Kinetics and Mechanism of Electron-transfer Reactions of Bis(1,4,7-triazacyclononane)nickel-(II) and -(III) Complexes

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The rates of the outer-sphere electron-transfer reactions involving the complex ion $[NiL^1{}_2]^{2+}$ (L^1 = 1,4,7-triazacyclononane) with a series of substituted polypyridine iron(III) ions, $[Fe(L{-}L)_3]^{3+}$, and various macrocyclic nickel(III) species and of the reduction of $[NiL^1{}_2]^{3+}$ by $[Co(L{-}L)_3]^{2+}$ species have been measured. Use of a Marcus cross-correlation leads to a self-exchange rate for the $[NiL^1{}_2]^{3+/2+}$ couple of $k_{22} = 6 \times 10^3$ dm^3 mol^{-1} s^{-1}. The data are of interest in that, unlike most other Ni^{II}–Ni^{III} couples measured, upon electron transfer there is retention of octahedral symmetry around the metal centre. Possible correlations of rates of electron exchange with bond extension in the primary co-ordination sphere are discussed.

Considerable progress has been made recently in stabilising higher oxidation states of nickel,[1-5] principally, although not exclusively,[6] using macrocyclic ligand systems. Difficulties persist, however, in the analysis of redox data owing to the change in geometry between the generally planar $NiN_4{}^{2+}$ systems and the pseudo-octahedral nickel(III) centres.[2,5] Attempts have been made to address this problem both in the case of a nickel oxime system [7,8] which incorporates a NiN_6 chromophore in nickel-(II), -(III), and -(IV) states and in the preparation of tris-bipyridyl [9,10] and other di-imine complexes where octahedral symmetry is retained in the bi- and ter-valent states. In the former system, however, proton-related ligand equilibria prevent the formation of a unique Ni^{II}–Ni^{III} couple [7,8] except at high pH (<9) and in the latter, ready oxidation of water is observed except at high hydrogen-ion concentrations (>1 mol dm^{-3}).

The complex ion bis(1,4,7-triazacyclononane)nickel(II), $[NiL^1{}_2]^{2+}$, which has been shown [11,12] to display octahedral geometry, has thermodynamic and kinetic stability approaching that of the tetra-aza-macrocyclic species. In these laboratories we have recently modified the synthesis of $[NiL^1{}_2][ClO_4]_2$.[13] The corresponding nickel(III) cation has been prepared using a variety of oxidants such as Co^{3+}(aq) in aqueous media and $NOBF_4$ in acetonitrile. The octahedral nature of the complex is maintained and the nickel(III) species is of such stability with respect to decomposition in aqueous media that electron-transfer studies may be made.

In this paper we present the results of an investigation of the oxidation of $[NiL^1{}_2]^{2+}$ by a series of substituted polypyridine complexes of iron(III), $[Fe(L{-}L)_3]^{3+}$, and of the reduction of $[NiL^1{}_2]^{3+}$ by $[Co(L{-}L)_3]^{2+}$ ions. The rate data may be used to evaluate the self-exchange parameters for the $[NiL^1{}_2]^{2+/3+}$ couple using the Marcus [14] correlation. The data are of interest in view of current studies of the intrinsic factors, especially those involving bond rearrangement, in the electron-transfer process. The results are compared with those obtained for other Ni^{II}–Ni^{III} couples.[8,15,16]

Experimental

The ligand 1,4,7-triazacyclononane was synthesised using a modification [13] of the method of Atkins *et al.* [17,18] and utilising the high degree of cyclisation achieved by the reaction of the disodium salt of *N*,*N*′,*N*″-tritosyldiethylenetriamine with the ditosyl derivative of 1,2-ethanediol (tosyl = ts = toluene-*p*-sulphonyl).

The nickel(II) complex was prepared by addition of an ethanol solution of nickel(II) perchlorate (2 mmol) to a warm solution of the ligand (4 mmol) dissolved in NaOH (12 cm^3, 1 mol dm^{-3}). After further warming (steam-bath) and adjustment of the pH to *ca.* 10.5 the colour of the solution became pink. Subsequent lowering of the pH to *ca.* 5 (1 mol dm^3 $HClO_4$) and cooling at 0 °C yielded light lilac crystals in almost quantitative yield. Recrystallisation from methanol–water and washing with propan-2-ol and then diethyl ether gave a product which was dried *in vacuo* (Found: C, 28.0; H, 5.75; Cl, 13.6; N, 16.0. Calc. for $C_{12}H_{30}Cl_2N_6NiO_8$: C, 27.95; H, 5.85; Cl, 13.75; N, 16.3%) (Canadian Microanalytical Services, Vancouver).†

The nickel(III) complex was formed by oxidation in *ca.* 1 mol dm^3 $HClO_4$ using a slight deficiency of Co^{3+}(aq). The olive-green complex produced was readily crystallised from 10^{-3} mol dm^{-3} $HClO_4$ solution (Found: C, 23.55; H, 4.95; Cl, 17.45; N, 13.55. $C_{21}H_{30}Cl_3N_6NiO_{12}$ requires C, 23.4; H, 4.90; Cl, 17.3; N, 13.65%). In distilled water, $\Lambda = 440$ S m^2 mol^{-1}, in agreement with that expected for a 3 : 1 electrolyte.

The complexes $[NiL^2][ClO_4]_2$[19] (L^2 = 1,4,8,11-tetra-azacyclotetradecane), $[NiL^3][ClO_4]_2$[20] (L^3 = *C*-*meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane), $[NiL^4][ClO_4]_2$ and $[NiL^5][ClO_4]_2$[21] (L^4 and L^5 are *C*-*rac*- and *C*-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane), $[NiL^6][ClO_4]_2$[20] (L^6 = 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene), and $[NiL^7][ClO_4]_2$[22] [L^7 = 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioximate (2−)] were prepared as described elsewhere. Their analytical purity was confirmed (Canadian Microanalytical Services).

The complexes $[Fe(L{-}L)_3][ClO_4]_2$, containing substituted 1,10-phenanthroline or 2,2′-bipyridine ligands (L–L), were prepared by mixing methanol solutions of ammonium iron(II) sulphate with those of the appropriate ligand (G. F. Smith). Addition of excess of $NaClO_4$ resulted in precipitation of the corresponding perchlorate complexes. The iron(III) species $[Fe(L{-}L)_3]^{3+}$ [L–L = 4,4′-dimethyl-2,2′-bipyridine (dmbipy), 4,7-dimethyl-1,10-phenanthroline (dmphen), or bipy = 2,2′-bipyridine] were generated in aqueous acidic solution by oxidation of the iron(II) complexes using PbO_2. Solutions of iron(III) species thus prepared in 5 mol dm^{-3} $HClO_4$ were stored at −5 °C and aliquots taken immediately prior to kinetic runs. U.v.–visible spectra of the species exhibited $\lambda_{max.}$ and ε values in excellent agreement with literature values. The complexes $[Co(phen)_3][NO_3]_2$ and $[Co(bipy)_3][ClO_4]_2$ were prepared using literature methods [23,24] and characterised by their spectra.[25,26]

Lithium nitrate (Reagent grade) was used without purification. Lithium perchlorate and lithium toluene-*p*-sulphonate were prepared by neutralisation of the moderately

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† CAUTION: Metal perchlorate complexes are hazardous and should be treated with caution.

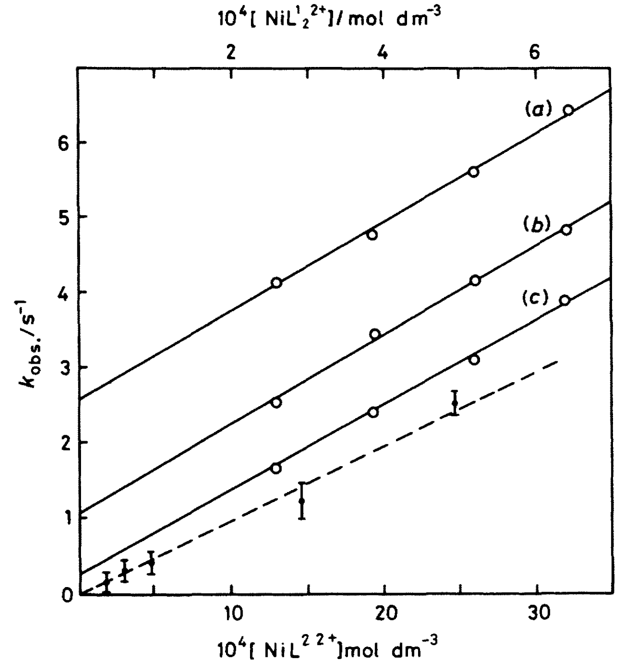

Figure 1. Plots of $k_{obs.}$ against $[\mathrm{NiL}^1{}_2{}^{2+}]$ at various concentrations of $[\mathrm{NiL}^2]^{2+}$ [see equation (1)]. The dotted line represents the dependence on $[\mathrm{NiL}^2{}^{2+}]$. $[\mathrm{NiL}^2{}^{2+}] = 24.8 \times 10^{-4}$ (*a*), 14.8×10^{-4} (*b*), and 2.8×10^{-4} mol dm^{-3} (*c*)

concentrated acid using $\mathrm{Li_2CO_3}$, and further recrystallised three times from water.

The stopped-flow and data-acquisition system have been described previously.[27] Nickel(III) macrocyclic complexes were prepared *in situ* by the oxidation of the corresponding nickel(II) species with a stoicheiometric deficiency of $\mathrm{Co^{3+}(aq)}$.[28] Ionic strength was maintained constant (1.00 mol dm^{-3}) using different reagents owing to solubility considerations; *e.g.* $\mathrm{HClO_4}$–$\mathrm{LiClO_4}$ for reactions of nickel(III) macrocycles and $[\mathrm{Co(bipy)_3}][\mathrm{ClO_4}]_2$, toluene-*p*-sulphonic acid and its lithium salt for $[\mathrm{Fe(L{-}L)_3}]^{3+}$, and $\mathrm{HNO_3}$–$\mathrm{LiNO_3}$ for reactions of $[\mathrm{Co(phen)_3}][\mathrm{NO_3}]_2$. Reactions were monitored at appropriate wavelengths over the range 400—600 nm. Experiments were carried out using pseudo-first-order conditions (>10-fold excess of reductant) and rate constants were derived from least-squares plots which were linear for more than three half-lives. In some instances where second-order conditions prevailed, k_2 (the second-order rate constant) was derived from plots of $\ln[(b/a - 1)(A_\infty - A_o)/(A_\infty - A_t) + 1]$ against t, where b and a are the initial concentrations of reactants. Reversibility was observed in the reduction of $[\mathrm{NiL}^1{}_2]^{3+}$ by $[\mathrm{NiL}^2]^{2+}$ owing to similarity of $E^\ominus$ values. In conditions of excess of $[\mathrm{NiL}^1{}_2]^{2+}$ and $[\mathrm{NiL}^2]^{2+}$ both the forward and reverse reactions [equation (1)] may be treated as pseudo-first order.

$$[\mathrm{NiL}^1{}_2]^{2+} + [\mathrm{NiL}^2]^{3+} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [\mathrm{NiL}^1{}_2]^{3+} + [\mathrm{NiL}^2]^{2+} \qquad (1)$$

The observed first-order rate constant, $k_{obs.}$, may thus be expressed in the form $k_{obs.} = k_f[\mathrm{NiL}^1{}_2{}^{2+}] + k_b[\mathrm{NiL}^2{}^{2+}]$. At constant $[\mathrm{NiL}^2{}^{2+}]$, plots of $k_{obs.}$ against $[\mathrm{NiL}^1{}_2{}^{2+}]$ should be linear and the intercepts obtained under differing concentration conditions a linear function of $[\mathrm{NiL}^2{}^{2+}]$. From these data both k_f and k_b may be derived (Figure 1). At 25 °C, $k_f = 5\,808 \pm 140$ dm^3 mol^{-1} s^{-1} and $k_b = 970 \pm 200$ dm^3 mol^{-1} s^{-1}.

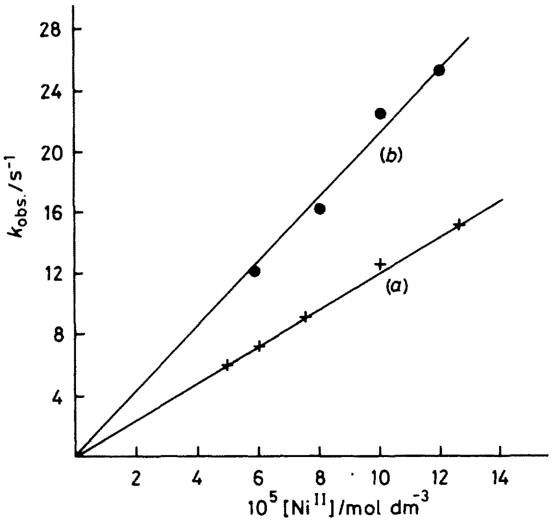

Figure 2. Dependence of observed rate constant ($k_{obs.}$) on $[\mathrm{NiL}^1{}_2{}^{2+}]$: (*a*) reaction with $[\mathrm{NiL}^4(\mathrm{H_2O})_2]^{3+}$ at 25 °C; (*b*) reaction with $[\mathrm{Fe(dmbipy)_3}]^{3+}$ at 25 °C

Results

For all reactions studied {oxidation of $[\mathrm{NiL}^1{}_2]^{2+}$ by nickel(III) macrocycles and iron(III) polypyridine complexes and reduction of $[\mathrm{NiL}^1{}_2]^{3+}$ by nickel(II) macrocycles and cobalt(II) polypyridine species} the stoicheiometry (to ±2%) may be represented by a one-electron transfer, *e.g.* as in equation (2) with a corresponding rate law (3). In Figure 2 is displayed the

$$[\mathrm{NiL}^1{}_2]^{2+} + [\mathrm{Fe(L{-}L)_3}]^{3+} \longrightarrow [\mathrm{NiL}^1{}_2]^{3+} + [\mathrm{Fe(L{-}L)_3}]^{2+} \qquad (2)$$

$$\text{Rate} = k_2[\text{Oxidant}][\text{Reductant}] \qquad (3)$$

first-order dependence of the observed rate constant ($k_{obs.}$) on [Reductant]. No dependence on hydrogen-ion concentration was observed over the range 0.1—1.0 mol dm^{-3}, as expected from the lack of any proton equilibria involving the reactants. For all reactions described, the hydrogen-ion concentration was maintained at 0.5 mol dm^{-3}. Rate data are presented in Table 1 together with associated activation parameters.

In the case of reaction (1) between the bis(nonane) complex and $[\mathrm{NiL}^2]^{3+}$, reversible behaviour was observed. Rate data at various concentrations of reagents are provided in Table 2.

Discussion

The substitution inertness of the iron(III) and cobalt(II) complexes and the retention of octahedral configuration of the $[\mathrm{NiL}^1{}_2]^{2+/3+}$ species requires an outer-sphere electron transfer. The Marcus theory [14,16] may be used to estimate the self-exchange rate constant for the bis(nonane) complex, using cross-reaction data. The rate constant, k_{12}, for a reaction such as (2) is related to those of the individual exchange reactions k_{11} and k_{22} and to the overall equilibrium constant, K_{12}, by expression (4). The work terms w_{12} and w_{21} correspond to

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}}W_{12} \qquad (4)$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/A_{11}A_{22}) + (w_{11} + w_{22})/RT]} \qquad (5)$$

$$W_{12} = \exp\,[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (6)$$

Table 1. Rate and activation parameters for the reactions of $[NiL^1_2]^{3+/2+}$ with various $[Fe(L–L)_3]^{3+}$, $[NiL(H_2O)_2]^{3+}$, and $[Co(L–L)_3]^{2+}$ complexes. $[H^+] = 0.5$, $I = 1.0$ mol dm^{-3}, $[NiL^1_2{}^{3+}] = (3–4) \times 10^{-6}$, $[NiL^1_2{}^{2+}] = (2–120) \times 10^{-6}$, $[Fe(L–L)_3{}^{3+}] = (1–4) \times 10^{-6}$, $[NiL^{3+}] = (4–8) \times 10^{-6}$, and $[Co(L–L)_3{}^{2+}] = (5–12) \times 10^{-5}$ mol dm^{-3}

Reaction [a]	Oxidant	Reductant	θ/°C	$10^{-4}k_2$/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
(i)	$[Fe(dmbipy)_3]^{3+}$	$[NiL^1_2]^{2+}$	9.3	9.0	35.8 ± 0.7	−22.7 ± 2.5
			14.8	12.1		
			19.5	16.0		
			25.0	21.1 ± 0.6		
(ii)	$[Fe(dmphen)_3]^{3+}$	$[NiL^1_2]^{2+}$	9.0	35.7	32.7 ± 2.4	−26.6 ± 7.0
			14.9	43.4		
			19.8	62.1		
			25.0	79.8 ± 0.8		
(iii)	$[Fe(bipy)_3]^{3+}$	$[NiL^1_2]^{2+}$	8.0	115	32.9 ± 2.8	−11.5 ± 9.7
			16.7	166 [b]		
			20.2	210 [b]		
			25.0	273 [b]		
(iv)	$[NiL^4]^{3+}$	$[NiL^1_2]^{2+}$	11.0	8.5	14.5 ± 1.5	−99 ± 5
			15.6	9.2		
			20.1	10.3		
			25.1	11.9 ± 0.8		
(v)	$[NiL^5]^{3+}$	$[[NiL^1_2]^{2+}$	10.2	10.8	25.5 ± 3.9	−58 ± 13
			15.5	12.2		
			19.9	14.8		
			25.0	19.4 ± 1.2		
(vi)	$[NiL^6]^{3+}$	$[NiL^1_2]^{2+}$	10.9	0.29	16.3 ± 1.6	−121 ± 6
			16.0	0.35		
			20.5	0.38		
			25.0	0.43 ± 0.02		
(vii)	$[NiL^1_2]^{3+}$	$[Co(phen)_3]^{2+}$	9.3	38.7	13.6 ± 2	−89 ± 4
			13.1	42		
			18.1	49		
			25.0	55.3 ± 2.1		
(viii)	$[NiL^1_2]^{3+}$	$[Co(bipy)_3]^{2+}$	25.0	42.6		
(ix)	$[NiL^7]^{2+}$	$[NiL^1_2]^{2+}$	25.0	0.002_7	*ca.* 45	*ca.* −70
(x)	$[NiL^2]^{3+}$	$[NiL^1_2]^{2+}$	25.0	0.58 [c]		
(xi)	$[NiL^1_2]^{3+}$	$[NiL^2]^{2+}$	25.0	0.097 [c]		

[a] Reactions (i)—(iii) studied in toluene-*p*-sulphonate solutions, (iv)—(viii), (x), and (xi) studied in perchlorate media, and (ix) studied in nitrate solutions. [b] Studied under second-order conditions. [c] Reaction showed reversibility (see Table 2).

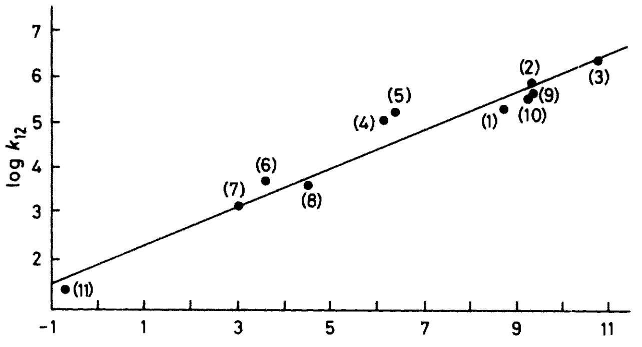

Figure 3. Plot of log k_{12} (k_{12} = second-order rate constant) against log $K_{12}k_{11}f_{12}$ [equation (8)]. Intercept = 1.89 = $\frac{1}{2}$ log k_{22}. k_{11} is the self-exchange rate constant of the complexes numbered in Table 3

$$\frac{A_{ii}}{\sigma^2} = \left(\frac{4\pi N v_n \delta r}{1\,000}\right)_{ii} \approx 3 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{Å}^{-2}\ \text{s}^{-1} \quad (7)$$

the energy associated with bringing the reactants and products, respectively, to a separation distance, r, in the activated complex. The terms w_{11} and w_{22} similarly apply to the self exchange reactions. A_{ii} is the diffusion rate for the species *ii*, σ the sum of the ionic radii, v_n the nuclear frequency which destroys the activated complex, and δr the thickness of the reaction layer. N = Avogadro's number.

For the systems under consideration the reactants and products are of similar charge and the work terms partially cancel. Also at an ionic strength of 1.00 mol dm^{-3} the values of W_{12} are generally small. Assuming W_{12} to be negligible, equation (4) may be expressed in the form (8) so that a plot

$$\log k_{12} = \tfrac{1}{2} (\log K_{12}k_{11}f_{12}) + \tfrac{1}{2} \log k_{22} \quad (8)$$

of log k_{12}, the measured second-order rate constant, against log $K_{12}k_{11}f_{12}$ should be linear with slope 0.5 and intercept $\frac{1}{2}$ log k_{22}. Using the various self-exchange parameters (Table 3) yields the plot shown in Figure 3. The slope 0.43 ± 0.06 (least-squares analysis with correlation factor 0.95) is in reasonable agreement with the predicted value. It is of interest that data obtained from both oxidation and reduction reactions are indistinguishable on the line. From the intercept, k_{22}, the rate constant for the $[NiL^1_2]^{3+/2+}$ exchange may be evaluated as 6×10^3 dm^3 mol^{-1} s^{-1}. Noteworthy is the fact that the nickel(III) macrocyclic complexes, *e.g.* $[NiL^4(H_2O)_2]^{3+}$, react *via* the outer-sphere route as is indicated by the relatively low $\Delta H^‡$ and negative $\Delta S^‡$ values. There are few data available on rates of substitution at nickel(III), but formation rates for halide complexes [3] are consistent with a solvent-exchange rate of $< 10^3$ dm^3 mol^{-1} s^{-1}. In the electron-transfer reactions under consideration, rates *ca.* 10^2 times greater are observed.

The wide variation of self-exchange rates for transition-metal redox couples has been interpreted, in part, in terms of

Table 2. Reaction of $[NiL^1_2]^{2+}$ with $[NiL^2]^{3+}$ at $I = 1.0$ mol dm^{-3} ($NaClO_4$), $[H^+] = 0.5$ mol dm^{-3}, 25 °C, and 402 nm in the presence of a large excess of $[NiL^2]^{2+}$; $[NiL^{2\,3+}] = (0.6\text{—}1.4) \times 10^{-5}$ mol dm^{-3}

$10^4[NiL^{1\,2+}]$/mol dm^{-3}		$10^4[NiL^{2\,2+}]$/mol dm^{-3}				
		1.8	2.8	4.8	14.8	24.8
2.59	$k_{obs.}$/s^{-1}	1.67 ± 0.06	1.80 ± 0.12	1.97 ± 0.10	2.52 ± 0.11	4.17 ± 0.15
3.89		2.36 ± 0.06	2.56 ± 0.10	2.16 ± 0.09	3.50 ± 0.09	4.79 ± 0.20
5.19		3.10 ± 0.13	3.19 ± 0.10	3.36 ± 0.12	4.16 ± 0.10	5.63 ± 0.15
6.48		3.93 ± 0.10	4.05 ± 0.15	4.24 ± 0.11	4.82 ± 0.12	6.46 ± 0.23
	Intercept/s^{-1}	0.134 ± 0.008	0.32 ± 0.1	0.41 ± 0.15	1.10 ± 0.2	2.57 ± 0.12
	Slope/dm^3 mol^{-1} s^{-1}	5 797 ± 180	5 689 ± 230	5 781 ± 350	5 829 ± 400	5 943 ± 200

Mean slope = k_f = 5 808 ± 140 dm^3 mol^{-1} s^{-1}. A plot of intercept *versus* $[NiL^{2\,2+}]$ yields k_b = slope = 970 ± 200 dm^3 mol^{-1} s^{-1} (intercept = $-5 \times 10^{-2} \pm 0.1$ *i.e.* not statistically different from zero).

Table 3. Marcus parameters for the redox reactions of $[NiL^1_2]^{2+}$ at 25 °C using $E^\ominus$ (n.h.e.) = 0.947 V for $[NiL^1_2]^{3+/2+}$

Reactant	$E^\ominus$/V	k_{11}/dm^3 mol^{-1} s^{-1}	K_{12}	$\log K_{12}k_{11}f_{12}$	$k_{12}(= k_2)$/dm^3 mol^{-1} s^{-1}
(1) $[Fe(dmbipy)_3]^{3+}$	0.96 [a]	3×10^8 [a]	1.66	8.70	2.11×10^5
(2) $[Fe(dmphen)_3]^{3+}$	1.00 [a]	3×10^8 [a]	7.86	9.35	7.98×10^5
(3) $[Fe(bipy)_3]^{3+}$	1.09 [a]	3×10^8 [a]	2.61×10^2	10.76	2.73×10^6
(4) $[NiL^4]^{3+}$	1.24 [b]	31.2 [c]	8.95×10^4	6.1	1.19×10^5
(5) $[NiL^5]^{3+}$	1.24 [b]	60	8.95×10^4	6.38	1.94×10^5
(6) $[NiL^2]^{3+}$	0.96 [b]	2×10^3 [b]	1.65	3.52	5.97×10^3
(7) $[NiL^2]^{2+}$	0.96 [d]	2×10^3	0.66	3.06 [d]	9.7×10^2
(8) $[NiL^6]^{3+}$	1.01 [e]	3×10^3 [e]	11.61	4.52	4.28×10^3
(9) $[Co(phen)_3]^{2+}$	0.37 [f]	8 [f]	5.64×10^9	9.34	5.53×10^5
(10) $[Co(bipy)_3]^{2+}$	0.37 [g]	7 [h]	5.64×10^9	9.29	4.26×10^5
(11) $[NiL^7]^{2+}$	0.65 [a]	6×10^4 [i]	9.56×10^{-6}	−0.684	26.8

[a] Ref. 15. [b] D. H. Macartney, A. McAuley, and T. Oswald, *J. Chem. Soc., Chem. Commun.*, 1982, 274. [c] O.Olubuyide, unpublished work. [d] Data for reverse reaction [equation (1)]. [e] K. Kumar, F. P. Rotzinger, and J. F. Endicott, personal communication. [f] B. R. Baker, F. Basolo, and H. M. Neumann, *J. Phys. Chem.*, 1959, **63**, 371. [g] E. Pagha and C. Siromi, *Gazz. Chim. Ital.*, 1957, **81**, 1125. [h] W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 1969, **73**, 1941. [i] Ref. 8.

the reorganisation of the inner co-ordination shells of the reactants. For the Ni^{II}–Ni^{III} couples where there is the transfer of a *d* σ* electron between the high-spin d^8 Ni^{II} and the low-spin d^7 Ni^{III} relatively few data are available for which structural data on bond lengths may be compared with kinetic parameters. The value of k_{22} in the present study may be compared with that of *ca.* 2×10^3 dm^3 mol^{-1} s^{-1} obtained for the exchange of tris(polypyridyl)nickel-(II) and -(III) complexes.[16] In the latter systems bond extensions of the order of *ca.* 0.1 Å have been suggested. The corresponding value for the $[NiL^2Cl_2]^{+/0}$ exchange has been determined recently in this laboratory,[29] $k_{11} = 3.4 \times 10^4$ dm^3 mol^{-1} s^{-1}. In this case *X*-ray crystallographic data are available for both the oxidised and reduced forms.[30,31] Different bond-length changes are observed in the axial and equatorial positions with Δd(Ni–Cl) = 0.04 Å and Δd(Ni–N) = 0.088 Å. The relatively small changes especially for the Ni–Cl bonds may favour a more rapid electron transfer. Detailed consideration of the present system must await structural data on the $[NiL^1_2]^{3+}$ ion. At present attempts are being made to prepare crystals suitable for analysis.

We are also undertaking the preparation of the corresponding triaza-cyclodecane and -cycloundecane complexes to determine the extent to which any asymmetry resulting from differing ring size and hence possibly differing bond lengths leads to variations in self-exchange rates.

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