcat^- , there is evidence for an inner-sphere process which may be substitution controlled. The rate constants are compared with the few data previously available, and are discussed with regard to the inner-sphere reorganisation required for electron transfer.

Reactions of the higher oxidation states of nickel continue to be of interest. Macrocyclic complexes of nickel(III) have been identified^{1–4} and the rates of redox reactions have been measured^{5–8} leading to self-exchange rate constants for the $\text{Ni}^{\text{III}}\text{L} - \text{Ni}^{\text{II}}\text{L}$ couples. In contrast, much less is known of the chemistry of nickel(IV). Early work by Drago and Baucom⁹ demonstrated an optimum arrangement for stabilising Ni^{IV} as a pseudo-octahedral array of nitrogen-donor atoms containing at least two oxime moieties. Chakravorty *et al.*^{10–12} extended this principle and synthesised a series of ligands containing oxime groups (L^2 , L^3) where both Ni^{III} and Ni^{IV} states have been stabilised. X-Ray determinations of the bis-oxime-nickel(III) and -nickel(IV) $\{[\text{Ni}^{\text{III}}(\text{L}^2)]$, $[\text{Ni}^{\text{IV}}(\text{L}^3)_2]\}$ complexes formed have been published.^{13–15} For L^1 only the Ni^{III} state is formed on oxidation.

To date, very few kinetic data have been reported on these systems, and investigations have centred mainly around the $\text{Ni}^{\text{III}}\text{L}$ and $\text{Ni}^{\text{IV}}\text{L}$ ions. The unusual stability of the $[\text{Ni}(\text{L}^2)]^{2+}$ ion ($\text{H}_2\text{L}^2 = 3,14\text{-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime}$) associated with the low-spin d^6 centre renders it especially suitable^{16,17} for kinetic studies. The one-electron reduction of $[\text{Ni}(\text{L}^2)]^{2+}$ to $[\text{Ni}(\text{L}^2)]^+$ is pH independent and can be monitored at $\text{pH} > 8.5$ ($E^\circ = 0.64 \text{ V}$ against n.h.e.). At lower pH (6–8) a second pH-dependent reduction is also evident, consistent with reactive protonated and deprotonated forms of the nickel(III) species. The rate of disproportionation of $[\text{Ni}^{\text{III}}(\text{HL}^2)]^{2+}$ is relatively slow ($k_0 \sim 4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) so that separate one-electron reductions ($\text{Ni}^{\text{IV}} \rightarrow \text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$) may be studied¹⁶ with reagents such as $[\text{Co}(\text{phen})_3]^{2+}$ and $[\text{Co}(\text{edta})]^{2-}$ (phen = 1,10-phenanthroline, edta = ethylenediaminetetra-acetate).¹⁸

In this paper, we wish to present kinetic data on two related



systems, using the ligands L^1 and L^3 . In the case of $[\text{Ni}(\text{L}^1)]^+$, the mono-oxime complex is oxidised exclusively to a nickel(III) low-spin species,¹³ the e.s.r. spectrum being consistent with the unpaired electron in the d_{z^2} orbital. The ligand L^3 affords an opportunity to examine both $\text{Ni}^{\text{IV}} - \text{Ni}^{\text{III}}$ and $\text{Ni}^{\text{III}} - \text{Ni}^{\text{II}}$ couples in a system, which, although somewhat less stable than L^2 , is still meridional in ligand disposition and where bond rearrangements accompanying electron transfer may be accomplished somewhat more easily. It is also of interest to compare self-exchange rates for these open chain systems with those of the $\text{Ni}^{\text{II}} - \text{Ni}^{\text{III}}$ macrocyclic complexes investigated recently.

† Supplementary data available (No. SUP 56718, 9 pp.); various rate data as specified in the text. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

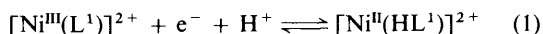
Experimental

(15-Amino-3-methyl-4,7,10,13-tetra-azapentadec-3-en-2-one oximate)nickel(III) Perchlorate, $[\text{Ni}(\text{L}^1)][\text{ClO}_4]_2$.—The preparation used was essentially that of Singh and Chakravorty *et al.*¹³ via butane-2,3-dione monoxime (biacetyl monoxime) and $\text{NH}(\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_2$ followed by complexation with nickel(II) leading to $[\text{Ni}^{\text{II}}(\text{HL}^1)][\text{ClO}_4]_2$ (Found: C, 27.20; H, 5.30; N, 15.85. Calc. for $\text{C}_{12}\text{H}_{28}\text{Cl}_2\text{N}_6\text{NiO}_9$: C, 27.25; H, 5.45; N, 16.0%).

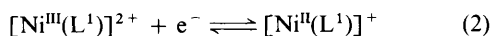
$[\text{Ni}(\text{HL}^1)][\text{ClO}_4]_2$ (0.2 g) was dissolved in aqueous NaOH (5 cm^3 , 0.2 mol dm^{-3}). The resulting brown solution was filtered and to the filtrate was added $[\text{NH}_4]_2[\text{S}_2\text{O}_8]$ (0.04 g) with continuous shaking. The reaction mixture turned a deep violet colour and 5 drops of saturated NaClO_4 solution were added. On cooling (0 °C), dark red crystals were deposited, which after filtration and washing with cold water, ethanol, and diethyl ether were dried *in vacuo* over calcium chloride (Found: C, 27.25; H, 5.15; N, 15.90. Calc. for $\text{C}_{12}\text{H}_{27}\text{Cl}_2\text{N}_6\text{NiO}_9$: C, 27.35; H, 5.30; N, 15.80%).

The u.v.–visible spectrum of $[\text{Ni}(\text{L}^1)]^{2+}$ is dominated by a metal–ligand charge-transfer band, λ_{max} , 498, $\epsilon = (2.7 \pm 0.2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, a feature used in the kinetic analysis. The e.s.r. frozen-solution (77 K) spectra of the Ni^{III} species are pH dependent. Above pH *ca.* 5 a near isotropic spectrum is observed ($g = 2.10$) but in more acidic conditions, axial symmetry ($g_{\parallel} = 2.03$ and $g_{\perp} = 2.13$) is found, with hyperfine interaction characteristic of two axially co-ordinated nitrogen centres. In this regard, the spectrum is identical to the room-temperature powder spectrum.¹⁰ The results are consistent with protonation of the oxime moiety at lower pH leading to greater tetragonal distortion, resulting in more pronounced hyperfine coupling. Protonation of the co-ordinated oxime is preferred to that at an amine or imine nitrogen which would result in dissociation of the complex.

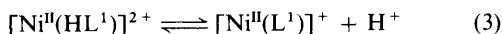
Over the pH range 5–8, cyclic voltammograms showed pH dependence and quasi-reversibility with peak–peak separations of *ca.* 70 mV. The formal potential for the couple given by equation (1) was computed¹³ as $E_p = 0.91 \pm 0.01 \text{ V vs. n.h.e.}$



This is close to that (0.904 V) [0.68 V *vs.* saturated calomel electrode (s.c.e.)] derived earlier.¹³ The potential for the related couple [equation (2)] has not been measured. A value may be



estimated based on (a) consistency with the observed changes in E° with pH as measured by cyclic voltammetry, and (b) it has been shown¹² that observed pH-dependent potentials can be separated into electron-transfer and proton-transfer contributions. For reaction (3) using a value of $\text{p}K_a = 6.8 \pm 0.5$, in



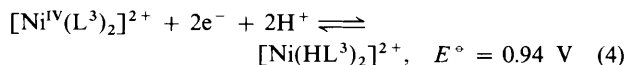
conformity with values for similar species¹² and with the observed cyclic voltammetry traces, together with the knowledge that $[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+}$ is a strong acid ($\text{p}K < 1$), gives $E^\circ = 0.49 \pm 0.03 \text{ V}$ for the couple (2). These potentials were used in subsequent analyses of the kinetic data.

Bis(6-amino-3-methyl-4-azaheX-3-en-2-one oxime)nickel(II) Perchlorate $[\text{Ni}(\text{HL}^3)]_2[\text{ClO}_4]_2$.—The free ligand 6-amino-4-azaheX-3-en-2-one oxime (HL^3) was prepared according to the literature method,¹² by reaction of ethylenediamine (1.2 g) with biacetyl monoxime (2.02 g) in dry di-isopropyl ether (10 cm^3). Yield 1.53 g. To the ligand (1.4 g) in ethanol was added an ethanolic solution of nickel perchlorate (1.8 g). After warming

with continuous stirring, and concentration, reddish brown crystals were deposited. These were recrystallised from ethanol to yield 1.6 g (50%) of pure product (Found: C, 26.7; H, 4.80; N, 15.20. Calc. for $\text{C}_{12}\text{H}_{26}\text{Cl}_2\text{N}_6\text{NiO}_{10}$: C, 26.65; H, 4.80; N, 15.40%). The corresponding nickel(IV) complex, $[\text{Ni}(\text{L}^3)]_2[\text{ClO}_4]_2$, was prepared using concentrated HNO_3 as oxidant, according to the method of Chakravorty and co-workers¹² (Found: C, 26.60; H, 4.55; N, 15.60. Calc. for $\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{N}_6\text{NiO}_{10}$: C, 26.60; H, 4.45; N, 15.50%).

The u.v.–visible spectrum of $[\text{Ni}(\text{L}^3)]^{2+}$ exhibits two maxima in the visible region, at 505 [$\epsilon = (6.1 \pm 0.1) \times 10^3$] and 419 nm [$\epsilon = (4.9 \pm 0.2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$].

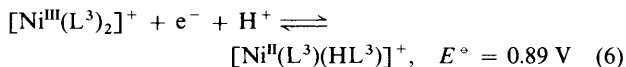
Cyclic voltammograms performed in buffered acetate or phosphate media, $I = 0.10 \text{ mol dm}^{-3}$ (NO_3^-), showed the electrochemistry to be dependent on hydrogen-ion concentration, as has been observed previously.¹⁰ Below pH 6, a single pH dependent, two-electron wave was observed, corresponding to the process given by equation (4). Above pH 6, two



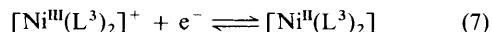
distinct one-electron waves were observed. The wave at higher potential was pH independent and corresponds to the process (5). The pseudo-reversible (peak separations $< 100 \text{ mV}$), pH-



dependent wave at lower potential has been attributed¹² to the reaction (6). Knowledge¹² of the successive $\text{p}K_a$ values of

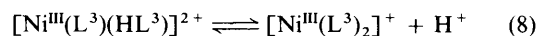


$[\text{Ni}^{\text{II}}(\text{HL}^3)]^{2+}$ (7.80 and 10.00, respectively) permits calculations of the potential for equation (7) as 0.30 V. These values

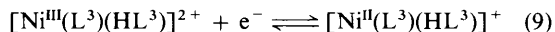


are identical ($\pm 0.01 \text{ V}$) to values reported earlier.¹²

In addition, the $\text{p}K_a$ value (4.43 ± 0.04) for equation (8)



available from kinetic data (see below), allows calculation of the potential for the couple (9) as $E^\circ = (0.63 \pm 0.02) \text{ V}$.



These non-proton-dependent potentials were used in the kinetic analyses.

Bis(1,4,7-triazacyclononane)nickel(II) Perchlorate, $[\text{Ni}(\text{L}^4)]_2[\text{ClO}_4]_2$.—The complex was prepared as described previously,⁵ affording lilac crystals. The $[\text{Ni}(\text{L}^4)]^{3+}$ ion for kinetic investigations was prepared in buffered acidic solution using a stoichiometric deficiency of hexa-aquacobalt(III) as oxidant.

Tris(1,10-phenanthroline)cobalt(II) Perchlorate, $[\text{Co}(\text{phen})_3]_2[\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$.—The complex was prepared according to a published method,¹⁹ and the yellow-orange crystalline product washed with ethanol, then diethyl ether, and dried *in vacuo*.

Hydroquinone (H_2quin) and *Catechol*.—Reagent grade hydroquinone (H_2quin) (Fisher) and catechol (H_2cat) (Aldrich) were purified by vacuum sublimation.

Table 1. Rate data for the reaction of $[\text{Ni}(\text{L}^1)]^{2+}$ and $[\text{Co}(\text{phen})_3]^{2+}$ ($T = 25.0^\circ\text{C}$; $I = 0.10 \text{ mol dm}^{-3}$ (NO_3^-); $[\text{Ni}^{\text{III}}] \text{ ca. } 1 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda = 500 \text{ nm}$)

pH	$10^{-4}[\text{Co}^{\text{II}}]/\text{mol dm}^{-3}$	$k_{\text{obs.}}/\text{s}^{-1}$	$10^{-3}k_{10}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
3.97	1.10	0.178	1.59 ± 0.07
	1.83	0.275	
	2.56	0.405	
4.38	3.12	0.495	1.69 ± 0.12
	1.10	0.193	
	1.83	0.282	
	2.56	0.427	
4.77	3.11	0.526	1.58 ± 0.03
	0.86	0.139	
	1.72	0.286	
	2.58	0.412	
4.85	3.44	0.543	1.71 ± 0.05
	1.10	0.180	
	1.83	0.315	
	2.56	0.435	
5.09	3.11	0.560	1.73 ± 0.07
	1.10	0.200	
	1.83	0.291	
	2.56	0.443	
5.78	3.11	0.552	1.61 ± 0.02
	0.86	0.138	
	1.72	0.274	
	2.58	0.413	
6.54	3.44	0.555	2.16 ± 0.04
	1.40	0.310	
	1.93	0.420	
	2.26	0.491	
	2.58	0.542	
mean $k_{10} = (1.65 \pm 0.06) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			

Results

Kinetic Studies.—The stopped-flow and data acquisition system have been described previously.²⁰ Absorbance data were collected and processed by an IBM PC microcomputer interfaced to the spectrometer via a Techmar Inc. PC-Mate Lab master module. The pH was maintained using acetate or phosphate buffers (0.02 mol dm^{-3}), and the ionic strength was held constant using LiNO_3 ($I = 0.10 \text{ mol dm}^{-3}$). Independent experiments indicated no dependence on buffer concentration. All experiments were carried out using pseudo-first-order conditions of excess (> 10 fold) reductant, and rate constants were derived from least-square plots of $\ln \Delta$ optical density vs. time which were linear for more than three half-lives.

1. **Reactions of $[\text{Ni}(\text{L}^1)]^{2+}$.**—Reactions were monitored at 500 nm, the absorbance maximum of the Ni^{III} complex. Identical results were obtained from solutions where Ni^{III} was generated electrochemically in solution, or solid Ni^{III} samples used.

Two reductants were used in this study. It is known from previous work that no hydrogen-ion dependences are associated with reactions involving $[\text{Co}(\text{phen})_3]^{2+}$.²¹ Using this reagent, any proton related pathways could be ascribed uniquely to Ni^{III} oxidant species. Hydroquinone (H_2quin) is a versatile reductant over a wide pH range. Many studies using this reagent display 'proton ambiguity', in that $[\text{H}^+]$ related reactions cannot be assigned to a specific process. The absence of any $[\text{H}^+]$ dependences for the Ni^{III} oxidant would then permit detailed examination of H_2quin and Hquin^- pathways.

$[\text{Co}(\text{phen})_3]^{2+}$ as reductant. A spectrophotometric titration, monitored at 500 nm, showed a $(1 \pm 0.005):1$ ratio of $\text{Ni}^{\text{III}}:\text{Co}^{\text{II}}$, consistent with the process in equation (10). The reaction was

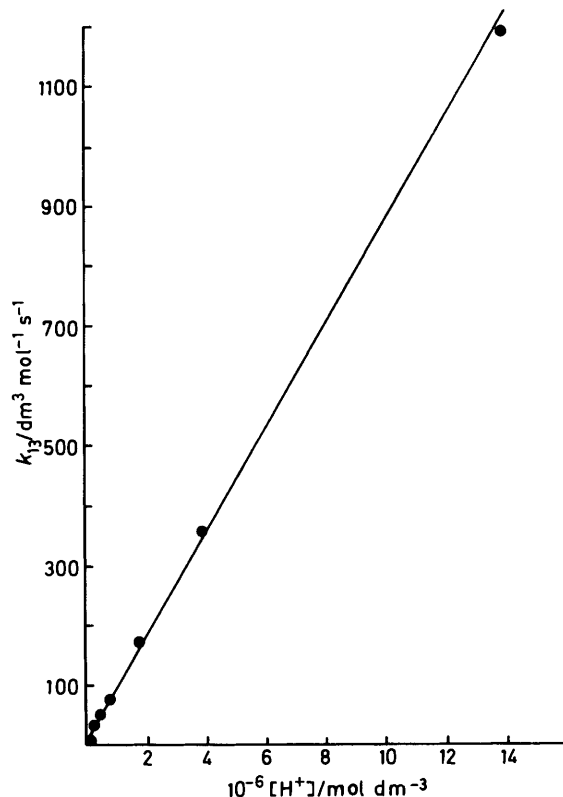
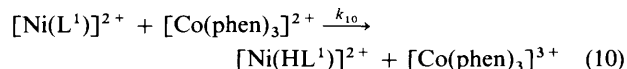


Figure 1. Plot of k_{13} against $[\text{H}^+]$ for the reaction of $[\text{Ni}(\text{L}^1)]^{2+}$ with hydroquinone

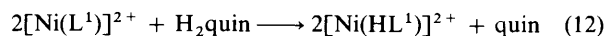


first order in both oxidant and reductant, corresponding to the rate law (11) with no dependence on pH over the range 3.97–5.78 and only a marginal increase at pH 6.54. The kinetic data

$$-d[\text{Ni}^{\text{III}}]/dt = k_{10}[\text{Ni}^{\text{III}}][\text{Co}^{\text{II}}] \quad (11)$$

are presented in Table 1. The data are consistent with reaction (10) with $k_{10} = (1.65 \pm 0.06) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. On reduction, there is a subsequent rapid protonation of the oxime bound to Ni^{II} leading to the product ion $[\text{Ni}(\text{HL}^1)]^{2+}$.

Hydroquinone as reductant. The reaction stoichiometry (pH 6.25, $\lambda = 500 \text{ nm}$) showed an oxidant:reductant ratio of $(2.0 \pm 0.05):1$ consistent with the process given by equation (12), when quin is quinone. A study at pH 5.4 revealed first-order



dependences on both $[\text{Ni}^{\text{III}}]$ and $[\text{H}_2\text{quin}]$ corresponding to the rate law (13). Investigation at various pH (see Supplementary

$$-d[\text{Ni}^{\text{III}}]/dt = k_{13}[\text{Ni}^{\text{III}}][\text{H}_2\text{quin}] \quad (13)$$

material, SUP 56718) over the range 4.22–7.15 showed a pronounced hydrogen-ion dependence with $k_{13} = k_a + k_b/[\text{H}^+]$ (see Figure 1). No spectroscopic changes of the Ni^{III} species were observed over the pH range studied, so that a proton equilibrium involving the reductant may be invoked.

Oxidation of $[\text{Ni}^{\text{II}}(\text{HL}^1)]^{2+}$ by $[\text{Ni}(\text{L}^4)_2]^{3+}$. The reaction stoichiometry (pH 3.9, $\lambda = 498 \text{ nm}$) showed an oxidant:

Table 2. Rate data for the reaction of $[\text{Ni}(\text{HL}^1)]^{2+}$ and $[\text{Ni}(\text{L}^4)_2]^{3+}$ $\{T = 25.0^\circ\text{C}, I = 0.10 \text{ mol dm}^{-3} (\text{NO}_3^-), \text{pH } 3.89, \lambda = 500 \text{ nm}\}$

$10^4[\text{Ni}(\text{HL}^1)]^{2+}/\text{mol dm}^{-3}$	$10^5[\text{Ni}(\text{L}^4)_2]^{3+}/\text{mol dm}^{-3}$	$10^4[\text{Ni}(\text{L}^4)_2]^{3+}/\text{mol dm}^{-3}$	$k_{\text{obs.}}/\text{s}^{-1}$
1.20	1.00	1.20	0.544
1.20	1.00	2.50	0.536
1.20	1.00	3.80	0.540
1.20	1.00	6.40	0.533
0.91	1.00	1.70	0.443
1.83	1.00	1.70	0.897
2.74	1.00	1.70	1.42
4.57	1.00	1.70	2.45
6.40	1.00	1.70	3.42

$$k_{14} = (4.84 \pm 0.32) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Table 3. Rate data* for the first reaction of $[\text{Ni}^{\text{IV}}(\text{L}^3)_2]^{2+}$ and $[\text{Co}(\text{phen})_3]^{2+}$ $\{T = 25.0^\circ\text{C}, I = 0.10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} (\text{NO}_3^-), [\text{Ni}^{\text{IV}}] \text{ ca. } 8 \times 10^{-6} \text{ mol dm}^{-3}, \lambda = 500 \text{ nm}\}$

pH	$10^{-5}k_{16}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
4.05	1.89
4.32	1.91
4.76	2.11
5.04	1.91
5.29	1.90
5.52	1.99
5.80	2.00
6.10	1.97
6.54	2.07

$$\text{mean } k_{16} = (1.97 \pm 0.07) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

* Each run represents the mean of four separate determinations.

Table 4. Hydrogen-ion dependence of the rate of reaction of $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^{2+}$ with $[\text{Co}(\text{phen})_3]^{2+}$ $\{T = 25.0^\circ\text{C}, I = 0.10 \text{ mol dm}^{-3} (\text{NO}_3^-), [\text{Ni}^{\text{IV}}] \text{ ca. } 8 \times 10^{-6} \text{ mol dm}^{-3}, \lambda = 500 \text{ nm}\}$

Buffer	pH	$10^{-3}k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Acetate	3.71	14.3 ± 0.02
Acetate	4.05	12.7 ± 0.02
Acetate	4.32	9.85 ± 0.28
Acetate	4.76	5.89 ± 0.05
Acetate	5.04	3.38 ± 0.09
Acetate	5.29	1.99 ± 0.05
Phosphate	5.52	1.60 ± 0.02
Acetate	5.80	0.92 ± 0.02
Acetate	6.10	0.70 ± 0.02
Phosphate	6.54	0.80 ± 0.04

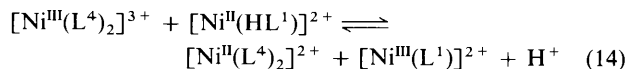
* Complete data set in Supplementary material, SUP 56718.

Table 5. Hydrogen-ion dependence on the rate of reaction of $[\text{Ni}^{\text{IV}}(\text{L}^3)_2]^{2+}$ with hydroquinone and catechol $\{T = 25.0^\circ\text{C}, I = 0.10 \text{ mol dm}^{-3} (\text{NO}_3^-), [\text{Ni}^{\text{IV}}] = 5 \times 10^{-5} \text{ mol dm}^{-3}, \lambda = 500 \text{ nm}\}$

Hydroquinone					
pH	3.61	3.65	4.10	4.45	4.53
$10^{-2}k_{18}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} *$	2.19 ± 0.29	2.39 ± 0.22	3.04 ± 0.20	6.07 ± 0.43	6.37 ± 0.75
intercept = $170 \pm 40 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$					
slope = $kK_a = (1.38 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$					
Catechol					
pH	5.86	6.01	6.30	6.34	6.59
$10^{-3}k_{18}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} *$	3.51 ± 0.2	7.5 ± 0.2	8.4 ± 0.3	8.9 ± 0.1	16.4 ± 0.9
intercept = $50 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$					
slope = $(4.4 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$					

* Second-order rate constant, $k_{\text{obs.}}/2[\text{H}_2\text{quin}]$; mean value derived from four independent determinations (see Supplementary material, SUP 56718).

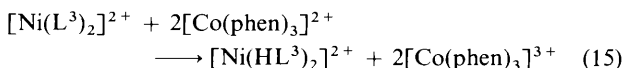
reductant ratio of $(1.00 \pm 0.05):1$ consistent with reaction (14). Kinetic studies (pH = 3.89), monitored at 500 nm, were



undertaken with excess of both $[\text{Ni}^{\text{II}}(\text{L}^4)_2]^{2+}$ and $[\text{Ni}^{\text{II}}(\text{HL}^1)]^{2+}$ present, in anticipation of some reversibility because of the small free energy change (E° for the $[\text{Ni}(\text{L}^4)_2]^{3+/2+}$ couple² is $0.947 \pm 0.004 \text{ V}$ so that $\Delta E^\circ = 0.06 \text{ V}$). Under such reaction conditions, both the forward and reverse steps of reaction (14) may be treated as pseudo-first order. The kinetic data (Table 2) are consistent with reaction (14) being irreversible under the experimental conditions, $k_{14} = (4.84 \pm 0.32) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

2. *Reactions of $[\text{Ni}(\text{L}^3)_2]^{2+}$.*—Kinetic studies were made under pseudo-first-order conditions of excess reductant and monitored at 500–505 nm, the absorbance maximum of both Ni^{IV} and Ni^{III} species.

$[\text{Co}(\text{phen})_3]^{2+}$ as reductant. The stoichiometry determined by titration, $(2 \pm 0.03):1$, is consistent with the overall reaction (15). Absorbance changes for the Ni^{IV} reduction were biphasic.



The initial fast step, first order in both $[\text{Ni}^{\text{IV}}]$ and $[\text{Co}^{\text{II}}]$ obeyed the rate law (16). The reaction yielding Ni^{III} was independent of

$$-d[\text{Ni}^{\text{IV}}]/dt = k_{16}[\text{Ni}^{\text{IV}}][\text{Co}^{\text{II}}] \quad (16)$$

pH over the range 4.05–7.13 and relevant rate data are provided in Table 3. The mean value for $k_{16} = (1.97 \pm 0.07) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

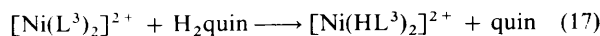
The second, slower step was well separated from the first, enabling independent treatment of the absorbance data. This reaction, also first order in both reagents, exhibits a pronounced pH dependence, with rates levelling off in the range 6.3–7.2. Rate data are presented in Table 4. Since the cobalt(II) species exhibits no proton equilibria in the range studied, the observed acid dependence is attributed to hydrogen-ion equilibria involving the nickel(III) ion, specifically protonation of one of the oxime groups, leading to $[\text{Ni}(\text{L}^3)(\text{HL}^3)]^{2+}$.

Hydroquinone or catechol as reductant. The reaction stoichiometry $(1.0 \pm 0.06):1$ was shown to be consistent with the process given in equation (17). Kinetic profiles were again pH

Table 6. Rate data for the reaction of $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^{2+}$ with hydroquinone and catechol hydrogen-ion dependences $\{T = 25.0^\circ\text{C}, I = 0.10 \text{ mol dm}^{-3} (\text{NO}_3^-), [\text{Ni}^{\text{IV}}]_{\text{initial}} \text{ ca. } 5 \times 10^{-5} \text{ mol dm}^{-3}, \lambda = 500 \text{ nm}\}$

Hydroquinone				
pH	5.08	5.18	5.19	5.31
$10^{-2}k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1a}$	5.20 ± 0.12 (5.02)	4.50 ± 0.07 (4.52)	4.40 ± 0.03 (4.47)	3.86 ± 0.04 (3.98)
pH	5.34	5.44	5.61	5.63
$10^{-2}k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1a}$	3.84 ± 0.03 (3.87)	3.44 ± 0.02 (3.56)	3.29 ± 0.89 (3.18)	3.17 ± 0.05 (3.14)
pH	6.10	6.29	6.55	6.62
$10^{-2}k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1a}$	3.19 ± 0.05 (2.94)	3.11 ± 0.10 (3.10)	3.50 ± 0.10 (3.55)	3.77 ± 0.09 (3.78)
Catechol				
pH	5.65	5.86	6.30	6.34
$10^{-2}k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1b}$	1.55 ± 0.03	1.71 ± 0.10	1.54 ± 0.02	1.55 ± 0.07
pH	6.41			
$10^{-2}k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1b}$	1.90 ± 0.08			

^a k_b = Second-order rate constant ($k_{\text{obs.}}/2[\text{H}_2\text{quin}]$) and represents the mean of at least four independent observations (see Supplementary material SUP 56718). The values in parentheses are those calculated using equation (25) with the constants in the text. ^b k_b = Second order rate constant ($k_{\text{obs.}}/2[\text{H}_2\text{cat}]$) and represent the mean of at least four independent observations (see Supplementary material, SUP 56718).



dependent. Below pH 4.6, the absorbance decay was monophasic, conforming to the rate law (18). Rate data in this region

$$-d[\text{Ni}^{\text{IV}}]/dt = k_{18}[\text{Ni}^{\text{IV}}][\text{H}_2\text{quin}] \quad (18)$$

are presented in Table 5 where it is seen that k_{18} increases with increasing pH. Above pH 4.6, a biphasic decay is observed ($\lambda = 500 \text{ nm}$) with a rapid absorbance increase followed by a slower decrease. A similar feature has been observed¹⁴ in the reduction of $[\text{Ni}^{\text{IV}}(\text{L}^2)]^{2+}$, the sexidentate ligand complex, with ascorbic acid. The spectrum of the Ni^{III} intermediate has been reported under such conditions, and, in view of the relevant E° values of the Ni^{III} and Ni^{IV} species, it is plausible to attribute the observations to the rapid reduction of $[\text{Ni}(\text{L}^3)_2]^{2+}$ followed by a slower reaction of the resulting Ni^{III} species. For the latter process, the rate law is given by equation (19). Rate data are shown in Table 6.

$$-d[\text{Ni}^{\text{III}}]/dt = 2k_1[\text{Ni}^{\text{III}}][\text{H}_2\text{quin}] \quad (19)$$

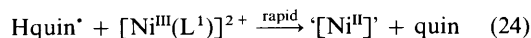
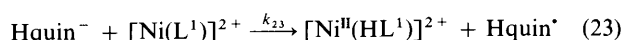
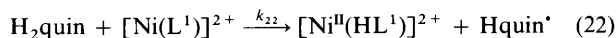
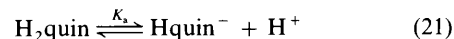
Discussion

Reactions of $[\text{Ni}(\text{L}^1)]^{2+}$.—The predominant form of the nickel(III) complex in the pH range studied is $[\text{Ni}(\text{L}^1)]^{2+}$ with the oxime group deprotonated. The absence of any hydrogen-ion dependence in the reaction with the outer-sphere reagent $[\text{Co}(\text{phen})_3]^{2+}$ permits calculation of the kinetic self-exchange of the $[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+}$ – $[\text{Ni}^{\text{II}}(\text{L}^1)]^+$ couple using a Marcus correlation.^{22,23} The second-order rate constant for an electron-transfer cross reaction, k_{ab} , is related to the individual self-exchange reactions, k_{aa} , k_{bb} , and the overall equilibrium constant, K_{ab} , by the expression (20). Detailed descriptions of

$$k_{\text{ab}} = (k_{\text{aa}}k_{\text{bb}}K_{\text{ab}}/f_{\text{ab}})^{1/2}W_{\text{ab}} \quad (20)$$

the formulation of work terms and related parameters for this expression have been provided in papers from these²⁴ and other laboratories.^{23,25} Treatment of the data for the $[\text{Co}(\text{phen})_3]^{2+}$ ^{19,21} reduction leads to a value for the kinetic self-exchange of the $[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+}$ – $[\text{Ni}^{\text{II}}(\text{L}^1)]^+$ couple of $k_{\text{exc.}} = (6 \pm 1) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

In the reaction with hydroquinone, the observed hydrogen-ion dependence may be attributed to equilibria involving the reductant. A scheme consistent with the data may be expressed as given in reactions (21)–(24), where Hquin^{\bullet} is the



semiquinone with no assumptions made as to its state of protonation. The rate expression (25) may then be written as follows. Since $K_a = 1.41 \times 10^{-10} \text{ mol dm}^{-3}$,²⁶ under the

$$-d[\text{Ni}^{\text{III}}]/dt = \frac{2(k_{22} + k_{23}K_a[\text{H}^+]^{-1})[\text{H}^+]}{(K_a + [\text{H}^+])} \cdot [\text{Ni}^{\text{III}}]_{\text{tot}} \cdot [\text{H}_2\text{quin}]_{\text{tot}} \quad (25)$$

prevailing experimental conditions $[\text{H}^+] \gg K_a$, so that [see equation (13)] $k_{13} = k_{\text{obs.}}/2[\text{H}_2\text{quin}]_{\text{tot}} = k_{22} + k_{23}K_a/[\text{H}^+]$. A linear plot of k_{13} against $[\text{H}^+]^{-1}$ has slope $k_{23}K_a$ and intercept k_{22} . Excellent linearity was observed (correlation coefficient = 0.999) leading to values of $k_{22} = 14.6 \pm 5$ and $k_{23} = (5.9 \pm 0.1) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. (A more accurate value of k_{22} may be obtained by examination of the data in Table 2 where a limiting value of $k_{22} = 5.4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is observed at low pH). The latter value was used in subsequent calculations.

The large difference in reactivity between the protonated ($k_{22} < 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and dissociated forms ($k_{23} = 5.9 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) of H_2quin may be rationalised in terms of the redox potentials and self-exchange parameters. The constant k_{23} (obtained from the slope of the plot in Figure 1) is the more precisely determined rate constant. Relatively few data are available for Hquin^- – Hquin^{\bullet} couples. An estimate of the E° value may be derived²⁷ from the expression (26), where pK_2

$$E_2^\circ = E_3^\circ + 0.059(pK_2 - pK_{r_2}) \quad (26)$$

refers to the dissociation equilibrium $\text{Hquin}^- \rightleftharpoons \text{H}^+ + \text{quin}^{2-}$ and pK_{r_2} to that of the radical ($\text{Hquin}^{\bullet} \rightleftharpoons \text{quin}^{\bullet-} + \text{H}^+$). E_3° is the potential for the process $\text{quin}^{\bullet-} + e^- \rightleftharpoons \text{quin}^{2-}$. Values of E_3° and the corresponding pK values used in equation (24) were determined experimentally or extrapolated from values for similar compounds using a linear relationship between E° and pK .^{28,29} Using $pK_2 = 11.4$ and $pK_{r_2} = 4.1$, E_2° may be estimated as 0.45 V. For the self-exchange rate, $k_{\text{exc.}}(\text{Hquin}^-$ – $\text{Hquin}^{\bullet})$, a value similar to that for the H_2quin – H_2quin^+ couple ($5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)²⁷ has been used. This is close to that for the corresponding resorcinol (*m*-dihydroxybenzene) couple determined recently³⁰ ($5.8 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) using $[\text{Ni}(\text{L}^4)_2]^{3+}$. Using these data, from the cross reaction (23) ($k_{23} = 5.9 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), the exchange rate for the $[\text{Ni}(\text{L}^1)]^{2+}$ – $[\text{Ni}(\text{L}^1)]^+$ couple is $3 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in excellent agreement (Table 7) with the value obtained using $[\text{Co}(\text{phen})_3]^{2+}$.

The value for the $[\text{Ni}(\text{L}^1)]^{2+}$ – $[\text{Ni}(\text{L}^1)]^+$ self-exchange rate calculated in a similar manner from the data for the cross-

Table 7. Self-exchange rate constants ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for Ni-L couples

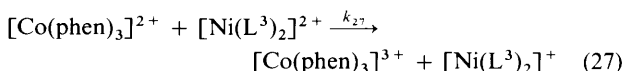
Reductants	$[\text{Co}^{\text{II}}(\text{phen})_3]^{2+}$	Hquin ⁻	Hcat ⁻
$[\text{Ni}^{\text{IV}}(\text{L}^3)_2]^{2+} - [\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$	$(7 \pm 1) \times 10^4$	$(5 \pm 2) \times 10^4$	$(12 \pm 2) \times 10^4$
$[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+ - [\text{Ni}^{\text{II}}(\text{L}^3)_2]$	8×10^3	$(3.2 \times 10^5)^a$	$(1.7 \times 10^6)^a$
$[\text{Ni}^{\text{III}}(\text{L}^3)(\text{HL}^3)]^{2+} - [\text{Ni}^{\text{II}}(\text{L}^3)(\text{HL}^3)]^+$	5×10^2	$(1.6 \times 10^4)^a$	$(1.1 \times 10^5)^a$
$[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+} - [\text{Ni}^{\text{II}}(\text{L}^1)]^+$	6×10^2	3×10^2	
$[\text{Ni}^{\text{III}}(\text{HL}^1)]^{3+} - [\text{Ni}^{\text{II}}(\text{HL}^1)]^{2+}$	$5.5 \times 10^2^b$		

^a Suggestive of inner-sphere reduction, see text. ^b Derived using the reaction with $[\text{Ni}(\text{L}^4)_2]^{3+}$.

reaction (22) ($4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is significantly different. This is perhaps not surprising since k_{22} (obtained as the intercept of the plot in Figure 1) is subject to considerable uncertainty, and there is a substantial negative driving force ($\Delta E^\circ = -0.60 \text{ V}$) for reaction (22), placing it outside the range where the Marcus relationship normally applies.

Reaction of $[\text{Ni}^{\text{III}}(\text{HL}^1)]^{2+}$ with $[\text{Ni}^{\text{III}}(\text{L}^4)_2]^{3+}$.—The observed irreversibility of reaction (14), despite the small value of ΔE° ($\sim 0.06 \text{ V}$), is attributable to the rapid and thermodynamically favoured deprotonation of the ion $[\text{Ni}^{\text{III}}(\text{HL}^1)]^{3+}$ formed initially to give $[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+}$, which is confirmed by the u.v.-visible spectrum of the product solution. Analysis, using $k_{\text{exc.}}\{[\text{Ni}(\text{L}^4)_2]^{3+} - [\text{Ni}(\text{L}^4)_2]^{2+}\} = 6.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,³¹ $\Delta E^\circ = 0.947 \text{ V}$, leads to a calculated value for the $[\text{Ni}^{\text{III}}(\text{HL}^1)]^{3+} - [\text{Ni}^{\text{II}}(\text{HL}^1)]^{2+}$ self-exchange rate of $5.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 7).

Reactions of $[\text{Ni}(\text{L}^3)_2]^{2+}$.—(a) *Reduction to Ni^{III} .* The first stage of the reaction with $[\text{Co}(\text{phen})_3]^{2+}$ shows no $[\text{H}^+]$ dependence (Table 4) and is consistent with reaction (27). Using



$\Delta E^\circ = 0.26 \text{ V}$, the self-exchange rate derived using the Marcus equation is $(7.0 \pm 1) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Since reaction (27) showed no acid dependence, the variation in rate of the first step in reduction by hydroquinone is the result of H_2quin and Hquin^- pathways similar to equations (21)–(25) above, yielding rate constants of $150 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (H_2quin) and $(9.5 \pm 0.2) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Hquin^-) respectively. For the reaction with H_2quin there is a substantial negative driving force ($\Delta E^\circ = -0.46 \text{ V}$). However, using the cross reaction with Hquin^- , the self-exchange rate constant for the $[\text{Ni}^{\text{IV}}(\text{L}^3)_2]^{2+} - [\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ couple is calculated to be $5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in excellent agreement with the $[\text{Co}^{\text{II}}(\text{phen})_3]^{2+}$ result. Further reactions were undertaken using catechol (H_2cat) as a reductant. The reaction stoichiometry is as observed with hydroquinone and a bi-phasic process was identified. For the $[\text{Ni}^{\text{IV}}(\text{L}^3)_2]^{2+} - [\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ reaction, the observed rate dependence on pH variation (see Table 5) was identical to that for the hydroquinone [equations (21)–(25)] with $k_{\text{H}_2\text{cat}} < 50 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{\text{Hcat}^-} = (1.25 \pm 0.2) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Using the latter rate constant in a Marcus correlation with $k_{\text{aa}} = 1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ³⁰ and $E^\circ = 0.48 \text{ V}$ ($\text{Hcat}^{-/0}$), a $\text{Ni}^{\text{IV}} - \text{Ni}^{\text{III}}$ self-exchange rate constant of $(12 \pm 2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is derived. This is in excellent agreement with the values determined above, $k(\text{Ni}^{\text{IV}} - \text{Ni}^{\text{III}}) = (8 \pm 3) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, confirming the outer-sphere nature of the reaction.

(b) *Reduction of $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ by $[\text{Co}(\text{phen})_3]^{2+}$.* The second stage of the reaction of $[\text{Ni}^{\text{IV}}(\text{L}^3)_2]^{2+}$ with Co^{II} is $[\text{H}^+]$ dependent. In this case, there is protonation of the nickel(III)

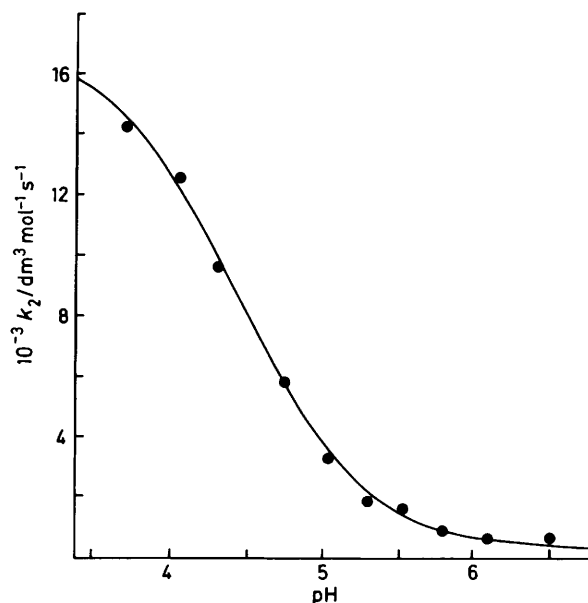
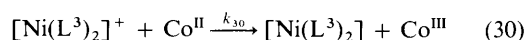
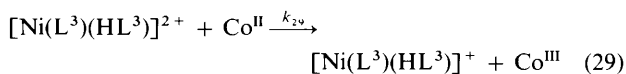
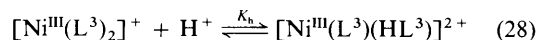


Figure 2. Hydrogen ion dependence of the rate of reduction of $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ by $[\text{Co}(\text{phen})_3]^{2+}$. The curve shown is calculated based on the parameters given in the text

oxidant. The observed data are consistent with the reaction scheme given by equations (28)–(30).



Using this scheme, the second-order rate constant k_2 (Table 4) is identified with $k_2 = k_{\text{obs.}}/[\text{Co}^{\text{II}}] = (K_h k_{29} + k_{30}[\text{H}^+]) / (K_h + [\text{H}^+])$. Analysis of the data in Table 4 by means of an iterative non-linear least-squares procedure gave best fit values of $K_h = (3.74 \pm 0.38) \times 10^{-5} \text{ mol dm}^{-3}$, $k_{29} = (1.73 \pm 0.05) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k_{30} = (3.1 \pm 1.7) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which yield the calculated curve shown in Figure 2. This value of K_h is used in calculating the potential for reaction (9). Marcus correlation derived values for the self-exchange rates for the protonated and deprotonated couples $[\text{Ni}(\text{L}^3)(\text{HL}^3)]^{2+/+}$ and $[\text{Ni}(\text{L}^3)_2]^{+/0}$ are 5×10^2 and $8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively.

(c) *Reduction of $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ by hydroquinone and catechol.* An increasingly complex $[\text{H}^+]$ dependence is observed in the second stage of the reaction of $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ with hydroquinone and catechol. In these systems, each of the reagents participates

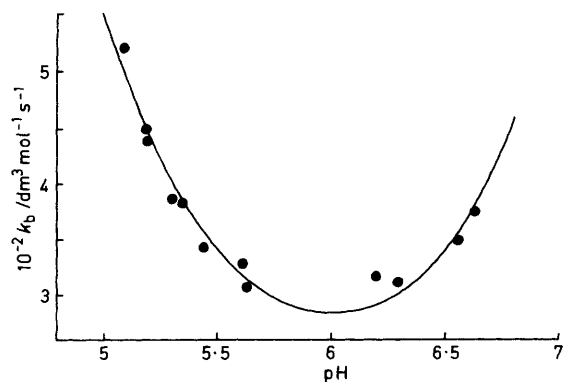
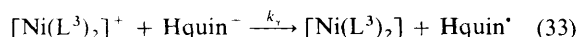
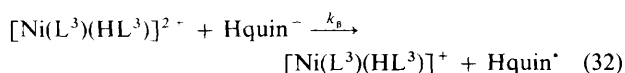
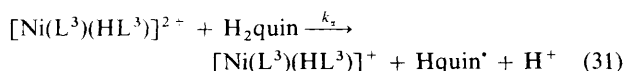


Figure 3. pH profile of the second-order rate constant for the reduction of $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ by hydroquinone. The curve shown is calculated based on the constants in the text

in a protonation equilibrium. This is confirmed in the nature of the pH profile where a shallow minimum is observed (Figure 3) for hydroquinone in the plot of k_b (the second-order rate constant) against pH. Based on reaction conditions and redox potentials, three principal reactions provide an excellent fit to the experimental data. Using equilibria (21) and (28), the reaction scheme may be presented as in equations (31)–(33).



The semiquinone radicals produced react rapidly *via* further metal-ion reduction. The rate may then be expressed as in equation (34). Thus the second-order rate constant is of the form given in equation (35).

$$R = 2 \left\{ \frac{k_x [\text{H}^+]}{K_h} + \frac{k_\beta \cdot K_a}{K_h} + \frac{k_\gamma \cdot K_a}{[\text{H}^+]} \right\} \cdot \frac{K_h}{([\text{H}^+] + K_h)} \cdot [\text{Ni}^{\text{III}}]_t [\text{H}_2\text{quin}]_t \quad (34)$$

$$k_b = \{A[\text{H}^+] + B + C/[\text{H}^+]\} \cdot K_h / ([\text{H}^+] + K_h) \quad (35)$$

Since K_a and K_h are known, individual rate constants may be evaluated using a non-linear least-squares iterative process. For hydroquinone, $k_x = (1.8 \pm 0.4) \times 10^3$, $k_\beta = (5.3 \pm 1) \times 10^7$, and $k_\gamma = (2.8 \pm 0.5) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. The corresponding values for catechol are $(4.72 \pm 0.3) \times 10^2$, $(1.43 \pm 0.15) \times 10^7$, and $(3.54 \pm 0.21) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These data, when considered in the Marcus treatment, yield values for the $[\text{Ni}(\text{L}^3)(\text{HL}^3)]^{2+/+}$ and $[\text{Ni}(\text{L}^3)_2]^{+/0}$ exchange rate constants 2–3 orders of magnitude greater than those derived using $[\text{Co}(\text{phen})_3]^{2+}$. An interpretation of these rates would involve a change in mechanism to an inner-sphere process in the case of these negatively charged ligands. One possible factor involving disproportionation of the $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ complex has been discounted since at the pH values at which rates were determined (pH > 5) any such reaction is very slow. Substitution rates at tetragonally distorted Ni^{III} centres have been shown to vary.

For the tetra-azamacrocycles,³¹ rates are *ca.* 10^2 – 10^3 s^{-1}

although where there is steric crowding in the ring, values of up to $3 \times 10^4 \text{ s}^{-1}$ are observed.³² On the other hand, in the case of the deprotonated polypeptide species where axial co-ordination is much less strong,³³ exchange rates of 10^6 – 10^7 s^{-1} are common. For the $[\text{Ni}(\text{L}^3)_2]^+$ complex, if the electron transfer is substitution controlled, a common value based on an inner-sphere rearrangement may be anticipated. The rate constants observed for reactions of Hcat[−] and Hquin[−] with this ion are 3.5×10^4 and $2.8 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. No account is taken of any pre-equilibrium association of the negatively charged ligand, although for steric reasons this may be anticipated to be small. The corresponding rates for the $[\text{Ni}(\text{L}^3)(\text{HL}^3)]^{2+}$ ion are again very close (1.43×10^7 and $5.3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively). This value is very large and may reflect the greater charge on the oxidant. To our knowledge the only other comparable data are for the sexidentate ligand complexes $[\text{Ni}^{\text{III}}\text{L}]^+$ and $[\text{Ni}^{\text{III}}(\text{HL})]^{2+}$, with the ascorbate ion (1.4×10^4 and $3 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Again, these rate constants are greatly in excess of the self-exchange rates and may refer to an inner-sphere reaction. If this is the case, then the 10–100-fold differences in rate between the $[\text{Ni}^{\text{III}}\text{L}^2]^+$ and $[\text{Ni}^{\text{III}}(\text{L}^3)_2]^+$ species may reflect the ease of rearrangement of the bis-oxime ligands compared to the single chain system where all six co-ordination sites may be affected. Of interest is the fact that in all three instances the protonated complex ion reacts more rapidly. Hydrogen bonding effects with the anion may be important, since on reduction to nickel(II) additional protonation is required. This could be achieved by exchange of the hydrogen on Hquin[−] leading not only to $[\text{Ni}(\text{H}_2\text{L}^2)]^{2+}$ or $[\text{Ni}(\text{HL}^3)_2]^{2+}$ but also to the quinone product observed.

Self-exchange rate data for the five couples under investigation are presented in Table 7. Striking differences are noted, especially for protonated species. In the case of the Ni^{IV} – Ni^{III} reduction of $[\text{Ni}(\text{L}^3)_2]^{2+/+}$, the mean rate constant (*ca.* $8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is almost identical to that ($6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)³⁴ for the hexadentate di-oxime ligand complex, $[\text{Ni}(\text{L}^2)]^{2+}$. In both cases, there is a change in electronic structure from the low-spin $t_{2g}^6 \rightarrow t_{2g}^6 e_g^1$ configuration and, although in the bis- L^3 complex there is no continuity of the 'back bone' of the ligand, the Ni–N bond length changes are virtually identical on reduction of the $[\text{Ni}(\text{L}^3)_2]^{2+}$ and $[\text{Ni}(\text{L}^1)]^{2+}$ complexes to the corresponding Ni^{II} systems.^{10,14,15} Unfortunately no data are available for Ni^{III} –N bond lengths in these systems. However, as has been seen previously,³⁵ these $\text{Ni}^{\text{IV}}\text{L}$ – $\text{Ni}^{\text{III}}\text{L}$ rates are markedly greater than for the d^6 – d^7 $\text{Co}^{\text{III}}\text{N}_6$ – $\text{Co}^{\text{II}}\text{N}_6$ couples, where, although inner-sphere reorganisation is important, there is also the energy associated with spin configuration changes.

In the case of the Ni^{III} – Ni^{II} bis-oxime couples, there are marked changes in the exchange rate constants upon protonation. For the deprotonated bis-oxime systems, $[\text{Ni}(\text{L}^3)_2]^{+/0}$ the rate observed, $8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, is suggestive of a ready inner-sphere reorganisation. The value is very close to that ($2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) obtained by Lappin *et al.*¹⁷ for the corresponding L^2 sexidentate complex in a study of the disproportionation of the nickel(III) species. There will be bond extension upon reduction, but the nickel(III) species (low-spin d^7) is subject to Jahn-Teller distortion. The self-exchange constant is similar to that of other Ni^{III} – Ni^{II} macrocycles where there is no hindrance in the axial sites.³²

An interesting result is that obtained for the mono-oxime $[\text{Ni}^{\text{III}}(\text{L}^1)]^{2+}$ – $[\text{Ni}^{\text{II}}(\text{L}^1)]^+$. For this sexidentate ligand (amine-oxime) $k_{\text{exc.}} = 6 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Values of exchange rate constants as low as this have been observed³² in Ni^{III} – Ni^{II} complexes only where there is considerable steric resistance to inner-sphere reorganisation or where there is protonation of the ligand. In the mono-oxime ligand there is the possibility of hydrogen bonding. In L^1 , the amine and N–O[−] groups will be

cis and an interaction of the type $-\text{N} \begin{array}{l} \text{H} \\ \diagdown \\ \text{H} \end{array} \text{---} \text{O} \text{---} \text{N}$ should result in a stabilised Ni^{III} species with a pseudo-macrocyclic N₆ framework. Charge effects would indicate little additional solvational reorganisation energy for the [Ni(L¹)]²⁺ ion. It appears that the inner-sphere bond reorganisation in the reduction process perturbs the facility for electron transfer, especially since an additional proton is required for stabilisation of the resulting nickel(II) ion. Using the outer-sphere reagent [Ni(L⁴)₂]³⁺ we have examined the reaction of the protonated [Ni^{II}(HL¹)]²⁺. The self-exchange rate constant ($6 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is very similar to that for [Ni(L¹)]^{2+/+} consistent with significant bond reorganisation in the redox process.

The considerable variation in the exchange rates and the possibility of inner-sphere processes in the complexes suggests that while there are electrostatic factors which are important, the nature of the ligands themselves must also be considered, especially where part of the charge formally on the metal ion is delocalised onto the ligand. Further work on macrocyclic N₆ systems, where there are configurational constraints imposed on the metal centres by ligand geometries, is also needed if variations such as those observed are to be interpreted further.

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