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Kinetics of the Reaction of the $[Ni^{III}cyclam(OH_2)_2]^{3+}$ Cation with Halide and Thiocyanate Ions in Aqueous Perchlorate Media

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The (1,4,8,11-tetraazacyclotetradecane)diaquonickel(III) cation, $[Ni^{III}L]^{3+}$, reacts with X^- ($=Cl^-$, Br^-, NCS^-) in aqueous perchloric acid according to the equation $[Ni^{III}L]^{3+} + X^- \rightleftharpoons [Ni^{III}LX]^{2+}$ ($K = k_1/k_{-1}$). The above equilibrium has been investigated by using both spectrophotometric and kinetic (stopped flow) techniques, and good agreement is observed in the values of K derived from both methods. In the reaction with NCS^-, carried out in excess $[Ni^{III}L]$, the rate law is of the form $R = k_2[[Ni^{III}L]][NCS^-]$, and the equilibrium constant is too large for a meaningful determination of the dissociation rate. Activation parameters and the associated rate constants are ($T = 25$ °C) as follows: $k_{1(Cl^-)} = 902$ L mol^{-1} s^{-1}, $\Delta H_1^‡ = 14.2 \pm 0.3$ kcal/mol, $\Delta S_1^‡ = -2.6 \pm 3$ cal deg^{-1} mol^{-1}; $k_{1(Br^-)} = 200 \pm 20$ L mol^{-1} s^{-1}, $\Delta H_1^‡ = 11.3 \pm 0.6$ kcal/mol, $\Delta S_1^‡ = 0.0 \pm 5$ cal deg^{-1} mol^{-1}; $k_{1(NCS^-)} = 1160 \pm 20$ L mol^{-1} s^{-1}, $\Delta H_1^‡ = 11.4 \pm 0.4$ kcal/mol, $\Delta S_1^‡ = -6.0 \pm 3$ cal deg^{-1} mol^{-1}. These are among the first data for substitution rates of a low-spin d^7 complex. Possible mechanisms of reaction are discussed. In the case of I^-, oxidation of the nucleophile occurs, and at 26 °C the second-order rate constant is $k_2' = 3020 \pm 90$ L mol^{-1} s^{-1}, with $\Delta H^‡ = 9.4 \pm 0.3$ kcal/mol and $\Delta S^‡ = -11.0 \pm 2.0$ cal deg^{-1} mol^{-1}. ESR techniques have been used to characterize the reaction products and to provide evidence for the formation of the monohalo- and *trans*-dihalonickel(III) cyclam complexes under conditions of excess ligand. These latter species are kinetically more stable in aqueous media than the precursor $[Ni^{III}L(OH_2)_2]^{3+}$ cation.

Introduction

The preparations of several macrocyclic complexes of Ni(III) have been reported recently.[1] In these complex ions, the saturated tetraaza ligand system is considered as being necessary in the stabilization of this oxidation state. In our laboratories, we have been investigating the mechanism of the cerium(IV) oxidation in acid media of the $[Ni(cyclam)]^{2+}$ {$[Ni(cyclam)]^{2+}$ = (1,4,8,11-tetraazacyclotetradecane)nickel(II)} cation and other related species to the corresponding nickel(III) complexes. Ni(III) macrocycles have been characterized[2,3] both in solution and in the solid state as low-spin, d^7 octahedral centers with two solvent molecules in the axial positions. The related complex from 2,3-Me_2-cyclam has been prepared[4] and is very stable in the solid state. Substitution of the axial solvent molecules in considerable excesses of halide, nitrate, and sulfate ion yielded the dihalide, dinitrato, and monosulfate complexes, respectively.

Very recently, further work on both unsaturated and saturated macrocyclic ligand systems has been published.[5–7] Flash photolysis and pulse radiolysis have been used in the oxidation of the nickel(II) complexes, and, in the case of saturated ligand systems, it has been shown that electrochemical methods produce nickel(III) complexes which are stable in acidic media over relatively long time periods.

To date, virtually no kinetic data are available on the substitution rates at the axial sites of these nickel(III) complexes. In the present study we report on an investigation into the rates of reaction with halide ions and thiocyanate. In the case of iodide, the macrocyclic complex oxidizes the ligand to yield triiodide ion. These data are of interest in view of current consideration being given to the mechanisms of substitution at tervalent metal centers.[8,9]

The use of ESR techniques has enabled us to examine the nature of the nickel(III) products in the presence of large excess concentrations of chloride, bromide, and thiocyanate. The *trans*-dichloro and -dibromo species are surprisingly stable in aqueous media and may be used as mild oxidants.

Experimental Section

The nickel(II)[10] and nickel(III)[11] complexes were prepared as the perchlorate salts as described previously. The nickel(III) cation, $[Ni^{III}L(OH_2)_2]^{3+}$, was characterized by using ESR ($g_\perp = 2.1928$; $g_\parallel = 2.0340$) and by UV/visible spectroscopy (λ_{max} 308 nm, ϵ_{max} 11 000 ± 100).

The dichloro and dibromo adducts of Ni(III) cyclam were obtained as their perchlorate salts by addition of an excess of a saturated sodium halide solution to one of the diaquo complex in 1.0 M perchloric acid. The products, being sparingly soluble in perchlorate media, were washed with 2 M acid and ice water and dried in vacuo. The products analyzed satisfactorily. Anal. Calcd for $[Ni(C_{10}H_{24}N_4)Br_2]ClO_4$: C, 23.2; H, 4.67; N, 10.8. Found: C, 23.5; H, 4.63; N, 10.8. Calcd for $[Ni(C_{10}H_{24}N_4)Cl_2]ClO_4$: C, 28.0; H, 5.63; N, 13.0. Found: C, 28.1; H, 5.71; N, 13.0.

ESR spectra were measured by using a Bruker 200 TT or a Varian E6S spectrometer. g values were determined from spectra run by using a scan range of 400 G. DPPH ($g = 2.0037$) was employed as an internal reference standard.

In kinetic runs, stock solutions of reagents were prepared immediately prior to each run, in order to minimize any decomposition of the nickel(III) complex in aqueous solution. This slow decay was arrested markedly in acid media, and kinetic data were derived by using solutions containing up to 1.0 M $HClO_4$. Reaction rates were monitored by using a modified Applied Photophysics stopped-flow instrument,[12] with appropriate thermostating being maintained to ±0.05°. Rate constants were computed by using a least-squares analysis of data collected with use of a PCM 12 microprocessor. Generally, between 25 and 100 data points were used, and first-order plots were found to be linear up to 6 reaction half-lives.

Absorbance measurements were made by using both Cary 17 and Varian 635 spectrophotometers with cell compartments thermostated to the appropriate temperature.

Results and Discussion

Spectrophotometric Measurements. Spectrophotometric titration of $[Ni^{III}L(OH_2)_2]^{3+}$ with I^- showed the stoichiometry of this reaction to be 1.02 (±0.05):1, the equation for the overall reaction being

$$2[Ni^{III}L]^{3+} + 3I^- \rightarrow 2[Ni^{II}L]^{2+} + I_3^-$$

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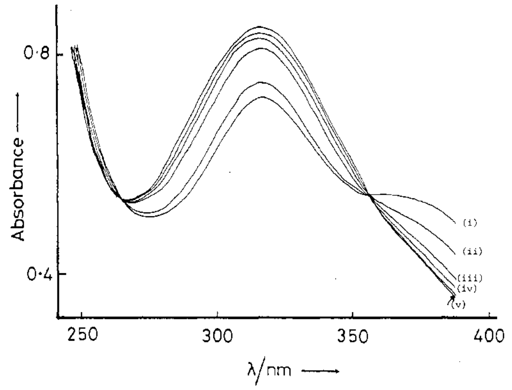

Figure 1. Spectrophotometric titration of $[\mathrm{Ni^{III}L(OH_2)_2}]^{3+}$ (8×10^{-5} M) against $\mathrm{Cl^-}$ ((i) 0, (ii) 0.001 M, (iii) 0.005 M, (iv) 0.010 M, (v) 0.02 M $\mathrm{Cl^-}$) at 23 °C. Ionic strength = 1.00 M.

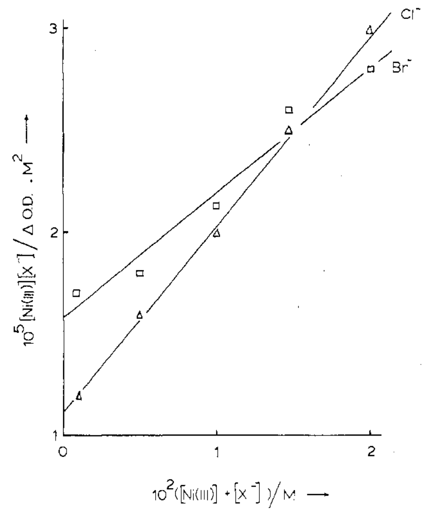

Figure 2. Relation of $1/\Delta\mathrm{OD}$ vs. [substrate] (according to eq 2) for the spectrophotometric titrations of $[\mathrm{Ni^{III}L(OH_2)_2}]^{3+}$ with chloride and bromide, at 25 °C. Ionic strength = 1.00 M.

To measure equilibrium constants for the $[\mathrm{Ni^{III}L}]^{3+}/\mathrm{X^-}$ systems (X = Cl, Br), we monitored absorbance changes in the UV spectra over the wavelength range 250–380 nm and the temperature range 6–34 °C (Figure 1). The nickel(III) complex concentration was maintained at 1.0×10^{-4} M in reactions with halide ions (10^{-4}–(2×10^{-2}) M). In the corresponding system with thiocyanate ion, where there is evidence for 1:2 complexing, the rates and spectra were measured in excess $[\mathrm{Ni^{III}L}]^{3+}$ ((1–16) $\times 10^{-3}$ M) with $[\mathrm{NCS^-}] \simeq$ (3–6) $\times 10^{-5}$ M.

The extent of equilibrium for reaction 1 may be measured

$$[\mathrm{Ni^{III}L}]^{3+} + \mathrm{X}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ni^{III}LX}]^{2+} \qquad (1)$$

by monitoring absorbance changes at the wavelength maximum for the monosubstituted species. The equilibrium constant ($K_1 = k_1/k_{-1}$) is derived by using eq 2 where ΔOD

$$\frac{[\mathrm{Ni^{III}L}]_0[\mathrm{X^-}]}{\Delta\mathrm{OD}} = \frac{[\mathrm{Ni^{III}L}]_0 + [\mathrm{X^-}]}{(\Delta\epsilon)l} + \frac{1}{K_1(\Delta\epsilon)l} \qquad (2)$$

represents the observed optical density change, Δϵ represents the difference in extinction coefficients between the complex ion and the adduct, and l is the optical path length. Figure 2 shows representative data for the reactions with chloride and bromide. The good linearity (eq 2) observed over the temperature range investigated confirms the formation of only 1:1 complexes in the concentration range studied. Even at the highest excess used (~200-fold $\mathrm{Cl^-}$ or $\mathrm{Br^-}$) there is little evidence for reaction with a second anion. Overall equilibrium constants derived are presented in Table I. In the case of iodide, the changes in UV spectra are consistent with reduction to nickel(II).

Table I. Equilibrium Constants ($K_1/\mathrm{M^{-1}}$) for Reactions of $[\mathrm{Ni^{III}L}]^{3+}$ with Ligands $\mathrm{X^-}$ (I = 1.0 M ($\mathrm{HClO_4}$))

	X	
T/°C	Cl⁻	Br⁻
6.0	150 ± 10[a]	25 ± 15[a]
6.6	146 ± 10[b]	23 ± 5[b]
13.7	150 ± 10[b]	30 ± 5[b]
19.4	170 ± 10[b]	36 ± 5[b]
23.0	179 ± 10[a]	50 ± 15[a]
25.0	210 ± 40[b]	34 ± 10[b]
30.0	185 ± 20[a]	

[a] Measured spectrophotometrically. [b] Measured kinetically.

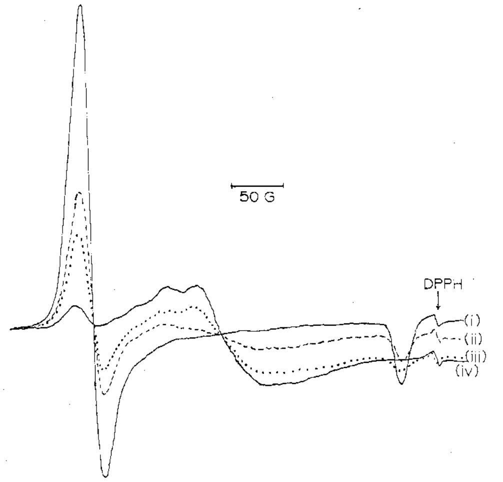

Figure 3. ESR "titration" of $[\mathrm{Ni^{III}L(OH_2)_2}]^{3+}$ with bromide in frozen 1.0 M perchloric acid at 77 K. $[\mathrm{Br^-}]$: (i) zero; (ii) 5×10^{-4} M; (iii) 1×10^{-3} M; (iv) 1×10^{-2} M.

ESR Measurements. Spectra were run at 77 K by using solid samples or frozen solutions of reacted mixtures, where appropriate. It may be seen from Figure 3 that marked changes in the spectra occur on complex formation, consistent with axial substitution. In some instances (vide infra), hyperfine splitting was observed, arising from coupling of the unpaired electron in the metal d_{z^2} orbital with the donor atom nucleus. Essentially an ESR "titration", analogous to those in visible spectroscopy, at 273 K indicated only one halide or thiocyanate ion to be coordinated over the concentration ranges employed in the kinetic studies (Figure 3). The dihalo complex cations, $[\mathrm{Ni^{III}LX_2}]^+$ (X = Cl, Br), were isolated as their perchlorate salts when exceedingly high concentrations (~5 M) of halide ion were employed. In these instances, ESR and UV spectra differ from those obtained in the present solution study. Previous ESR solution and frozen solution studies with dimethyl sulfoxide as solvent have been reported.[13] Under these conditions both the monohalo solvents and dihalo complexes were characterized although in the case of bromide as axial ligand, the presence of concentrated hydrobromic acid was required to counter the dissociation reaction $[\mathrm{NiBr_2L}]^+ \rightleftharpoons [\mathrm{NiBrL}]^{2+} + \mathrm{Br^-}$. We consider this supportive evidence that over the concentrations used in the present kinetic investigations, the product ions are the monoligated complex ions. ESR parameters for appropriate nickel(III) complex cations are listed in Table II.

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[13] A. Desideri, J. B. Raynor, and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2051 (1977).

Table II. ESR Parameters for the Nickel(III) Complex Cations $[Ni^{III}LX_2]^{n+}$ (in Frozen 1.0 M Perchloric Acid, at 77 K)

X	$g_\parallel$	$g_\perp$	X	$g_\parallel$	$g_\perp$
MeCN	2.0250	2.2148	OH_2[a]	2.0386	2.2138
OH_2	2.0332	2.2193	NO_3	2.0334	2.2402[b]

[a] Products of reaction of Co(III) and Ce(IV) with $[Ni^{II}L]^{2+}$.
[b] Solid sample.

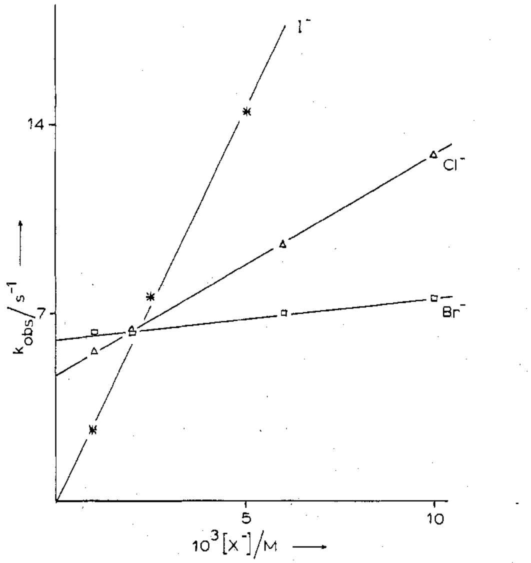


Figure 4. Plot of observed first-order rate constant (k_{obsd}/s^{-1}) vs. halide ion concentration, $[X^-]$, at 25 °C in 1.0 M perchloric acid (I^- data (*) at temperature of 26 °C refer to the redox reaction observed).

Kinetic Measurements. The observed first-order rate constants, k_{obsd}, were found to vary linearly with anion concentration. Data are presented in Table III, and as may be seen from Figure 4, whereas the curves for Cl^- and Br^- show intercepts, those for I^- (and NCS^-) pass through the origin. For reaction 1, rate law 3 may be derived.

$$\frac{d[Ni^{III}LX]}{dt} = k_{obsd}[Ni^{III}L] = (k_1[X^-] + k_{-1})[Ni^{III}LX] \quad (3)$$

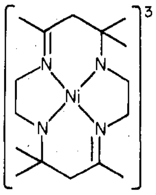
Equilibrium quotients obtained kinetically show good agreement with those derived spectrophotometrically (Table I). Thermodynamic parameters have been derived (Table III) for the formation and dissociation reactions of these complexes.

Reactions with Chloride and Bromide. As may be seen from Table I, in keeping with the relatively small absorbance changes, equilibrium constants are generally low and show little variation with temperature. K_1 for the chloro complex (~170 M^{-1}) is about 5–6 times greater than for the bromo species (~30 M^{-1}). This difference derives largely from the formation rate constants (at 25 °C, $k_{1(Cl^-)} = 902\ M^{-1}\ s^{-1}$ compared with $k_{1(Br^-)} = 207\ M^{-1}\ s^{-1}$). Replacement of a solvent molecule is generally considered to proceed via an outer-sphere species (eq 4). Values for K_{os} for a complex of this charge type may be

$$[Ni^{III}L]^{3+} + [X^-] \underset{}{\overset{K_{os}}{\rightleftharpoons}} [Ni^{III}L,X^{2+}] \xrightarrow{k_f} [Ni^{III}LX]^{2+} + H_2O \quad (4)$$

calculated[14] in 1.0 M ionic strength to be 1.7–1.8 M^{-1}, depending on the radii of the cation and anions, respectively. For these calculations, the nickel(III) cyclam radius was assumed in our approximation to be identical with that of the nickel(II) complex, and the halide is considered to approach along the axial direction. Experimental values of K_{os} at $I \approx 1.0$ M, for the reaction of $(H_2O)_6Cr^{3+}$ with NCS^- and Cl^-, are 1.0 and 0.9 M^{-1}, respectively.[15,16] Agreement between the theoretical and experimental values for these similar charge types is considered good, since it is known that at higher ionic strengths it is increasingly difficult to determine parameters for the encounter complex and hence values for the inner-sphere complexing constants.[17] If the value of unity for K_{os} is of the correct magnitude, the k_f values for complex formation are 902 s^{-1} (Cl^-) and 207 s^{-1} (Br^-), respectively. On axial coordination of halide, not only is the ESR spectrum modified (Figure 3) but changes in the UV–visible are also evident (Figure 1). An interesting feature is that in halide media the $[Ni^{III}LX_2]^+$ ions are more stable with respect to decomposition than the diaquo complexes. Indeed, whereas the ion $[Ni^{III}L(OH_2)_2]^{3+}$ decomposes fairly rapidly (~1 h) at pH >2–3, the dichloro species is stable for a period of days. A similar effect has been noted recently by Meyerstein[7] with the $[Ni^{III}(Me_6\text{-cyclam})SO_4]^+$ ion where coordination by an anion appears to impart increased thermodynamic and kinetic stability.

Some comparisons of reactions of nickel(III) complexes with halide ions may be derived from recent studies. Laurence[6] has shown that for the saturated ligand complex $[Ni^{III}(Me_6\text{-cyclam})]^{3+}$ and for the *trans*-14-diene analogue (A),



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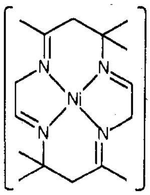

B

reaction with Br^- and I^- produces halogen. The reaction kinetics were studied at low pH. No similar redox reactions between Ni(III) complexes and Cl^- were observed even at high (0.1–0.5 M) Cl^- concentrations. For the more strongly oxidizing species B the reaction with Cl^- (0.1 M) showed a second-order decay of the complex. The linear dependence of the second-order rate constant on $[Cl^-]$ implied that under these conditions a high proportion of B was in a form in which at least one chloride ion is bound. This is in agreement with the present study where under the concentrations of halide ions noted above there is a mixture of $[Ni^{III}LCl]^{2+}$ and $[Ni^{III}LCl_2]^+$. The diene complexes are known to have higher redox potentials than the saturated cyclam species, and our finding of a stable *trans*-dichloronickel(III) cyclam ion is in keeping with this observation. The reaction of A and Br^- has been investigated independently by Meyerstein and co-workers.[5] The second-order rate law in [A] is again observed. The experimental conditions have a lower (~10^{-2} M) concentration of halide, and in this study the oxidation is considered to proceed via several stages, with the initial reaction ($[A] = [Ni^{III}L']^{3+}$).

$$[Ni^{III}L']^{3+} + Br^- \underset{k_b}{\overset{k_a}{\rightleftharpoons}} [Ni^{III}L'Br]^{2+}$$

At pH ~3, $k_a \approx 1300 \pm 300\ M^{-1}\ s^{-1}$ ($I \approx 0.01$ M). This value may be compared with $k_f = 207\ M^{-1}\ s^{-1}$ for the corresponding reaction of $[Ni^{III}cyclam]^{3+}$ ($I = 1.00$ M). Again the strong oxidizing power of the unsaturated ligand complex forces the production of Br_2, whereas in the present system there is no

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[14] R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, p 183.

[15] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

[16] D. F. C. Morris and S. D. Hammond, *Electrochim. Acta*, **13**, 545 (1968).

[17] G. A. K. Thomson, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **16**, 2880 (1977).

Table III. Observed First-Order Rate Constants, k_{obsd}/s^{-1}, for Reaction of the $[Ni^{III}L(OH_2)_2]^{3+}$ Cation with Halide Ions (X^-) (in 1.0 M Perchloric Acid, at Various Temperatures)

		X = Cl			X = Br		
$T/°C$	$10^3[X^-]/M$	k_{obsd}/s^{-1}	$k_1{}^a/M^{-1}\ s^{-1}$	$k_{-1}{}^b/s^{-1}$	k_{obsd}/s^{-1}	$k_1{}^a/M^{-1}\ s^{-1}$	$k_{-1}{}^b/s^{-1}$
6.6	1.0	1.25			2.66		
	2.0	1.60			2.75	59 ± 10	2.61 ± 0.10
	6.0	2.09	168 ± 5	1.15 ± 0.10	2.94		
	10.0	2.86			3.21		
13.7	1.0	2.52			3.73		
	2.0	2.93			4.08	110 ± 15	3.71 ± 0.20
	6.0	4.00	329 ± 10	2.19 ± 0.15	4.25		
	10.0	5.56			4.85		
19.4	1.0	3.61			4.69		
	2.0	4.47	490 ± 10	3.26 ± 0.10	5.19	160 ± 15	4.66 ± 0.15
	6.0	6.07			5.51		
	10.0	8.22			6.30		
25.0	1.0	5.55			6.30		
	2.0	5.87 ± 0.5[c]	902 ± 7	4.27 ± 0.20	6.30 ± 0.5[c]	207 ± 20	6.07 ± 0.20
	6.0	9.72 ± 0.2[c]			7.28 ± 0.30[c]		
	10.0	13.3 ± 0.4[c]			7.80 ± 0.23[c]		
			$\Delta H^{\ddagger} = 14.2 \pm 0.3$ kcal mol^{-1}			$\Delta H^{\ddagger} = 11.3 \pm 0.6$ kcal mol^{-1}	
			$\Delta S^{\ddagger} = 2.6 \pm 3.0$ cal deg^{-1} mol^{-1}			$\Delta S^{\ddagger} = 0 \pm 5.0$ cal deg^{-1} mol^{-1}	

[a] Values calculated as the slope of a least-squares plot of k_{obsd} vs. $[X^-]$. [b] k_{-1} values are the intercepts of such plots, according to eq 3. [c] Mean of two independent determinations.

Table IV. Observed First-Order and Derived Second-Order Rate Constants for Reaction of Thiocyanate Ion ((3–6) × 10^{-5} M) with Excess $[Ni^{III}L]^{3+}$ Cation (at Various Temperatures; Medium = 1.0 M $HClO_4$)[a]

$T/°C$	$10^4[[Ni^{III}L]^{3+}]/M$	k_{obsd}/s^{-1}	$k_2/M^{-1}\ s^{-1}$
10.0	2.35	0.103	
	4.69	0.204	439 ± 5
	9.38	0.412	
15.5	3.08	0.202 (0.208)[b]	
	6.17	0.408	623 ± 9
	12.3	0.810	
24.9	3.17	0.354	
	6.34	0.78	
	9.51	1.06	1160 ± 20
	12.7	1.48	
	15.9	1.85	
34.2	2.78	0.681	
	5.56	1.32	2370 ± 30
	11.1	2.67	

[a] Activation parameters: $\Delta H^{\ddagger} = 11.4 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -6 \pm 3$ cal deg^{-1} mol^{-1}. [b] $[H^+] = 0.1$ M; ionic strength = 1.0 M ($LiClO_4$).

redox observed. A preliminary study[2] of the reaction of Ni^{II}cyclam with Br_2 is consistent with the formation of $[Ni^{III}cyclamBr]^{2+}$. From the comparison of the rates it appears that substitution of differing nitrogen donor types in the equatorial positions of the coordination sphere of nickel(III) has only a small effect on the rate of substitution of the axial aquo ligands. In this regard, the situation resembles that of nickel(II) complexes where for *trans*-diaquotetraammine complexes the $Ni^{II}OH_2$ exchange rates vary by only an order of magnitude.[18]

Reaction with Thiocyanate. In this system, where the metal ion complex was present in excess, the rate law is of the form

$$\frac{d[[Ni^{III}LNCS]^{2+}]}{dt} = k_2[[Ni^{III}L]^{3+}][NCS^-]$$

No variation in rate with $[H^+]$ was observed (Table IV). The product spectrum is consistent with the formation of the 1:1 complex under these conditions. This has been confirmed by ESR measurents. There is no evidence for any dissociation reaction similar to that observed in the case of Cl^- and Br^-.

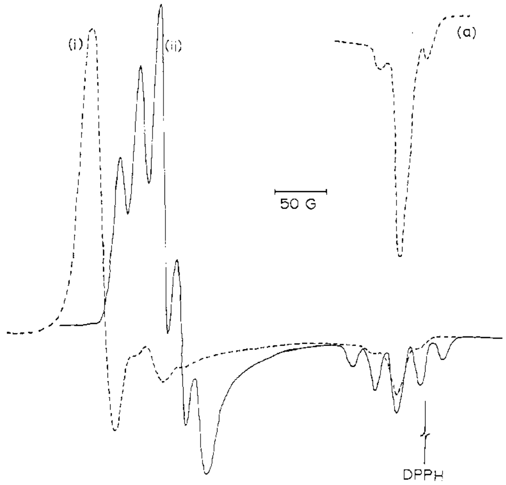

Figure 5. ESR spectra of (i) the $[Ni^{III}L(NCS)(OH_2)]^{2+}$ cation (---) in presence of an excess of $[Ni^{III}L(OH_2)_2]^{3+}$ ((a) amplitude doubled) and (ii) the $[Ni^{III}L(NCS)_2]^+$ cation (—) in frozen 1.0 M perchloric acid at 77 K.

It thus appears that the equilibrium constant for formation of the complex $[Ni^{III}LNCS]^{2+}$ is at least an order of magnitude greater than that for the monochloro species. The absence of any positive intercept in the plot of rate constant against $[Ni^{III}L]$ (eq 3) is consistent with these data. (At 25 °C, a least-squares plot yields an intercept equal to $9 \times 10^{-5} \pm 1 \times 10^{-3}$.) Evidence for nitrogen bonding in the thiocyanate complex has been suggested from several observations. It is known that Ni(III) species will oxidize thiols and thioureas. Also the d–d band maximum in the NCS complex (295 nm) is shifted compared to that of the nickel(III) cyclam aquo ion (λ_{max} 308 nm). In the case of the monochloro and monobromo ions, the corresponding λ_{max} values are identical (306 nm). This observation confirms the view of an NCS^- nitrogen donor atom since when this ligand is S bonded, the thiocyanate ion is close to Cl^- in the spectrochemical series.

In the spectra, the hyperfine interaction of the N-bonded ligand has been observed. As is seen in Figure 5, the appearance of a triplet in the $g_{\parallel}$ signal is attributable to the interaction of the electron in the d_{z^2} orbital with the nitrogen nucleus ($I = 1$). A similar observation has been made by Busch et al.[11] in the oxidation of a pentadentate nickel(II) complex where one of the nitrogen atoms is in the axial site.

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In conditions of excess thiocyanate, the formation of the complex ion $[Ni^{III}L(NCS)_2]^+$ is accompanied by a change in the spectrum where now the expected quintet is observed for two axial nitrogen donor atoms and where there is evidence of the hyperfine splitting in the $g_\perp$ region. It is of interest to note that the corresponding cobalt(III) complex has an identical bonding mode.[19] One observation currently under investigation in this laboratory is that in acetonitrile solutions, the thiocyanate complex undergoes a redox reaction, suggesting that in this solvent the ligand may be sulfur-bonded.

Although only three substitution reactions have been studied in detail, it appears that the rate constants for reaction show a spread of less than an order of magnitude and may reflect an dissociative process. The general mechanism for many tervalent metal complexes (especially aquo ions) is via an I_a process.[8] The possible exception to this is in cobalt(III) systems. This study represents the first investigation of a low-spin d^7 M(III) substitution mechanism. This spin system is more labile than the corresponding low-spin d^6 (e.g., cobalt) and so may require less help from the entering nucleophile. Also since Ni(III) is smaller than Co(III), there will be less tendency to increase the coordination number. For these reasons there may be more I_d behavior for Ni(III) relative to the I_a mechanisms for Cr(III). Supportive evidence for an I_d process comes from a comparison with the I_a reactions of $Cr(H_2O)_6^{3+}$[20] or $Mo(H_2O)_6^{3+}$[9] with NCS^- and Cl^-. Ratios of $k_f(NCS^-)/k_f(Cl^-)$ in these systems are 62 and 59, respectively, compared with a value of 1.5 for the nickel(III) cyclam complex. This may also be the case for the reactions of complexes A and B although data for these systems are extremely limited.

Although all our ESR evidence to date is consistent with octahedral mono(aquo ligand)nickel(III) complex ions, an interesting observation worthy of further investigation is that, in dimethyl sulfoxide, although the dihalo cations have local D_{4h} symmetry, there is a change to lower symmetry in the monochloro species.[13]

Reaction with Iodide. Over the range of concentrations of (excess) iodide studied, the rate law is of the form $R = k_2[[Ni^{III}L]^{3+}][I^-]$. The reaction was monitored in an excess of the $[Ni^{III}L]^{3+}$ cation in several cases, yielding identical rate data. In this system, however, the very significant band at 308 nm associated with the nickel(III) state diminished as the reaction proceeded. The redox reaction was also confirmed by monitoring the formation of I_3^-. Rate data are presented in Table V where it is seen that rate constants ($k_2' = 3020$ $M^{-1}\ s^{-1}$ at 26 °C) are greater than for the other ions studied. No rate variation was observed over the range $[H^+] = 0.2–1.0$ M, indicating that no protonation of the nickel(III) cyclam complex occurs.

Three mechanisms may be proposed which are consistent with the rate data. If complex formation precedes an intramolecular electron transfer, a scheme may be written as

$$[Ni^{III}L]^{3+} + I^- \underset{}{\overset{K_1}{\rightleftharpoons}} [Ni^{III}L\cdot I]^{2+} \xrightarrow[\text{redox}]{k} [Ni^{II}L]^{2+} + I\cdot$$

$$I\cdot + I\cdot \xrightarrow{\text{fast}} I_2 \xrightarrow[I^-]{\text{fast}} I_3^-$$

Table V. Observed First-Order Rate Constants and Derived Second-Order Coefficients for the Redox Reaction of Iodide Ion with the $[Ni^{III}L(OH_2)_2]^{3+}$ Cation (at Various Temperatures; Ionic Strength = 1.0 M (Lithium Perchlorate/Perchloric Acid))[a]

T, °C	$10^3[I^-]/M$	k_{obsd}/s^{-1}	$10^{-3}k_2'/M^{-1}\ s^{-1}$
10.2	1.0	0.98	
	2.5	3.02	1.18 ± 0.08
	5.0	5.39	
	10.0	11.6	
15.1	1.0	1.82	
	2.5	3.79	1.63 ± 0.09
	5.0	7.80	
	10.0	16.4	
22.4	1.0	2.60	
	2.5	5.22	
	5.0	11.3	2.37 ± 0.17
	10.0	25.3	
26.0	2.5	7.70	3.02 ± 0.9
	5.0	14.4	
	10.0	31.0	
30.5	1.0	4.11	
	5.0	19.3	3.92 ± 0.13
	10.0	38	

[a] Activation parameters: $\Delta H^\ddagger = 9.45 \pm 0.3$ kcal mol^{-1}; $\Delta S^\ddagger = -11.0 \pm 2$ cal $deg^{-1}\ mol^{-1}$.

(a) The data may be interpreted in terms of the rate-determining formation of an iodo complex as envisaged for the other halide ion reactions, followed by a very rapid reaction as a second step. For a dissociative process of the type described above, the rate would be expected to be lower than that observed. (b) A second mechanism involves the rate-determining molecular redox reaction of the iodo complex. From trends in the equilibrium constants of the chloro and bromo complexes an upper limit of $K_1 \approx 10–15\ M^{-1}$ may be postulated for the iodo complex. If the preequilibrium complexation was of this order of magnitude with a rate-determining redox step, some curvature might be expected in the plots of k_{obsd} against $[I^-]$, especially at higher concentrations. There was no evidence for such deviations from linearity. For a complex with $K_1 < 1$, however, a first-order dependence on I^- would be observed. (c) A third, possibly more likely proposal, especially if steric effects are significant, is that of an outer-sphere reaction. In this regard, the system resembles that of the corresponding cobalt(III) aquo ion reactions[21] where the oxidations of Br^- and NCS^- are considered to proceed via a substitution-controlled process, whereas the reaction with I^- is thought to be outer sphere.

Further work, currently in progress on the oxidations of quinols which appear to be outer sphere and of the reactions of the *trans*-dihalo complexes (as inner-sphere oxidants) with metal ions, should help, at least in part, to resolve some of these problems.

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Registry No. $[Ni^{III}L(OH_2)_2]^{3+}$, 72360-42-0; $[Ni^{II}L(OH_2)_2]^{2+}$, 64616-26-8; $[Ni^{III}L(Cl)_2]ClO_4$, 60105-35-3; $[Ni^{III}L(Br)_2]ClO_4$, 60105-37-5; $[Ni^{III}L(NCS)(OH_2)]^{2+}$, 72360-43-1; $[Ni^{III}L(NCS)_2]^+$, 72360-44-2; $[Ni^{III}L(MeCN)_2]^{3+}$, 47099-85-4; $[Ni^{III}L(NO_3)_2]^+$, 72360-45-3; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; SCN^-, 302-04-5.

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