



Structure and Kinetics of Oxidation of Amphiphilic Nickel(II) Pentaazamacrocycles by Peroxodisulfate and by a Nickel(III) Pendant-Arm Macrocycle

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Abstract

Three nickel(II) pentaazamacrocycles bearing pendant alkyl tails have been synthesized, and the crystal structure of one (bearing an octyl tail) is reported. The redox potentials of the complexes, for oxidation of the nickel(II) centre, is 0.72 V (*versus* S.H.E.) in all cases, indicating that the pendant alkyl tails have no effect on the redox site. The kinetics of oxidation of the complexes by peroxodisulfate, $S_2O_8^{2-}$ and by aqua(5, 5, 7, 12, 12, 14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetato)nickel(III), $[Ni(hmca)(OH_2)]^{2+}$ have been studied. Oxidation by $S_2O_8^{2-}$ occurs by ion-pairing of the reactants, followed by electron transfer with concomitant peroxo bond fission. Oxidation by $[Ni(hmca)(OH_2)]^{2+}$ occurs by an outer sphere electron transfer process. Redox kinetics at the nickel centre provides a probe for supramolecular interactions at the pendant tails in such complexes.

Abbreviations: hmca = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetato tacn = 1,4,7-triazacyclononane

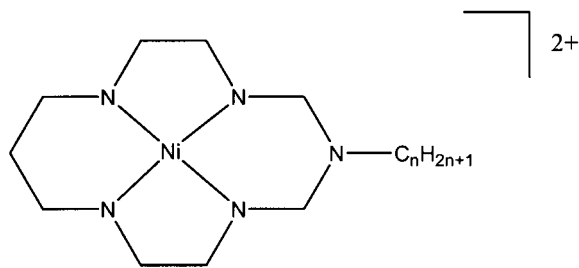
Introduction

There is a rich chemistry centred on the reactivity of macrocycles [1], with a variety of donor atoms that complex to metal ions. In recent years there has been a great deal of interest in the functionalization of macrocycles, producing pendant-arm complexes [2]. The synthesis and chemistry of polyazamacrocycles bearing pendant arms has been reviewed [3]. Pendant-arm macrocyclic complexes as biological models has also been reviewed [4]. Azamacrocycles having one alkyl pendant-arm can be incorporated into liquid membranes [5]. Catalytic activity in solution can be greatly affected by the ability of a reagent to aggregate in solution, forming structured assemblies such as micelles, vesicles and lipid bilayers. This ability is dependent on the reagent having certain structural and electronic characteristics, such as a charged hydrophilic “headgroup” and a long hydrophobic “tail” [6]. Hexaazamacrocycles containing six attached long aliphatic tails have been prepared, and have been shown to form a tubular mesophase (liquid crystal) by stacking the macrocyclic units [7]. Amphiphilic ferrocene-containing micelles have been shown to be disrupted by oxidation to the Fe(III) state, but re-micellize on reduction back to Fe(II) [8]. More recently, there has been a significant interest aroused in the ability of amphiphilic complexes to exhibit liquid crystal behaviour [9]. While many of the systems were of penta- or

octahedral coordination, improved liquid crystal behaviour is found for systems with square planar geometry, since structural anisotropy of the ligand is not compromised.

Polyazamacrocycles have been long known to stabilize unusual oxidation states in transition metals [10] and much work has been published on electron transfer kinetics, particularly for the nickel(II/III) system [11]. In spite of the interest in the redox kinetics of transition metal macrocycles, there have to date been no kinetic studies of redox reactions involving amphiphilic macrocyclic complexes. In this work we have synthesized several nickel(II) pentaazamacrocycles bearing pendant alkyl “tails” ($[NiL^4]^{2+}$, $[NiL^8]^{2+}$ and $[NiL^{12}]^{2+}$, where the superscripts refer to the length of the carbon chain in the alkyl “tails” and in one case we have characterized the complex crystallographically. We have examined their oxidation kinetics by the peroxodisulfate anion and by the octahedral cationic nickel(III) complex of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1-acetic acid, $[Ni(hmca)(OH_2)]^{2+}$ (where the pendant acetic acid is deprotonated and coordinated to the nickel(III) centre). The mechanisms of these oxidations are discussed, and the potential for such redox centres to be used as probes for supramolecular interactions is suggested.

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$[\text{NiL}^n]^{2+}$ (where $n = 4, 8$ or 12)

amine (carbon chain 4 to 12) (1 equivalent) in methanol solvent were refluxed with aqueous formaldehyde (2 equivalents) for 24 h. Addition of excess perchloric acid to the individual cooled, filtered reaction mixtures resulted in precipitation of the yellow products, which were filtered, washed thoroughly with methanol, diethyl ether and air-dried. The complexes were characterized by elemental analysis, infrared spectroscopy, and for the octyl-complex, $[\text{NiL}^8](\text{ClO}_4)_2$, by X-ray crystallography. Analytical data are reported in Table 1.

Caution! Compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

Crystallography

X-ray quality crystals were obtained by the diffusion method using acetonitrile/diethyl ether. The X-ray structure determination was performed on a Mercury CCD area detector coupled with a Rigaku AFC8 diffractometer, using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The orange plate crystal was mounted on a glass fibre. Full tabulations of atomic coordinates; all bond lengths and angles (with anisotropic displacement parameters); hydrogen coordinates (with isotropic displacement parameters); and observed and calculated structure factors have been deposited as supplementary material.

Electrospray mass spectrometry

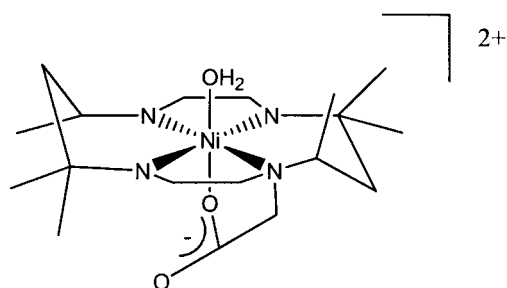
The mass spectrometry measurements were obtained on a VG quadrupole mass spectrometer with an atmospheric pressure electrospray source. Samples, in distilled water, were introduced into the source at a flow rate of 5 mL min^{-1} .

Cyclic voltammetry

Cyclic voltammograms were measured using a Princeton Applied Research model 482 fast-scanning electrochemical apparatus, in aqueous 0.10 M trifluoromethanesulphonic acid, under an argon atmosphere. A 1 mm diameter Pt disk working electrode, a platinum wire counter electrode and a Ag/AgCl (sat. KCl) reference electrode were used.

Kinetics

All kinetic experiments were carried out in aqueous media, using deionized, doubly-distilled water. For the oxidations involving the nickel(III) macrocycle $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$ as oxidant, kinetic measurements were made using a Hi Tech SF61-DX2 stopped flow spectrometer, thermostatted to $\pm 0.1 \text{ }^\circ\text{C}$ with a Lauda model RM6 refrigerated recirculating water bath. Pseudo-first-order conditions were maintained, using an excess of the appropriate nickel(II) amphiphilic macrocycle. A constant ionic strength of 0.100 M ($\text{NaClO}_4/\text{HClO}_4$) was maintained for all experiments. Perchlorate was used as an inert, non-coordinating ion. The ionic strength was limited since the perchlorate salts of



$[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$

Experimental

Materials

Potassium peroxodisulfate (BDH) was recrystallized twice from cold distilled water prior to use. The $[\text{Ni}(\text{hmca})(\text{OH}_2)](\text{ClO}_4)_2$ complex was prepared as reported previously [12]. The nickel(III) form was prepared *in situ* by oxidation with a stoichiometric deficiency of Co(III)(aq) . Stock solutions of the latter were prepared by electrochemical oxidation of cobalt(II) perchlorate solutions in perchloric acid. Cobalt(III) solutions were analysed by titration (for perchloric acid concentration) and by UV/visible spectrophotometry (for Co(III) , molar absorptivity = $35.3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [13]. All other reagents and solvents were of AnalaR grade and were used as received. All solutions were prepared using distilled, deionized water.

Synthesis of the $[\text{NiL}^{4,8,12}](\text{ClO}_4)_2$ complexes

The general "padlock" method of Suh and Kang was followed, where a template condensation of a polyamine and a primary amine with formaldehyde was carried out in the presence of nickel(II) [14]. Stoichiometric amounts of nickel(II) chloride hexahydrate (1 equivalent), 1,4,8,11-tetrazaundecane (1 equivalent) and the appropriate alkyl

Table 1. Elemental analyses of $[\text{NiL}^{4,8,12}](\text{ClO}_4)_2$

Compound	% C		% H		% N	
	Calc.	Found	Calc.	Found	Calc.	Found
$[\text{NiL}^4](\text{ClO}_4)_2$	30.32	30.19	6.07	5.94	13.60	13.39
$[\text{NiL}^8](\text{ClO}_4)_2$	35.75	34.87	6.88	6.66	12.26	12.16
$[\text{NiL}^{12}](\text{ClO}_4)_2$	40.21	40.15	7.55	7.59	11.17	11.05

the nickel complexes have low solubility, which would be decreased further by increased ionic strength. The reactions were followed by monitoring net absorbance changes at 440 nm due to formation of the $[\text{NiL}^{4,8}]^{3+}$ products. Pseudo-first-order rate constants were determined by non-linear least-squares fitting of absorbance-time data, using Hi Tech's "Kinetasyst" software, on a Dell 466MHz Pentium III computer.

For oxidations by peroxodisulfate, kinetic measurements were made using a Hewlett-Packard 8453 diode array UV/visible spectrophotometer. Ionic strength was maintained at 0.30 mol dm^{-3} using potassium sulfate. Potassium sulfate was used to maintain the ionic strength rather than perchlorate, since it better resembles the nature of the oxidant ion in solution and, more importantly, provides a stabilizing medium for the nickel(III) product. This stabilizing effect is well known [10]. Sulfate could not be used in the oxidations using $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$ since it would react with the oxidant, thus altering the nature of the electron transfer mechanism. Pseudo-first-order conditions were maintained using an excess of oxidant. Due to the low solubility of the $[\text{NiL}^{12}](\text{ClO}_4)_2$ complex it was not possible to study its oxidation kinetics.

Results and discussion

Crystallography

Diffraction quality crystals of $[\text{NiL}^8](\text{ClO}_4)_2$ were obtained by diffusion of diethyl ether into an acetonitrile solution of the nickel(II) complex. The crystal data are given in Table 2. The crystal structure consists of monomeric $[\text{NiL}^8]^{2+}$ cations, in which the nickel atom is coordinated to four nitrogen atoms in a square-planar fashion, with two non-interacting perchlorate anions. The octyl pendant-tail is attached to the non-coordinating nitrogen of the ligand, with the macrocycle taking up a *trans-III* configuration [15]. The structure of the complex cation is shown in Figure 1. Selected interatomic bond lengths and angles are given in Table 3, and are typical for nickel(II) polyazamacrocycles [16].

Electrospray mass spectra

Table 4 lists the mass spectral peaks for the three complexes. In all cases the major peak corresponded to the parent mononuclear complex cation, $[\text{NiL}^{4,8,12}]^{2+}$. Peaks corresponding to the monoperchlorate ion pairs, $\{[\text{NiL}^{4,8,12}](\text{ClO}_4)\}^+$ were also detectable, as is common for multipli-charged

Table 2. X-Ray crystallographic data for $[\text{Ni}(\text{II})\text{L}^8](\text{ClO}_4)_2$

Empirical formula	$\text{C}_{17}\text{H}_{39}\text{Cl}_2\text{N}_5\text{O}_8\text{Ni}$
Crystal colour, habit	orange, plates
Crystal dimensions	$0.08 \times 0.22 \times 0.40 \text{ mm}$
Formula weight	$571.13 \text{ g mol}^{-1}$
Crystal system	triclinic
Lattice type	primitive
Space Group	P-1 (#2)
$a(\text{\AA})$	8.2751(13)
$b(\text{\AA})$	8.3691(13)
$c(\text{\AA})$	22.916(5)
α	$97.078(10)^\circ$
β	$90.573(13)^\circ$
γ	$115.494(10)^\circ$
V	$1418.1(5) \text{\AA}^3$
D_{calc}	1.337 g cm^{-3}
Z value	2
Absorption coefficient, μ	6.88 cm^{-1}
F_{000}	604.00
Reflections collected	13910
Reflections with $I > 2.00\sigma(I)$	3839
Goodness of fit	2.84
R	0.082
wR2	0.284

$$R = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}; R_W = \left[\frac{\sum w(|F_0| - |F_c|)^2}{\sum w F_0^2} \right]^{1/2}.$$

Table 3. Selected bond distances (\AA) and angles ($^\circ$) for $[\text{NiL}^8](\text{ClO}_4)_2$

Bond	Distance	Bonds	Angle
Ni(1)–N(4)	1.936(5)	N(4)–Ni(1)–N(3)	86.8(2)
Ni(1)–N(2)	1.951(5)	N(4)–Ni(1)–N(1)	92.7(2)
Ni(1)–N(3)	1.963(6)	N(3)–Ni(1)–N(1)	179.3(2)
Ni(1)–N(1)	1.957(6)	N(4)–Ni(1)–N(2)	178.8(3)
Cl(1)–O(1)	1.39(1)	N(2)–Ni(1)–N(3)	94.2(2)
Cl(1)–O(2)	1.397(10)	N(2)–Ni(1)–N(1)	86.3(2)
Cl(1)–O(4)	1.39(1)	O(1)–Cl(1)–O(2)	109.77(14)
Cl(1)–O(3)	1.399(10)	O(1)–Cl(1)–O(4)	109.53(14)
N(1)–C(9)	1.495(11)	O(2)–Cl(1)–O(4)	109.69(14)
N(1)–C(1)	1.493(10)	O(1)–Cl(1)–O(3)	109.32(15)
N(2)–C(2)	1.443(9)	C(8)–N(5)–C(9)	112.9(6)
N(3)–C(5)	1.483(11)	C(8)–N(5)–C(10)	110.9(7)
N(4)–C(7)	1.480(9)	C(9)–N(5)–C(10)	118.9(8)
N(4)–C(8)	1.485(11)	C(9)–N(1)–C(1)	112.1(7)
N(5)–C(8)	1.446(12)	C(9)–N(1)–Ni(1)	116.5(5)
N(5)–C(9)	1.442(12)	C(1)–N(1)–Ni(1)	107.2(4)
N(5)–C(10)	1.448(3)		

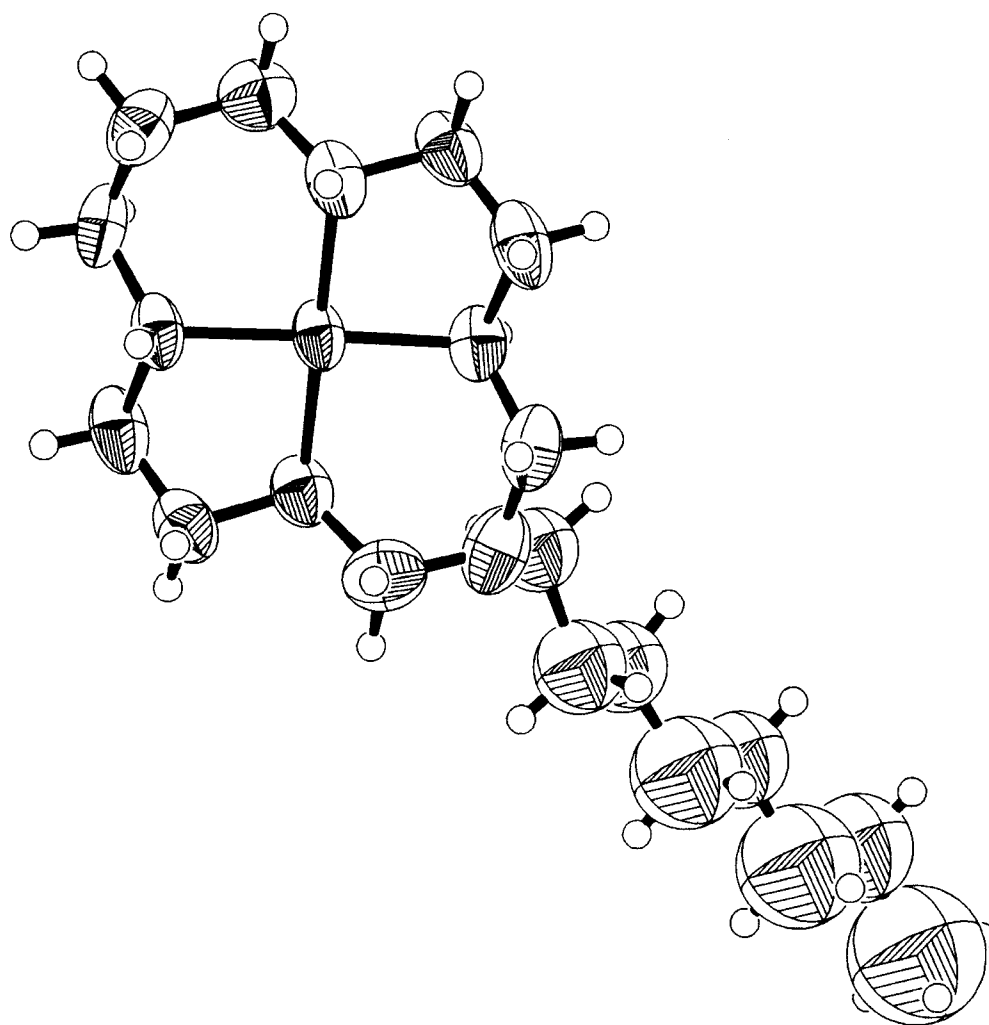


Figure 1. ORTEP Drawing of the $[\text{NiL}^8]^{2+}$ cation.

Table 4. Electrospray mass spectral data

Species	m/e (calc.)	m/e (found)	%BPI
$[\text{NiL}^4]^{2+}$	158.5	157.5	(major)100
$[\text{NiL}^4](\text{ClO}_4)^+$	416	416	5.99–11.59
$[\text{NiL}^8]^{2+}$	186.5	185.6	(major)100
$[\text{NiL}^8](\text{ClO}_4)^+$	472	470.3	2.17–5.19
$[\text{NiL}^{12}]^{2+}$	215	213.8	(major)100
$[\text{NiL}^{12}](\text{ClO}_4)^+$	528.5	528.3	0.48–3.22

complex cations. The data not only confirm the molecular formulae of the complexes, but also that they remain intact in solution.

Electrochemistry

Figure 2 shows the cyclic voltammogram for $[\text{NiL}^4](\text{ClO}_4)_2$ in 0.1 M triflic acid, showing reversible one-electron transfer. Similar reversibility was observed for all complexes. The redox potentials for the complexes are 0.72 V (versus

Ag/AgCl) with peak separations of 60 mV. Interestingly, no difference in redox potentials was found between the complexes, suggesting that the lipophilic tails do not interfere with the electron transfer process from/to the metal centre.

Kinetics

Oxidation by peroxodisulfate

The nickel(II) pendant-arm macrocycles oxidized smoothly to the trivalent state. Figure 3 shows the time dependence of the UV/visible spectrum of $[\text{NiL}^4](\text{ClO}_4)_2$ with peroxodisulfate, displaying a clean isosbestic point at 237 nm. Excellent first-order kinetics were observed over at least five half-lives for the appearance of the nickel(III) products. Addition of the radical scavenger allyl acetate had no effect on the reaction rates. Table 5 lists the observed first-order rate constants for the oxidation of the nickel(II) macrocycles by peroxodisulfate in aqueous solution, as a function of oxidant concentration and temperature. Plots of k_{obs} versus $[\text{S}_2\text{O}_8^{2-}]$ are non-linear, indicating the rapid formation of an ion pair between the reactants prior to electron transfer.

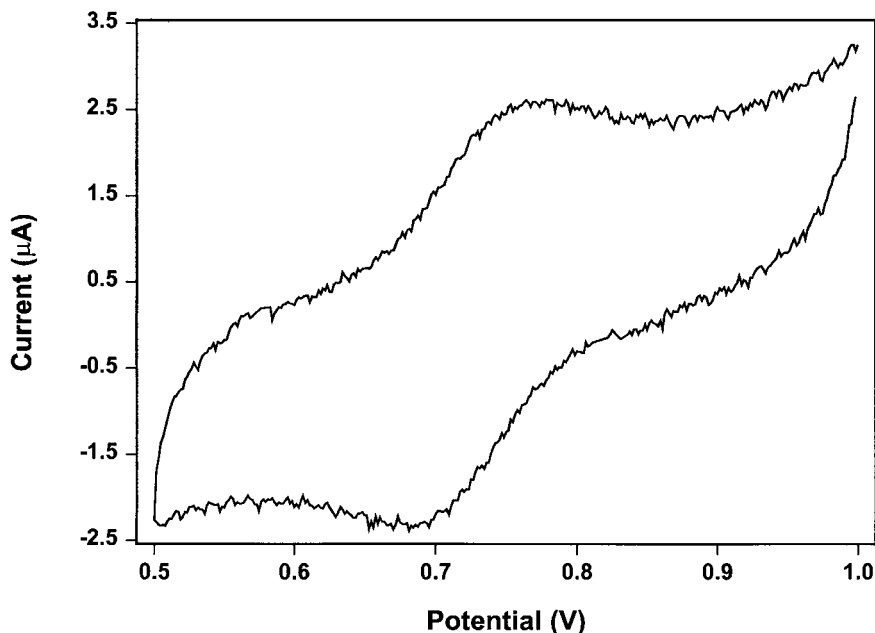


Figure 2. Cyclic voltammogram for $[\text{NiL}_4](\text{ClO}_4)_2$ in 0.1 M triflic acid, at 25 °C under argon atmosphere.

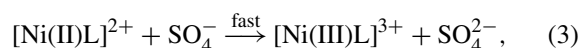
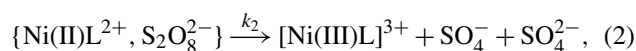
Table 5. Observed first-order rate constants, k_{obs} for the oxidation of $[\text{NiL}^4]^{2+}$ and $[\text{NiL}^8]^{2+}$ cations by peroxodisulfate at 298 K; and for the oxidation of $[\text{NiL}^4]^{2+}$ for a series of temperatures, as a function of oxidant concentration ($I = 0.30 \text{ mol dm}^{-3}$)

	Temperature (K)				
	293.7	298.0	302.5	307.4	312.1
$[\text{S}_2\text{O}_8^{2-}] (\text{mol dm}^{-3})$	$k_{\text{obs}}/\text{s}^{-1}$				
$[\text{NiL}^4]^{2+}$					
0.001	0.0181	0.0255	0.0270	0.0810	0.119
0.002	0.0319	0.0435	0.0478	0.117	0.171
0.003	0.0429	0.0539		0.140	0.196
0.004	0.0523	0.0748	0.0791	0.161	
0.005	0.0571	0.0760	0.0913	0.170	0.234
0.006				0.190	
$[\text{NiL}^8]^{2+}$					
0.001		0.0351			
0.002		0.0481			
0.003		0.0600			
0.004		0.0652			
0.005		0.0724			

It is well known [17] that for square-planar nickel(II) tetraazamacrocycles, $[\text{Ni}(\text{mac})]^{2+}$ there exists in solution an equilibrium between the yellow, square planar $[\text{Ni}(\text{mac})]^{2+}$ (diamagnetic) and the blue, octahedral $[\text{Ni}(\text{mac})\text{S}_2]^{2+}$ (where S = solvent). Solutions of such nickel(II) complexes show paramagnetic line broadening in their NMR spectra. We have measured the H-1 NMR spectra of $[\text{NiL}^4](\text{ClO}_4)_2$ in the ionic strengths used in our kinetic studies, and found no difference. Interestingly, there is very little line-broadening, suggesting that the equilibrium favours the square-planar form for the amphiphilic complexes studied in this work. Hence we have assumed that the high-spin

octahedral/low-spin square-planar equilibrium does not play a significant role in the present system.

The general mechanism for oxidation of transition metal complexes by the peroxodisulfate anion is well known [18]. Reduction of peroxodisulfate characteristically proceeds *via* rate-determining fission of the peroxo-bond, a step that may be assisted by the presence of a metal ion. In oxidations of, for example, organic substrates the sulfate radicals produced either thermally or photolytically play a key role and their formation is rate determining [19]. In the present study, the lack of dependence of reaction rate on the radical scavenger indicates that there is no significant build up of sulfate radicals, and the oxidation reaction occurs *via* electron transfer from the metal centre to the peroxodisulfate oxidant, with concomitant peroxo-bond fission. The general mechanism for oxidation of cationic nickel(II) macrocycles by the peroxodisulfate anion is:



The overall reactions corresponds to:



For oxidation of nickel(II) complexes of neutral square planar macrocycles, the nickel(III) product is known to co-ordinate sulfate ion, forming the $[\text{Ni}(\text{III})\text{L}(\text{SO}_4)]^+$ cation

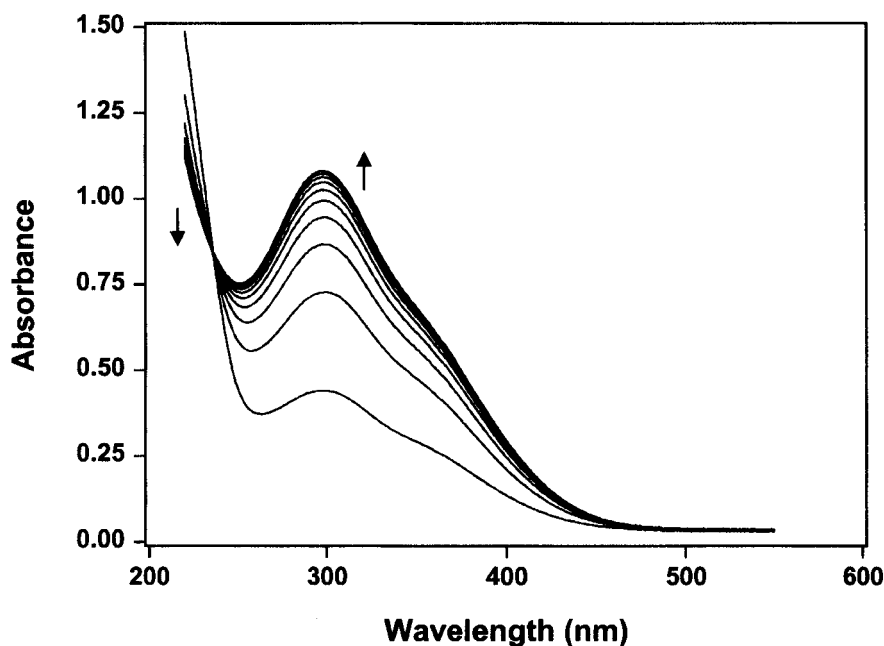


Figure 3. UV/visible spectral changes during the oxidation of $[\text{NiL}^4](\text{ClO}_4)_2$ by peroxodisulfate, at 25 °C. Scans were taken at 18 s intervals ($[\text{S}_2\text{O}_8^{2-}] = 0.00300 \text{ mol dm}^{-3}$). Arrows indicate direction of absorbance change with time.

[20]. Hence the products of Equation (4) may be written as $2[\text{Ni(III)L}(\text{SO}_4)]^+$. This has no effect on the kinetic interpretation. The rate law that derives from Equations (1)–(3) is:

$$\begin{aligned} \text{Rate} &= +d[\text{Ni(III)}]/dt = 2k_{\text{obs}}[\text{Ni(II)L}]_{\text{tot}} \\ &= \frac{2k_2K_{ip}[\text{S}_2\text{O}_8^{2-}][\text{Ni(II)L}]_{\text{tot}}}{1 + K_{ip}[\text{S}_2\text{O}_8^{2-}]}, \end{aligned} \quad (5)$$

where k_2 is the rate of electron transfer from the nickel(II) centre to the oxidant, within the ion-pair solvation shell and K_{ip} is the ion-pairing constant. The factor of 2 stems from the stoichiometry of the reaction. Values for K_{ip} for $[\text{NiL}^4]^{2+}$ and $[\text{NiL}^8]^{2+}$ at 298 K, obtained by a non-linear least-squares fit of the kinetic data to Equation (5), are 170 ± 30 and 160 ± 20 respectively. These are reasonable values for ion-pairing between two doubly-charged species. The fact that the values are very similar to one another suggests that the closeness of approach of the participating ions is similar, and remote from the lipophilic tails. It is known that in aqueous solution, an equilibrium exists between low-spin, square-planar $[\text{NiL}]^{2+}$ and high-spin, octahedral $[\text{NiL}(\text{OH}_2)_2]^{2+}$. Previous kinetic studies have shown that there is little effect on the ion-pairing constant due to this equilibrium.

The rate constants for oxidation of $[\text{NiL}^4]^{2+}$ and $[\text{NiL}^8]^{2+}$ are also very similar to one another, supporting the hypothesis that the lipophilic tails are directed away from the macrocyclic centre in solution, as they are in the solid state. Thus they do not influence the rate of electron transfer from the nickel(II) centre to the peroxodisulfate anion.

The activation enthalpy and entropy for the oxidation of the $[\text{NiL}^4]^{2+}$ complex were determined as $30 \pm 5 \text{ kJ mol}^{-1}$ and $-160 \pm 50 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively from the temper-

Table 6. Observed first-order rate constants, k_{obs} and calculated second-order rate constants, k_6 for the oxidation of $[\text{NiL}^4]^{2+}$ and $[\text{NiL}^8]^{2+}$ by $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$ as a function of reductant concentration at 298 K

10^4 [reductant]/(mol dm ⁻³)	$[\text{NiL}^4]^{2+}$	$[\text{NiL}^8]^{2+}$
	$k_{\text{obs}}/\text{s}^{-1}$	
1.00	0.794	0.756
2.00	1.59	1.44
3.00	2.40	2.35
4.00	3.20	2.86
5.00	3.95	3.58
$k_6/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	7960 ± 70	7080 ± 310

ature dependence data. These are very similar to activation parameters for oxidation of a wide range of transition metal complexes by peroxodisulfate [18, 21]. The magnitudes of the ion pairing constants are in keeping with those for other systems, and it appears that the length of the alkyl tail has little or no effect on K_{ip} .

Oxidation by $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$

We have previously examined the electron transfer kinetics involving the $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$ complex, which undergoes outer-sphere electron transfer with $[\text{Ni}(\text{tacn})_2]^{2+}$ [12]. The self-exchange rate, k_{11} for the $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{+/2+}$ system was calculated as $870 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The redox potential for the $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{+/2+}$ couple has been measured at 0.845 V (vs Ag/AgCl in 3M NaCl), and so is sufficiently strong to oxidize the amphiphilic complexes in the present study. Table 6 lists the observed first-order rate constants for oxidation of the $[\text{NiL}^4]^{2+}$ and $[\text{NiL}^8]^{2+}$

Table 7. Observed first-order rate constants, k_{obs} for the oxidation of $[\text{NiL}^4]^{2+}$ by $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$ and calculated second-order rate constants, k_6 as a function of temperature. Concentrations of $[\text{NiL}^4]^{2+}$ $[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}$ were 1.00×10^{-4} mol dm^{-3} and 1.00×10^{-5} mol dm^{-3} respectively ($I = 0.10$ mol dm^{-3})

T/K	Replicate observed first-order rate constants $k_{\text{obs}}/\text{s}^{-1}$					$k_6/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
285	0.610	0.590	0.619	0.618	0.591	6000 ± 250
289	0.687	0.669	0.669	0.658	0.697	6760 ± 160
293	0.742	0.737	0.736	0.733	0.750	7400 ± 70
302	0.840	0.823	0.826	0.821	0.820	8260 ± 80
306	0.855	0.872	0.855	0.863	0.897	8680 ± 180

complexes in 0.10 M NaClO_4 , at 25 °C, together with the derived second-order rate constants. The reaction obeys a second-order rate law

$$\text{Rate} = k_6[[\text{NiL}^{4,8}]^{2+}][[\text{Ni}(\text{hmca})(\text{OH}_2)]^{2+}] \quad (6)$$

and was found to be independent of acid. The temperature dependence of the rate constant for the $[\text{NiL}^4]^{2+}$ complex (Table 7) gave activation parameters of 11 ± 1 kJ/mol and -130 ± 10 J/mol K for the activation enthalpy and entropy respectively. These values are typical for outer-sphere redox processes.

According to Marcus theory [22], for an outer-sphere electron transfer mechanism, the rate constant for the cross-reaction (k_{12}) is related to the rate constants for the self-exchange rates of the components, k_{11} and k_{22} , and the cross reaction equilibrium constant (K_{12}) by the expression:

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}w'_{12}, \quad (7)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/A_{11}A_{22}) + (w_{11} + w_{22})/RT]} \quad (8)$$

and $w'_{12} = \exp[-w_{12} + w_{21} - w_{11} - w_{22}]/2RT$, where $w_{ij} = Z_i Z_j e^2 / D_s \sigma_{ij} (1 + \beta \sigma_{ij} (\mu^{1/2}))$; $A_{ij} = 4\pi N \sigma^2 \nu b \gamma r / 1000_{ij}$, where w_{ij} is the work required to bring the ions i and j (with charges Z_i and Z_j respectively) to the separation distance σ_{ij} . This distance is assumed to be equal to the sum of the radii of the ions i and j ; $\beta (= 8\pi N e^2 / 1000 D_s k T)^{1/2}$; νb is the nuclear frequency that destroys an activated complex configuration; and γr is the thickness of the reaction layer (~ 0.8 Å); D_s is the dielectric constant of the medium.

From the observed second-order rate constants at 298 K, the self-exchange rate for the oxidant and the redox potentials of the reactants, the self-exchange rates for the n -butyl- and n -octyl-tailed nickel macrocycles have been estimated as 930 and 750 $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ respectively. The estimate of k_{11} is in good agreement with self-exchange rates of other nickel(II/III) tetraazamacrocyclic systems [23], which have self-exchange rates in the region of 1500 $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$.

The presence of lipophilic tails appended to the macrocyclic ligand does not affect the electron transfer process

at the nickel centre. Thus nickel(II/III) redox kinetics may be useful as a probe of supramolecular properties of the lipophilic tails. Current work in our laboratory explores the host-guest properties of these tails with cyclodextrins, where we are able to estimate the binding constants for the supramolecular interaction of the amphiphilic macrocycles with α - and β -cyclodextrins. This work is to be reported later.

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