agent used for plutonium decorporation. The difference in specificity between DTPA and 3,4,3-LICAMS confirms that catechoylamides may provide a promising alternative to DTPA for chelation therapy of plutonium contamination.

An interesting correlation is observed if one compares the pM value of each metal to its charge to ionic radius ratio. Figure 6 is a graph of charge to ionic radius ratio vs. pM for MECAMS. A similar correlation exists for 4-LICAMS and 3,4,3-LICAMS. The ionic radii used for Zn(II) and Cu(II) were those listed by Shannon[11] for four-coordinate species. The other ions were assumed to be six-coordinate. Copper(II) is the smallest of the divalent metals studied, and it demonstrates the greatest affinity for the catechoylamide. Ferric ion, with its high charge and small size, demonstrates the greatest stability. Plutonium(IV) also exhibits a high charge to ionic radius ratio, and this explains the qualitative observation of its high affinity for poly(catechoylamide) ligands. Work in progress includes titrations of trivalent lanthanides with 3,4,3-LICAMS to analyze the extent to which the correlation mentioned above can be extended.

Summary

The synthetic poly(catechoylamide) ligands generally form very stable complexes with ferric ion and other ions of high charge to ionic radius ratios including Pu(IV) and Th(IV).[10] The common divalent metals that are present in the body, e.g., Mg(II) and Ca(II), are large enough and are of sufficiently low charge not to be chelated effectively by the poly(catechoylamides). The effectiveness of the ligands as a whole can be attributed not only to the intrinsic affinity of the phenolic oxygens for ligation of highly charged ions but also can be attributed to the structural design of the entire complex for encapsulation of the desired ion. It is the combination of these two factors which contributed to the excellent selectivity of the poly(catechoylamides) to sequester Fe(III) or Pu(IV).

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Registry No. 4-LICAMS, 73630-97-4; MECAMS, 71353-06-5; 3,4,3-LICAMS, 82044-95-9; Fe, 7439-89-6; Cu, 7440-50-8; Zn, 7440-66-6; Ni, 7440-02-0; Co, 7440-48-4; Mg, 7439-95-4; Ca, 7440-70-2.

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Kinetics and Mechanism of the Oxidation of Hydroquinone and Catechol by $[Ni^{III}cyclam]^{3+}$ in Aqueous Perchlorate Media

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Detailed rate studies have been made of the oxidation of hydroquinone (H_2Q) and catechol (H_2Cat) by Ni^{III}cyclam, $[Ni^{III}L]^{3+}$, complexes. Over the pH range 0–2.9, the rate of loss of Ni(III) may be represented by the equation $-d[Ni(III)]/dt = \{2(k_1 + k_2K_h/[H^+] + k_3K_aK_h/[H^+]^2)K_3[H^+][Ni(III)]_t[H_2Q]_t\}/\{([H^+] + K_h)([H^+] + K_3)\}$, where K_h and K_3 represent hydrolysis and dissociation constants of $[Ni^{III}cyclam]^{3+}$ and protonated dihydroxybenzene, respectively. The rate constants are $k_1([Ni(III)] + [H_2Q]) = 1.09 \times 10^4$ (H_2Q) and 6.98×10^2 (H_2Cat) $M^{-1}\ s^{-1}$, respectively ($T = 25$ °C), and other constants involving $[Ni(OH)L]^{2+} + H_2Q$ have been evaluated from hydrogen ion dependence measurements. There is also evidence for a pathway involving $H(Cat)^-$ as a reductant. Sulfate ion has a marked effect on the rates, showing pronounced retardation owing to the formation of sulfate complexes with lower redox potentials. The data have been interpreted with a Marcus cross correlation and are considered outer sphere in character. Self-exchange rates for Ni(II)/Ni(III) macrocycles are discussed.

Introduction

With recent observations[2,3] that the nickel(III) state can be stabilized with nitrogen-donor macrocyclic ligands, several reports have been published[4-8] describing various ligand types and some chemical and physical properties of the nickel(III) complexes. The broader aspects of the chemistry of this oxidation state have also been the subject of a recent review.[9]

The nickel(III) species offer a wide range of oxidizing potentials,[10] but to date there have been relatively few data describing the kinetics and mechanisms of reaction with reducing substrates. In some systems where the transient nickel(III) complexes were generated at relatively high pHs (2–5) with pulse radiolysis[11] or flash photolysis[12] techniques, the reactions with Br^-, SCN^-, and H_2O_2 have been monitored. In general, the rate data show a second-order dependence on metal complex and first or second order on substrate, suggesting the involvement of inner-sphere complexes. The rate, however, varies with both pH and reductant concentration.

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In contrast, although Ni^{III}cyclam ($[Ni^{III}L]^{3+}$, L = cyclam = 1,4,8,11-tetraazacyclotetradecane) forms complexes with Cl^-, Br^-, and NCS^-, the redox reaction with I^- shows a first-order dependence on reductant and on [Ni(III)].[13] In the latter case, the reaction rates were not markedly different from those of formation of the complexes and no firm conclusion could be inferred as to the mechanism although an outer-sphere process was proposed. Very recently the reaction of I^- by the nickel(III) complex of tri-α-aminoisobutyric acid has been investigated,[14] and in the major reaction pathway two electrons are transferred in one concerted reaction step which proceeds via a transition state composed of two nickel centers and two iodides.

In this paper we report the results of a kinetic study of the oxidation of hydroquinone (1,4-dihydroxybenzene) and catechol (1,2-dihydroxybenzene) by Ni^{III}cyclam. Unlike previous data from these laboratories[13] where the reaction conditions were maintained at $[H^+] = 1.00$ M, the dependence of rates on pH has been monitored up to pH ~3. In this way the pathways ascribed to the monohydroxy complex $[NiL(OH)(OH_2)]^{2+}$ may also be evaluated. Sulfate ions have been shown to stabilize these macrocyclic complexes through inner-sphere axial coordination. The effect of $[SO_4^{2-}]$ present in solution is to retard the rates owing to lower redox potentials of the sulfato species.

Experimental Section

$[Ni^{II}L](ClO_4)_2$ and the corresponding nickel(III) complex were prepared as described previously.[13] Stock solutions of $[Ni^{III}L]^{3+}$ were also prepared by electrolysis of $\sim 10^{-3}$ M solutions of $[NiL]^{2+}$ at 1.2 V (Pt electrodes) in 2 M $HClO_4$. Nickel(III) was determined spectrophotometrically ($\epsilon_{308} = 11\,200$ M^{-1} cm^{-1}) and $[H^+]$ of the oxidant stock solutions by standard titration with base. Such stock solutions were stable for several weeks if kept in the dark at 0 °C. Another sample of $[Ni^{III}L]^{3+}$ was obtained as a perchlorate salt. Electrolysis at 1.5 V of a slurry of $[Ni^{II}L]^{2+}$ in 4.0 M $HClO_4$, followed by evaporation in vacuo of the dark green solution produced a red-brown solution from which reddish crystals were obtained. On dissolution of such material in water or dilute perchloric acid, the characteristic green solutions of $[Ni^{III}L]^{3+}$ were produced with spectroscopic (UV–visible and ESR) and kinetic properties identical with those of the samples used previously. This material has been identified tentatively as $[Ni^{III}L](ClO_4)_3$ with no axially coordinated solvent molecules. Further work is currently under way to characterize these crystals.

Hydroquinone and catechol (Fisher Reagent) were recrystallized from ethanol and washed with ether. Lithium perchlorate was prepared by neutralization of Li_2CO_3 with moderately concentrated (~5 M) $HClO_4$ and further recrystallized three times from water. Special care was taken to eliminate sulfate ions as shown by the absence of cloudiness on addition of $Ba(ClO_4)_2$.

The stopped-flow apparatus and data acquisition system used have been described previously.[15] Reactant solutions were prepared immediately before use. Experiments were carried out in the presence of excess reductant. The ionic strength was maintained at 1.00 M with use of where appropriate, mixtures of $HClO_4$, $LiClO_4$, or Li_2SO_4. The disappearance of $[Ni^{III}L]^{3+}$ was monitored at 350 nm, and pseudo-first-order plots from which least-squares slopes were derived were linear for more than 3 half-lives.

Table I. Rate Data for the Reaction of $[Ni^{III}cyclam]^{3+}$ with 1,4-Dihydroxy- and 1,2-Dihydroxybenzene

1,2-Dihydroxybenzene Dependence: $T = 25.0$ °C, $[Ni(III)] \approx 4 \times 10^{-5}$ M

pH 0.0

$10^3[H_2Cat]/M$	0.59	1.00	1.02	1.09	1.5	2.0
k_{obsd}/s^{-1}	0.68	1.13	1.14	1.30	1.68	2.25

$k_a = 569 \pm 9$ M^{-1} s^{-1}

pH 2.74

$10^3[H_2Cat]/M$	0.578	1.035	2.59
k_{obsd}/s^{-1}	3.14	6.10	14.8

$k_a = 2857 \pm 93$ M^{-1} s^{-1}

Dependence of Rate Constant on $[H^+]$[a]

1,2-dihydroxybenzene		1,4-dihydroxybenzene	
$10^4[H^+]/M$	$10^{-3}k_a/M^{-1}$ s^{-1} [b]	$10^4[H^+]/M$	$10^{-3}k_a/$ M^{-1} s^{-1} [b]
5.37	12.64 (12.99)	3.09	22.0 (22.5)
12.4	5.44 (5.17)	11.17	17.7 (17.6)
18.2	2.86 (3.49)	25.56	15.1 (14.7)
50.0	1.64 (1.55)	83.90	13.4 (12.2)
83.9	1.19 (1.18)	90.60	13.3 (12.2)
419	0.769 (0.793)	107.5	13.0 (12.0)
1000	0.724 (0.736)	240	11.4 (11.4)
2100	0.710 (0.698)	419	10.2 (11.0)
10000	0.569 (0.559)	881	11.0 (10.9)
		1000	11.3 (10.8)
		4190	9.9 (10.0)
		7970	9.1 (9.1)
		10000	9.0 (9.0)

[a] $[Ni(III)] \approx (1-5) \times 10^{-5}$ M; $I = 1.0$ M $HClO_4/LiClO_4$. [b] $k_a = k_{obsd}/2[H_2Q]$, where $[H_2Q]$ was in the range $(5-8) \times 10^{-4}$ M. Numbers in parentheses are values calculated with use of (10) with parameters presented in Table III (see text).

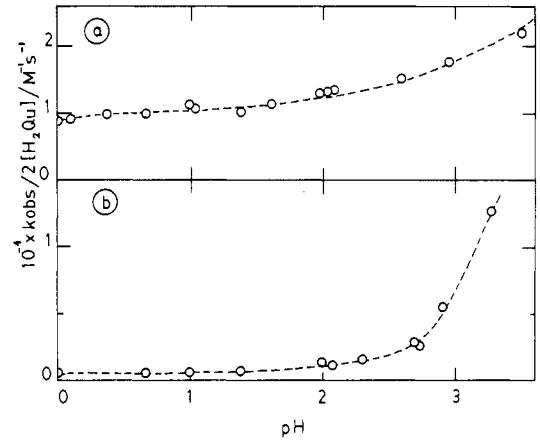

Figure 1. Plots of $k_{obsd}/2[H_2Q]$ against pH. $T = 25.0$ °C; $[H_2Q] = (5-8) \times 10^{-4}$ M; $[Ni(III)] = (1-5) \times 10^{-5}$ M. The dotted lines are fitted values using eq 10 and 12 (see text): (a) $[Ni^{III}L]^{3+}$ + hydroquinone; (b) $[Ni^{III}L]^{3+}$ + catechol.

Results

Comparison of UV–visible spectra taken before and after mixing of nickel(III) and excess quinol showed that all the metal ion oxidant was consumed, with the production of $[Ni^{II}L]^{2+}$. The reaction stoichiometry was measured with a spectrophotometric titration, and for each quinol, the Ni(III) consumed per mole of reductant was found to be 2.0:1 within experimental error (3%) consistent with reaction 1, where H_2Q and Q represent the quinol and the corresponding quinone, respectively.

$$2[Ni^{III}L]^{3+} + H_2Q \rightarrow 2[Ni^{II}L]^{2+} + Q + 2H^+ \quad (1)$$

At a constant hydrogen ion concentration, the reactions were first order in both oxidant and reductant. Typical dependences are shown in Table I for the reaction with catechol at pH 0 and pH 2.74. There was, however, a marked dependence on $[H^+]$, with increasing acidity being accompanied by a decrease in the observed rate constant. In Figure 1 is shown the pH profiles of the second-order rate constant ($T = 25$ °C) for the two reductants. Over the range studied (0 < pH < 3.5) no simple order in $[H^+]$ was found. The rate data at various

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Table II. Rate and Equilibrium Constants for Reactions of Ni^{III}cyclam Complexes with Hydroquinone and Catechol (I = 1.00 M ($LiClO_4$))

Hydroquinone

	T/°C				
	10.1	15.5	20.5	25.0	30.8
$10^{-3}k_1{}^a$	4.8 ± 0.4	5.1 ± 0.4	6.9 ± 0.7	11.0 ± 0.5	20.0 ± 1.5
	$\Delta H^{\ddagger}$ = 11.5 ± 4,^{d} $\Delta S^{\ddagger}$ = −1 ± 7^e				
$10^3K_h{}^b$	1.0 ± 0.2	1.3	0.8 ± 0.2	0.8 ± 0.2	0.6
$10^{-3}k_2{}^a$	8.0 ± 0.4	10.8 ± 0.8	21 ± 2	26 ± 9	33 ± 1
	$\Delta H^{\ddagger}$ = 10.5 ± 4,^{d} $\Delta S^{\ddagger}$ = −3 ± 6^e				
$K_3{}^b$	4.1 ± 1.2	5.7 ± 1.7	4.5 ± 1	4.5 ± 0.8	2.2 ± 1.2
$10^{10}K_a{}^c$			0.45		
$10^{-2}k_4{}^a$			6.6 ± 1.2		
($K_f{}^b$)			(1.7 × 10^3)		
$10^{-3}k_5{}^a$			1.4 ± 0.4		
($K_b{}^b$)			(300)		

Catechol

	T/°C		
	15.7	25.0	31.6
$10^{-2}k_1{}^a$	3.62 ± 0.3	7.50 ± 0.5	9.7 ± 0.4
	$\Delta H^{\ddagger}$ = 11 ± 4,^{d} $\Delta S^{\ddagger}$ = −10 ± 9^e		
$K_3{}^b$	(3.3)	3.3 ± 0.7	(3.3)
$10^{10}K_a{}^{b,c}$	1.4	1.4	1.4
$10^{-10}k_3{}^a$	1	6	6
$10^{-2}k_4{}^a$		1.05	
$10^{-2}k_5{}^a$		1.95	

^{a} In M^{-1} s^{-1}. ^{b} In M. ^{c} Reference 27. ^{d} In kcal mol^{-1}. ^{e} In cal K^{-1} mol^{-1}.

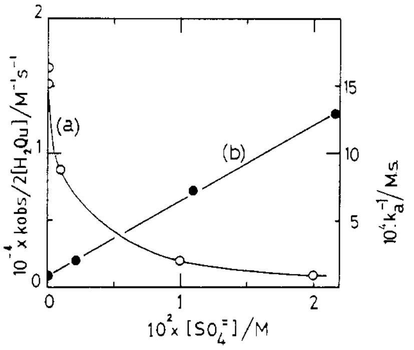

Figure 2. (a) Plot of $k_{obsd}/2[H_2Q]$ against $[SO_4{}^{2-}]$ T = 25.0 °C; pH 2.95; $[Ni^{III}L]^{3+}$ = 5 × 10^{-5} M; $[H_2Q]$ = 5 × 10^{-4} M. (b) Plot of $k_a{}^{-1}$ against $[SO_4{}^{2-}]$ (eq 19).

temperatures are presented in Table II.

Meyerstein et al.[5,16,17] have shown that sulfate ions form complexes with $[Ni^{III}L]^{3+}$ and related species and that the stability of these species toward reduction is greatly increased. Electrochemical measurements provide values of the redox potentials $E°([Ni^{III}L]^{3+}/[Ni^{II}L]^{2+})$ = 0.75 V and $E°([Ni^{III}L(SO_4)_2]^-/Ni^{II}L)$ = 0.46 V with respect to the Ag/AgCl reference electrode used in ref 16. The corresponding values with a standard hydrogen electrode are 0.97 and 0.69 V, respectively.

Table III. Dependence of Rates on Sulfate Ion (T = 25 °C, I = 1.00 M ($LiClO_4$))

Hydroquinone

$10^2[SO_4{}^{2-}]$/M	$10^{-4}k_a$/ M^{-1} s^{-1}	$10^2[SO_4{}^{2-}]$/M	$10^{-4}k_a$/ M^{-1} s^{-1}
	$[H^+]$ = 1.12 × 10^{-3} M		
0.0	1.73 (1.76)	1.012	0.19_6 (0.22)
0.0101	1.51 (1.57)	2.024	0.097 (0.15)
0.101	0.87_7 (0.92)		
	$[H^+]$ = 8.93 × 10^{-3} M		
0.0	1.34 (1.23)	2.05	0.064 (0.13)
1.025	0.13_5 (0.18)		
	$[H^+]$ = 4.19 × 10^{-2} M		
0.0	1.02 (1.10)	2.05	0.078_4 (0.17)
1.095	0.16 (0.24)		
	$[H^+]$ = 0.214 M		
0.0	(1.00) (1.08)	1.025	0.23_4 (0.31)
0.512	0.35 (0.44)	2.05	0.12_8 (0.23)
	$[H^+]$ = 0.419 M		
0.0	0.99 (1.00)	1.01	0.27 (0.32)
0.505	0.40 (0.45)		

Catechol

$10^2[SO_4{}^{2-}]$/M	$10^{-3}k_a$/ M^{-1} s^{-1}	$10^2[SO_4{}^{2-}]$/M	$10^{-3}k_a$/ M^{-1} s^{-1}
	$[H^+]$ = 8.39 × 10^{-3} M		
0.0	1.19 (1.19)	2.05	0.10_6 (0.16)
1.025	0.21 (0.21)		
	$[H^+]$ = 4.19 × 10^{-2} M		
0.0	0.77 (0.77)	2.049	0.07 (0.17)
1.025	0.14_6 (0.20)		
	$[H^+]$ = 0.2 M		
0.0	0.71 (0.71)	2.05	0.13 (0.22)
1.025	0.23 (0.27)		
	$[H^+]$ = 1.00 M		
0.0	0.57 (0.56)	1.089	0.30_8 (0.24)
0.218	0.47 (0.39)		

In agreement with these observations, it was found that addition of $SO_4{}^{2-}$ (up to 2 × 10^{-2} M) drastically slowed down the reactions. A typical result is shown in Figure 2 for the hydroquinone reaction at pH 2.95. Variations of the second-order rate constants with pH at a constant $[SO_4{}^{2-}]$ were more complex. Increasing the pH from 0 to ~2 under these conditions resulted first in a decrease in rate and then in an increase up to the highest pH studied (ca. 3.4). The rate data are presented in Table III.

Discussion

(a) Hydrogen Ion Dependences. As indicated earlier, the rate variations were not a simple function of $[H^+]$. Two regions were therefore examined separately, namely, 0.1 < $[H^+]$ < 1.0 M and $[H^+]$ < 0.05 M.

(i) 0.1 < $[H^+]$ < 1.0 M. Quinols have been used as reductants for a wide variety of metal oxidants including $Fe(phen)_3{}^{3+}$,[18] $IrCl_6{}^{2-}$,[19] Mn(III),[20,21] V(V),[22] Np(VI),[23] $Mo(CN)_8{}^{3-}$,[24] and $CoW_{12}O_{40}{}^{5-}$,[25] since, with various ring-sub-

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stituted derivatives, they offer a series of reacting substrates exhibiting a large range of redox potentials.

In the present study, at pH <1.0 there is a small but reproducible retardation of the reaction rate on increasing $[H^+]$. Two possibilities for this behavior were investigated. If a protonated form of $[Ni^{III}L]^{3+}$ was produced, one of the ring nitrogens would be involved. This would be expected to result in instability of the complexes with respect to further dissociation and intramolecular redox of $[Ni^{III}L]^{3+}$. No spectroscopic changes (which would accompany such a process) were observed in the range 0.1–4.0 M $HClO_4$. The alternative, a protonation of the quinol, is therefore preferred (eq 2).

$$H_3Q^+ \rightleftharpoons H^+ + H_2Q \quad K_3 \tag{2}$$

The rate scheme for the oxidation may be written as shown in eq 3 and 4, where SQ· represents the semiquinone radical

$$[Ni^{III}L]^{3+} + H_2Q \xrightarrow{k_1} [Ni^{II}L]^{2+} + SQ\cdot \tag{3}$$

$$[Ni^{III}L]^{3+} + SQ\cdot \xrightarrow{\text{fast}} [Ni^{II}L]^{2+} + Q \tag{4}$$

with no assumption made as to the state of its protonation. If (3) is rate-determining, the rate equation may be expressed in the form shown in eq 5, consistent with a first-order de-

$$\frac{-d[Ni^{III}L^{3+}]_t}{dt} = \frac{2k_1[H_2Q]_t[Ni(III)]_tK_3}{[H^+] + K_3} \tag{5}$$

pendence on [Ni(III)] and $[H_2Q]$ at constant $[H^+]$. The observed second-order rate constant, $k_a = k_{obsd}/2[H_2Q]$, may be written as $k_1K_3/([H^+] + K_3)$. Rearranging yields eq 6, such

$$k_a = k_1 - k_a[H^+]/K_3 \tag{6}$$

that a plot of k_a against $k_a[H^+]$ should be linear with intercept k_1 and slope $-1/K_3$. With use of the data in Table I, such plots showed good linearity over the $[H^+]$ range under consideration, providing values (T = 25°C) for $k_1(H_2Q) = (1.1 \pm 0.05) \times 10^4$ M^{-1} s^{-1} and $k_1(H_2Cat) = 730 \pm 40$ M^{-1} s^{-1} and $K_3 = 4.5 \pm 1.2$ and 3.3 ± 0.9 M for hydroquinone and catechol, respectively. Although there are no previous data for these systems, values of K_3 for alcohols have been shown to lie in the range 1–10 M,[26] the value for phenol being 3.9 M. Also, in an acid-dependence study with catechol similar to the present investigation but with $IrCl_6^{2-}$ as oxidant,[19] the retardation was ascribed in part to a medium effect. The differences involved, however, are considered larger than that expected solely from this source. With use of the data in ref 19 and with incorporation of equilibrium 2, the results obtained for the oxidation of catechol by Ir(IV) are $K_3 = 5.3 \pm 2$ M and $k_1(H_2Cat) = (3.1 \pm 0.3) \times 10^3$ M^{-1} s^{-1} with no detectable rate of reaction of H_3Q^+. Comparison of the equilibrium constant with the present data is considered reasonable.

(ii) $[H^+]$ < 0.05 M. Hydroquinone. Since the pK_a for formation of the hydroquinone anion is 10.35,[27] in the pH range (1.5–3.2) studied, the substrate is present predominantly as the undissociated species. The increase in rate on a decrease of $[H^+]$ (Figure 2) may thus be attributed to reaction of a second nickel(III) species with rate constant k_2 (eq 7 and 8).

$$[Ni^{III}L(OH_2)_2]^{3+} \rightleftharpoons [Ni^{III}L(OH)(OH_2)]^{2+} + H^+ \quad K_h \tag{7}$$

$$[Ni^{III}L(OH)(OH_2)]^{2+} + H_2Q \xrightarrow{k_2} [Ni^{II}L]^{2+} + SQ\cdot \tag{8}$$

Under these conditions, k_a may be written in the form shown in eq 9, and a plot of $k_a(K_h + [H^+])$ should be linear with slope

$$k_a = (k_1[H^+] + k_2K_h)/(K_h + [H^+]) \tag{9}$$

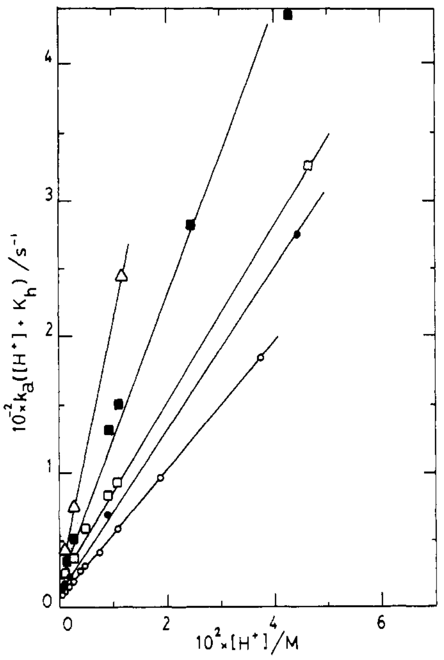

Figure 3. Plots of $k_a([H^+] + K_h)$ against $[H^+]$ at various temperatures (see text): (○) T = 10.1 °C; (●) T = 15.5 °C; (□) T = 20.5 °C; (■) T = 25.0 °C; (△) T = 31.8 °C.

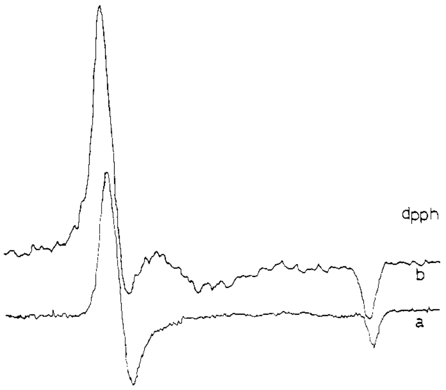

Figure 4. ESR spectra of (a) $[Ni(cyclam)(OH_2)_2]^{3+}$ (pH 0) and of (b) the monohydroxo complex $[Ni(cyclam)(OH)(OH_2)]^{2+}$ (pH 3.5), both at T = 77 K.

k_1 and intercept k_2K_h. From pulse radiolysis studies on $[Ni^{III}Me_6cyclam]^{3+}$ (Me_6cyclam = *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) a pK_h value of 3.7 has been reported,[16] and a similar value has been indicated for the $[Ni^{III}L]^{3+}$ complex.[17] A measure of pK_h may be obtained in the present study by plotting $k_a(K_h + [H^+])$ against $[H^+]$ for differing values of K_h until the best straight line is produced. The data representing best fits at various temperatures are presented for hydroquinone in Figure 3. The values of k_1, k_2, and K_h derived are presented in Table II. At 25 °C, $K_h = 8 \times 10^{-4}$ M (pK_h = 3.1), a value in reasonable agreement with previous data which were obtained at lower ionic strengths. Confirmation of the magnitude of K_h comes from the slopes of curves in Figure 3 (k_1), which agree to within 4–8% with the k_1 values obtained in the higher hydrogen ion concentration studies (eq 6). An identical K_h value has been derived in this laboratory with use of a similar kinetic analysis in the reaction of $[Ni^{III}L]^{3+}$ with H_2O_2.[28] Further evidence for the monohydroxy complex comes from ESR measurements on frozen solutions at 77 K. At $[H^+]$ = 1.00 M, the spectrum of $[Ni(L)(H_2O)_2]^{3+}$ shows the two lines $g_\perp = 2.21$ and $g_\parallel = 2.024$ characteristic of a low-spin d^7 ion in

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a D_{4h} symmetrical environment. Measurements on solutions at $[H^+] = 10^{-3}$ M show much greater fine structure in the $g_\perp$ region compatible with a loss of symmetry. A similar finding has been proposed from photochemical measurements of these nickel(III) complexes.[29] The spectra are shown in Figure 4.

Using the individual rate and equilibrium constants, it is possible to calculate the rate constant for reaction over the range $[H^+] = 3.5 \times 10^{-4}$ to 1.00 M with the relationship

$$k_a = \frac{(k_1 + k_2K_h/[H^+])[H^+]K_3}{([H^+] + K_3)([H^+] + K_h)} \qquad (10)$$

The data are presented in Table I, and excellent agreement is observed with the experimental points.

Catechol. In the pH range 1.5–3.4, a more marked increase in rate at higher pHs is observed than for the hydroquinone system. In this case, however, the pK_a for $H(Cat)^-$ formation is lower (9.85),[27] leading to the possibility of the reaction

$$[Ni^{III}L(OH)(OH_2)]^{2+} + H(Cat)^- \xrightarrow{k_3} [Ni^{II}L]^{2+} + SQ\cdot \qquad (11)$$

at pH >2.7. With use of reactions 3, 8, and 11 the rate expression is of the form

$$k_a = \frac{(k_1 + k_2K_h/[H^+] + k_3K_hK_a/[H^+]^2)K_3[H^+]}{([H^+] + K_h)([H^+] + K_3)} \qquad (12)$$

Rearrangement yields

$$f(k) = \left(\frac{k_a([H^+] + K_3)([H^+] + K_h) - k_1}{K_3[H^+]}\right)[H^+] = k_2K_h + k_3K_hK_a/[H^+] \qquad (13)$$

so that a plot of the function $f(k)$ against $[H^+]^{-1}$ should be linear with intercept k_2K_h and slope $k_3K_hK_a$. Good linearity was observed at all temperatures studied, and individual rate constants are presented in Table II. The calculation of the rate profile against pH (Figure 1b) has been made, and the comparison with experimental data over the range $[H^+] = 2.75 \times 10^{-4}$ to 1.00 M (eq 12) is good.

(b) Sulfate Dependences. Nickel(III) species are known to form complexes with anions such as SO_4^{2-}:

$$[Ni^{III}L]^{3+} + SO_4^{2-} \rightleftharpoons [Ni^{III}LSO_4]^+ \quad K_f \qquad (14)$$

Also, under conditions of moderate hydrogen ion concentration, the equilibrium

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \quad K_2 \qquad (15)$$

exists with $K_2 = 1.2 \times 10^{-2}$ M.[30]

Under conditions used in this study, at relatively low $[SO_4^{2-}]$ ($\leq 2 \times 10^{-2}$ M) equilibria involving only the monosulfate complexes are considered significant. This is confirmed by a reasonable linear slope of $1/k_a$ against $[SO_4^{2-}]$ see (Figure 2). The dramatic decrease in rate (Figure 2) may be ascribed to the sulfato complexes reacting more slowly than the aquo ions. If, in the presence of sulfate, the kinetic pathways (16) and (17) are present in addition to (3) and (8), then the rate constant may be expressed in the form (18), where K_b represents the constant for association of a proton with the nickel(III) species. Under conditions of low $[SO_4^{2-}]$ ($\leq$0.01 M) and at $[H^+] < 0.4$ M

$$[Ni^{III}LSO_4]^+ + H_2Q \xrightarrow{k_4} [Ni^{II}L]^{2+} + SQ\cdot + SO_4^{2-} \qquad (16)$$

$$[Ni^{III}L(H)(SO_4)]^{2+} + H_2Q \xrightarrow{k_5} [Ni^{II}L]^{2+} + SQ\cdot + HSO_4^- \qquad (17)$$

$$k_a = K_3\{(k_1 + k_2K_h/[H^+] + k_3K_hK_a/[H^+]^2) + (k_4K_fK_2 + k_5K_b[H^+])[SO_4^{2-}]_t/([H^+] + K_2)\}/\{([H^+] + K_3)(1 + K_h/[H^+] + ([SO_4^{2-}]_t/([H^+] + K_2)) \times (K_fK_2 + K_b[H^+]))\} \qquad (18)$$

$$(k_1 + k_2K_h/[H^+] + k_3K_aK_h/[H^+]^2)\ (=\alpha) > (k_4K_fK_2 + k_5K_b[H^+])[SO_4^{2-}]_t/([H^+] + K_2)\ (=\beta)$$

so that

$$\frac{1}{k_a} = \frac{([H^+] + K_3)([H^+] + K_h)}{K_3[H^+]\alpha} + \frac{([H^+] + K_3)(K_fK_2 + K_b[H^+][SO_4^{2-}]_t)}{([H^+] + K_2)K_3\alpha} \qquad (19)$$

Plots of k_a^{-1} against $[SO_4^{2-}]_t$ showed linearity at constant $[H^+]$ (see Figure 2). With use of (19) it may be seen that

$$\frac{(\text{slope})([H^+] + K_2)([H^+] + K_h)}{(\text{intercept})[H^+]} = K_fK_2 + K_b[H^+] \qquad (20)$$

Utilizing both the hydroquinone and the catechol data (T = 25 °C) plots according to (20) yielded a straight line of slope $K_b = 250 \pm 100$ and intercept $(K_fK_2) = 18 \pm 8$. An iterative analysis was then employed to obtain resolved values of rate constants k_4 and k_5 in (18). The calculated data based on $k_4 = 600 \pm 50$ M^{-1} s^{-1} and $k_5 = 1420 \pm 120$ M^{-1} s^{-1} (hydroquinone) and $k_4 = 105 \pm 30$ M^{-1} s^{-1} and $k_5 = 195 \pm 80$ M^{-1} s^{-1} (catechol) with $K_fK_2 = 20 \pm 6$ and $K_b = 300 \pm 130$ M are shown in Table II in reasonable agreement with the observed data. Deviations at higher $[SO_4^{2-}]$ may be due to further complexing of sulfate. At high pH, there exists the possibility of another $[H^+]^{-1}$ pathway deriving from hydrolysis of the aquo–sulfato complex. The value of $K_f = (1.7 \pm 0.6) \times 10^3$ M may be compared[17] with that for $[Ni^{III}Me_6cyclam]^{3+}$ (3×10^3 M) obtained from pulse radiolysis studies. An estimate of $K \approx 10^5$ M^2 for the bis(sulfato) complex of $[Ni^{III}cyclam]$ has been made,[31] suggesting a value of $\sim 10^2$ M for the second complexation constant of $[Ni^{III}L(SO_4)]^+$ with sulfate ions. The reduced values of k_4 and k_5 compared to k_1 and k_2 are consistent with the diminished oxidative reactivity of the sulfate species.

As has been observed for previous reactions with these substrates,[19-24] the reduction of hydroquinone is $\sim 10^2$ faster than that for catechol. Also the rate constant (k_2) for the monohydroxynickel(III) complex ion is ~3 times greater (for hydroquinone) than that (k_1) for the $[Ni^{III}L(OH_2)_2]^{3+}$ ion. In our treatment we have assigned reaction 8 exclusively to that of the hydrolyzed cation with H_2Q. A proton ambiguity persists here in that an equivalent representation of (8) is via reaction of $[Ni^{III}L]^{3+} + HQ^-$. There will probably be a contribution from this source in the k_2K_h value derived for catechol. The rapid reaction $[Ni(L)(OH)]^{2+} + H(Cat)^-$ ($k_3 \approx 6 \times 10^{10}$ M^{-1} s^{-1}) is in keeping with the greatly increased reduction potential of the anion. No similar reaction was observed for HQ^- in the present pH range, probably owing to the slightly greater pK_a value (10.35 against 9.85 for catechol). With the assumption of a similar value ($k_3 \approx 6 \times 10^{10}$ M^{-1} s^{-1}) for the hydroquinone reaction, the term $k_3K_aK_h$ contributes less than 0.2% to the reaction rate at pH 2. We feel therefore that the concentration of HQ^- is sufficiently low

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Table IV. Comparison of the Kinetic Data and Evaluation of Free Energy Parameters for the Oxidation if 1,2- and 1,4-Benzenediol by Various Substrates at 25 °C

			ΔG^*_{12}[a]		k_{12}[b]		
oxidant	ΔG°_{12}[a]	ΔG^*_{11}[a]	obsd	calcd	obsd	calcd	ref
Reductant: 1,2-Dihydroxybenzene							
$[IrCl_6]^{2-}$	4.91	8.0	10.05	9.92	3.1×10^3[c]	5.36×10^3	19
$[IrCl_5(H_2O)]^-$	1.89	8.0	8.47	8.22	6.2×10^4	9.26×10^4	18
$IrCl_4(H_2O)_4$	3.39	8.0	7.09	9.04	6.4×10^5	2.33×10^4	18
$[IrBr_6]^{2-}$	6.64	5.2	10.33	9.64	2.7×10^3	8.48×10^3	18
$[Fe(phen)_3]^{3+}$	2.54	3.0	6.11	6.10	1.65×10^6[d]	3.33×10^6	18
$[Fe(5\text{-}mphen)_3]^{3+}$	2.36	3.0	6.64	6.64	6.5×10^5[d]	1.35×10^6	18
$[Mo(CN)_8]^{3-}$	8.53	4.0	12.31	10.38	9.5×10	2.43×10^3	23
$[Co(W_{12}O_{40})]^{5-}$	3.92	15.36	10.94	12.98	9.5×10^2	3.03×10	25
$[Ni^{III}L]^{3+}$	4.84	9.5	11.08	10	7.2×10^2	2.17×10^3	*f*
$[NiLSO_4]^+$	9.23	9.5	12.25	12.62	1.05×10^2	5.6×10	*f*
Reductant: 1,4-Dihydroxybenzene							
$[IrCl_6]^{2-}$	2.84	8.0	8.37	8.74	7.3×10^4	3.89×10^4	19
$[IrCl_5(H_2O)]^-$	−0.19	8.0	6.90	7.16	8.8×10^5	5.65×10^5	19
$[IrBr_6]^{2-}$	4.57	5.2	8.36	8.36	7.4×10^4	7.41×10^4	19
$[Fe(CN)_6]^{3-}$	8.53	8.0	13.64	12.14	10	1.2×10	24
$[Fe(phen)]^{3+}$	0.46	3.0	4.34	4.98	4.0×10^7[d]	2.22×10^7	18
$[Fe(5\text{-}mphen)]^{3+}$	1.38	3.0	5.37	5.47	1.0×10^7[e]	9.81×10^6	18
$[Fe(dimphen)]^{3+}$	2.54	3.0	4.77	6.10	2.8×10^7[e]	3.33×10^6	18
$[Mo(CN)_8]^{3-}$	6.46	4.0	9.49	8.98	1.1×10^4	4.3×10^3	24
$[Co(W_{12}O_{40})]^{5-}$	1.85	15.36	9.34	11.86	1.43×10^4	1.45×10^2	25
Np(VI)	−1.38	14.85	8.66	10.00	4.52×10^4	4.66×10^3	23
$[Ni^{III}L]^{3+}$	2.77	9.5	9.50	9.39	1.09×10^4	1.29×10^4	*f*
$[NiLSO_4]^+$	6.92	9.5	11.21	11.58	6.6×10^2	3.24×10^2	*f*

[a] In kcal mol^{-1}. [b] In M^{-1} s^{-1}. [c] Reevaluated–see text. [d] $T = 6$ °C. [e] $T = 20$ °C. [f] Present work.

to permit identification of (8) as shown.

The Marcus cross relationship has been used widely to correlate the free energy of activation (ΔG^*_{12}) with the free energy of reaction (ΔG°_{12}) for outer-sphere electron-transfer reactions.[32-36] The relationship may be expressed in the form

$$\Delta G^*_{12} = W_{12} + \lambda(1 + \Delta G^{\circ}_{12}/\lambda)^2/4 \qquad (21)$$

where the observed rate constant $k_{12} = Z \exp(-\Delta G^*_{12}/RT)$. (The collision number Z used was 10^{11} M^{-1} s^{-1}; $\lambda = 2(\Delta G^*_{11} - W_{11} + \Delta G^*_{22} - W_{22})$.) The terms ΔG^*_{11} and ΔG^*_{22} refer to the free energies of activation for the self-exchange reactions of the oxidizing and reducing agents, respectively, and W_{11}, W_{22}, W_{12}, and W_{21} to the various work terms arising from Coulombic forces in bringing together the reactants and separating the products. Attempts have been made to include the work terms[24,33] in the correlation. There is from this source, however, only a small contribution to the rate at this ionic strength, and work terms have been neglected here. A value for quinols of $\Delta G^*_{22} = 6.5$ kcal mol^{-1} has been proposed[19] for a series of dihydroxybenzenes. This value has been used in the present study. In the case of ΔG^*_{11}, recent ESR and kinetic studies using $^{61}Ni^{III}L$ and reactions of $[Fe^{III}(phen)_3]^{3+}$[36] are consistent with a value of 9.5 ± 1.5 kcal mol^{-1}. The E° value for the couple $[NiL(SO_4)]^+/[NiL]^{2+}$ (0.77 V) has been calculated from the potential (0.97 V) of the $[NiL(OH)_2]^{3+}/[NiL]^{2+}$ couple. For the $SQ\cdot/H_2Q$ couples, the corresponding values are 1.17 and 1.08 V for catechol and hydroquinone, respectively.[37] Using the same ΔG^*_{11} parameter for the reactions of aquo and sulfate species, we have calculated with use of (21) the rate of oxidation of both substrates. Comparison with observed values shows rates to be in generally good agreement, confirming the outer-sphere designation for these reactions (Table IV). The measure of agreement is comparable with that obtained previously. It is known from studies[38] on cobalt macrocycles of this type ($CoN_4X_2^{3+/2+}$) (N_4 = *trans*-[14]diene) that self-exchange rates are sensitive to the nature of group X. Further studies on nickel(III) systems with various axial groups are required, however, to confirm whether similar effects are present.

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Registry No. H_2Q, 123-31-9; H_2Cat, 120-80-9; $[Ni^{III}L]^{3+}$, 66199-97-1; $[NiLSO_4]^+$, 71603-84-4.

Supplementary Material Available: Listings of rate data, equilibrium constants, dependence of rates on sulfate ion, and comparison of kinetic data and evaluation of free energy parameters (7 pages). Ordering information is given on any current masthead page.

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