perimentally correspond to such displacements, the calculations of the coupling constants V and V_2 were carried out for displacements in the Q_θ component. The metal–ligand matrix elements specifying the relative effects of the various ligands in a complex distorted along both components of the ϵ_g mode are given in ref 44.

In the procedure given in ref 20 it is assumed that the σ-antibonding energy of a d-orbital Δ' varies inversely as the nth power of the bond distance. For a displacement Q along the Q_θ component of the ϵ_g mode (Figure 1b) at angle $\phi = 0°$ (a tetragonal elongation) the energies of the $d_{x^2-y^2}$ and d_{z^2} orbitals are given by

$$E(d_{z^2}) = \frac{2}{3}\Delta'\left(1 + \frac{2CQ}{r_0}\right)^{-n} + \frac{1}{3}\Delta'\left(1 - \frac{CQ}{r_0}\right)^{-n} \qquad \text{(A1a)}$$

$$E(d_{x^2-y^2}) = \Delta'\left(1 - \frac{CQ}{r_0}\right)^{-n} \qquad \text{(A1b)}$$

where $C = 1/12^{1/2}$ is the appropriate normalization constant (see eq 1a of text). Expanding to second order gives

$$E(d_{z^2}) = \Delta'\left(1 - \frac{nCQ}{r_0} + \frac{3n(n+1)C^2Q^2}{2r_0^2}\right) \qquad \text{(A2a)}$$

$$E(d_{x^2-y^2}) = \Delta'\left(1 + \frac{nCQ}{r_0} + \frac{n(n+1)C^2Q^2}{2r_0^2}\right) \qquad \text{(A2b)}$$

The terms relevant to the Jahn–Teller distortion of the complex are those that discriminate in energy between $d_{x^2-y^2}$ and d_{z^2}; the term in Q^2 affecting the baricenter of d_{z^2} and $d_{x^2-y^2}$ is effectively included in the force constant, since for the copper(II) complex this is estimated as the average of the corresponding nickel(II) and zinc(II) complexes. If the difference in the number of electrons between the two orbitals is m, the electronic contribution to the potential is

$$m[E(d_{z^2}) - E(d_{x^2-y^2})]/2 = \frac{-nm\Delta'Q}{12^{1/2}r_0} + \frac{m\Delta'n(n+1)Q^2}{24r_0^2} \qquad \text{(A3)}$$

A reversal in the electronic occupancy of the two orbitals simply reverses the sign of both contributions, and since it is conventional to define the first- and second-order electronic contributions V and V_2 in absolute terms, this yields the relationships

$$V = \frac{nm\Delta'}{12^{1/2}r_0} \qquad V_2 = \frac{m\Delta'n(n+1)}{24r_0^2}$$

Registry No. $Cu(H_2O)_6^{2+}$, 14946-74-8; $Cu(C_5H_5NO)_6^{2+}$, 47839-68-9; $Cu(NO_2)_6^{4-}$, 28111-94-6; $Cu(tach)_2^{2+}$, 46934-10-5; $Ni(diamine)_3^{2+}$, 15276-13-8; $Cr(NH_3)_6^{3+}$, 14695-96-6; PtF_6^{2-}, 16871-53-7.

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Kinetics and Mechanism of Chloride and Bromide Substitution of Diaquonickel(III) Macrocyclic Complexes

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The complex cations $[NiM_m(OH_2)_2]^{3+}$ (M_m = [α]-*C-meso*-5,12-dimethylcyclam), $[NiM_r(OH_2)_2]^{3+}$ (M_r = *C-rac*-5,12-dimethylcyclam), and $[NiE_m(OH_2)_2]^{3+}$ (E_m = *C-meso*-5,12-diethylcyclam) (cyclam = 1,4,8,11-tetraazacyclotetradecane) react with Cl^- and Br^- in aqueous perchloric acid according to the equation $NiL(OH_2)_2^{3+} + X^- \rightleftharpoons NiLX(OH_2)^{2+}$ ($K = k_1/k_{-1}$). Stopped-flow studies provide details of forward and reverse rate constants: at 25 °C k_1 for the reaction of $[NiM_m]^{3+}$ with Cl^- is 2180 ± 66 $M^{-1}\ s^{-1}$ and for that with Br^- is 889 ± 31 $M^{-1}\ s^{-1}$; at 25 °C k_1 for the reaction of $[NiE_m]^{3+}$ with Cl^- is (3.1 ± 0.4) × $10^3\ M^{-1}\ s^{-1}$ and with Br^- is (2.8 ± 0.2) × $10^3\ M^{-1}\ s^{-1}$; at 13.4 °C, k_1 for the reaction of $[NiM_r]^{3+}$ with Cl^- is (1.4 ± 0.2) × $10^4\ M^{-1}\ s^{-1}$. The data are consistent with a dissociative mechanism, the effect of axial steric groups in the M_r ligand causing an increase in the rate. A second ligand and metal ion independent reaction has also been identified, which is postulated as a reorganization of the octahedral ions to more stable pentacoordinate complexes. ESR evidence is presented consistent with a more distorted geometry for the monochloro complex ions.

Although there has been considerable recent interest in the redox reactions of nickel(III) complexes,[1-4] there is still a dearth of information on the substitution reactions at these centers.[5-7] Such studies are of interest, in that, whereas cobalt(III) complexes appear to react via dissociative-interchange[8,9] mechanisms, many other trivalent metal ions show some associative character on

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ligand replacement.[10] However, this may be a function of cation size. As steric crowding becomes a factor, dissociative behavior is anticipated. Ni(III) species contain a metal center formally at least as small as cobalt(III) ions, and further investigation of mechanisms is warranted.

Complexed nickel(III) ions have been shown to be stabilized as octahedral, or tetragonally distorted octahedral, low-spin d^7 species.[3,11,12] In tetraazamacrocyclic complexes, $NiN_4L_2^{n+}$, the axial positions are taken up by solvent molecules in the absence of other ligating species. Axial coordination by halides,[5,13] sulfate,[2,13,14] and phthalate[13] has been shown to give kinetically stable nickel(III) centers. Values of the forward and reverse rates of (1) were derived with use of pulse radiolysis methods[15] (L = *trans*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (*trans*-Me$_6$diene), X^- = Br^-), where k_1 = (1.3 ± 0.3) × 10^3 M^{-1} s^{-1} and k_{-1} = 120 s^{-1}.

$$[NiL(H_2O)_2]^{3+} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [NiL(H_2O)X]^{2-} + H_2O \quad (1)$$

A study of the ligand substitution process in $[Ni(cyclam)(H_2O)_2]^{3+}$ has been published,[5] where X^- in eq 1 is Cl^-, Br^-, and SCN^-. The small variation of the rate constants with the anions studied suggests that the mechanism is an interchange process, but there are insufficient data to identify the activation process.

Margerum[6] has recently published a study of axial coordination of monomeric ligands with Ni(III) peptide complexes. In this case, the Ni(III) complexes carry an overall charge of 0 or 1−, and complexation was not observed with the negatively charged halide ions. Coordination and stabilization by N-containing ligands such as NH_3, pyridine, and imidazole was observed. The rates of complexation, however, were too fast to be observed by stopped-flow methods.

In the present investigation, three nickel(III) macrocyclic complexes were reacted with Cl^- and Br^- ions and the rates of substitution measured. Differences in rates observed between the various complexes are attributed to steric effects in the macrocycles, and the mechanism of substitution is discussed.

Experimental Details

The nickel(II) complexes $[NiM_m](ClO_4)_2$ (M_m = [α]-*C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), $[NiM_r](ClO_4)_2$ (M_r = *C-rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), and $[NiE_m](ClO_4)_2$ (E_m = *C-meso*-5,12-diethyl-1,4,8,11-tetraazacyclotetradecane) were prepared as described previously.[16]

Solutions of the diaquonickel(III) complexes were prepared by electrochemical oxidation of the nickel(II) complex in acetonitrile, by removal of the solvent and dissolution of the solid Ni(III) complex in an aqueous acidic solution, or by chemical oxidation, a stoichiometric deficiency of hexaaquocobalt(III) being added to an aqueous acidic solution of the Ni(II) complex.

The kinetic experiments were performed over the temperature range 8–25 °C in aqueous 1.0 M perchloric acid. The stopped-flow apparatus has been described previously.[17] Pseudo-first-order conditions of excess halide ion were employed, and the reactions were monitored at 390–405 nm (Cl^- reactions) or 420–430 nm (Br^- reactions), where contributions from a second step were minimal. Absorbance data were collected and processed by an IBM PC microcomputer interfaced to the spectrophotometer via a Techmar Inc. PC-Mate Lab Master Module. Plots of ln $(A_\infty - A_t)$ against time were linear for greater than 3 half-lives.

Results

The kinetics of the reactions of $[NiM_m(H_2O)_2]^{3+}$, $[NiM_r(H_2O)_2]^{3+}$, and $[NiE_m(H_2O)_2]^{3+}$ with Cl^- and Br^- ions were studied by a stopped-flow method. UV-visible spectroscopic and ESR studies showed that there was no evidence of any dihalide species being formed under these conditions. The high acid concentration was necessary to inhibit reduction of the Ni(III) reactants by water; no change in rate was observed when the acid concentration was decreased at constant ionic strength. The observed first-order rate constants, k_{obsd}, were found to vary linearly with anion concentration. Rate data are presented in Table I, and plots of k_{obsd} vs. halide concentration were found to be linear. Figure 1 shows a plot of k_{obsd} vs. $[Cl^-]$ for each of the three complexes studied. In the case of $[NiM_r(H_2O)_2]^{3+}$, the rate of Cl^- substitution was too fast for measurement at 25 °C and data measured at lower temperatures were extrapolated to estimate a value at this temperature. The rate of Br^- substitution of $[NiM_r(H_2O)_2]^{3+}$ was very fast, and precise determination of the rate was not possible.

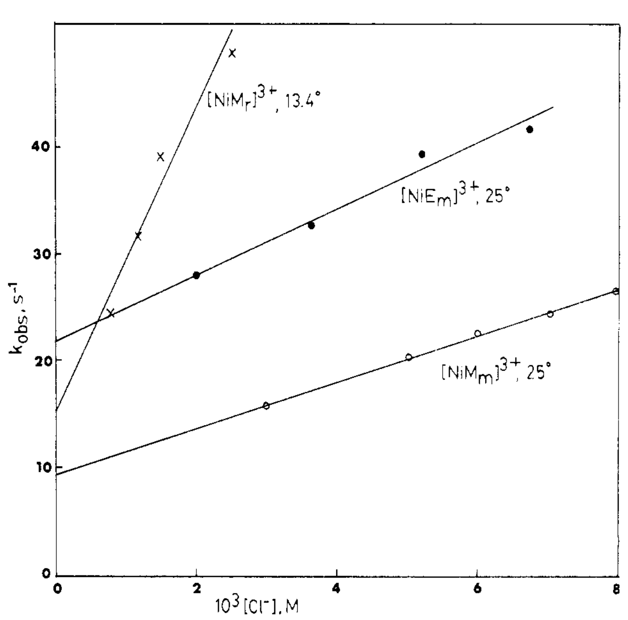

Figure 1. Graphs of observed rate constant for chloride substitution vs. chloride concentration.

The absorbance changes in the complexation reactions were also fairly small, particularly in the case of the bromide reactions. Furthermore, the diaquonickel(III) macrocyclic complexes were slowly reduced by water, especially at higher temperatures, which reduced the amount of absorbance change on some repeat runs. However, this did not affect the observed rate constant, since pseudo-first-order conditions of excess halide concentration were used.

The rate data are consistent with eq 2, for which the rate law can be derived.[8] Thus the intercepts of the lines in Figure 1

$$-d[Ni^{III}L]/dt = k_{obsd}[Ni^{III}L] = (k_1[X^-] + k_{-1})[Ni^{III}L] \quad (2)$$

correspond to k_{-1}, and the slopes correspond to k_1. Table II summarizes the values of k_1 and k_{-1} found for each complex at 25 °C, as well as the reported values of these parameters for other Ni(III) complexes.

For the $[NiM_m(H_2O)_2]^{3+}$ complex, equilibrium constants derived kinetically showed good agreement with those derived spectrophotometrically. Absorbance changes in the UV-visible spectra were monitored over the wavelength range 250–450 nm at 25 °C as a function of halide ion. The value of the equilibrium constant *K* was derived with use of eq 3, where ΔAbs is the

$$[Ni^{III}L][X^-]/\Delta Abs = [X^-]/(\Delta\epsilon)l + 1/K(\Delta\epsilon)l \quad (3)$$

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. For the reaction of $[NiM_m(H_2O)_2]^{3+}$ with Cl^-, the value of 217 ± 53 M^{-1} derived from this plot agrees well with 233 ± 17 M^{-1} derived kinetically.

In all of the reactions studied, after the initial fast reaction, a second, slower reaction was observed. The rate was first order

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Table I. Observed Rate Constants for Halide Substitution of Ni(III) Macrocyclic Complexes (I = 1.0 M, [Ni(III)] ≈ 5 × 10^{-5} M)

$[NiM_m]^{3+} + Cl^-, Br^-$

$[NiM_m]^{3+} + Cl^-$					$[NiM_m]^{3+} + Br^-$				
T, °C	$10^3[Cl^-]$, M	k_{obsd}, s^{-1}	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	T, °C	$10^3[Br^-]$, M	k_{obsd}, s^{-1}	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}
25.0	3.00	15.7	2180 ± 66	9.35 ± 0.40	25.1	2.00	23.7	889 ± 31	21.8 ± 0.3
	5.00	20.6				4.00	24.9		
	6.00	22.5				6.00	27.3		
	7.00	24.5				10.0	30.8		
	8.00	26.7				15.0	35.0		
20.0	3.00	7.92	1483 ± 71	3.42 ± 0.39	20.2	2.0	14.8	689 ± 34	13.2 ± 0.3
	5.00	10.9				6.00	17.3		
	6.00	12.1				10.0	19.8		
	7.00	14.0				15.0	23.8		
15.0	3.00	4.76	852 ± 31	2.28 ± 0.19	15.0	2.00	6.90	520 ± 16	5.8 ± 0.1
	5.00	6.62				4.00	7.80		
	6.00	7.38				6.00	8.98		
	7.00	8.36				10.0	10.75		
	8.00	8.96				15.0	13.71		
10.0	3.00	3.61	441 ± 11	2.28 ± 0.07	10.0	2.00	4.83	323 ± 12	4.1 ± 0.1
	5.00	4.50				4.00	5.23		
	6.00	4.86				6.00	6.06		
	7.00	5.37				10.0	7.20		
	8.00	5.83				15.0	8.98		
8.5	3.00	3.06	345 ± 56	1.90 ± 0.34					
	5.00	3.51							
	6.00	3.91							
	7.00	4.09							
	8.00	4.90							

$[NiE_m]^{3+} + Cl^-, Br^-$

$[NiE_m]^{3+} + Cl^-$					$[NiE_m]^{3+} + Br^-$				
T, °C	$10^3[Cl^-]$, M	k_{obsd}, s^{-1}	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	T, °C	$10^3[Br^-]$, M	k_{obsd}, s^{-1}	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}
25.0	2.00	27.9	(3.1 ± 0.4) × 10^3	22 ± 2	25.1	2.33	32.2	(2.8 ± 0.2) × 10^3	26 ± 1
	3.64	32.8				4.66	38.7		
	5.20	39.5				6.98	43.6		
	6.76	41.8				9.31	51.9		
20.0	2.0	15.7	(2.3 ± 0.2) × 10^3	10.5 ± 0.9	20.0	2.33	17.4	(1.6 ± 0.1) × 10^3	13.3 ± 0.5
	3.64	18.3				4.66	20.0		
	5.20	22.5				6.98	23.9		
	6.76	26.7				9.31	27.5		
						11.64	31.7		
15.0	2.00	9.6	(1.22 ± 0.06) × 10^3	7.4 ± 0.4	15.0	2.00	11.0	690 ± 16	9.5 ± 0.1
	3.64	11.9				4.58	12.6		
	5.20	14.2				6.86	14.2		
	6.96	16.0				9.15	16.0		
	8.56	17.6				11.44	17.4		
11.0	1.61	6.68	912 ± 86	4.8 ± 0.5	11.0	2.29	8.56	428 ± 24	7.5 ± 0.2
	3.75	8.0				4.58	9.20		
	5.35	9.32				6.86	10.5		
	6.96	10.9				9.15	11.5		
	8.56	13.1				11.44	12.3		

$[NiM_r]^{3+} + Cl^-$

	k_{obsd}, s^{-1}		
$10^3[Cl^-]$, M	13.4 °C	10.6 °C	7.8 °C
0.80	24.5	18.1	13.5
1.20	31.9	22.1	16.4
1.50	39.1	25.4	18.4
2.50	49.0	34.3	26.4
3.50			31.3
$10^{-3}k_1$, M^{-1} s^{-1}	14 ± 2	9.4 ± 0.2	7.8 ± 0.3
k_{-1}, s^{-1}	15 ± 3	10.8 ± 0.4	7.1 ± 0.6

and was independent of halide concentration. The reaction was also monitored when a run was carried out under conditions of 10 times excess Ni(III), and the rate was found to be independent of Ni(III) concentration. Figure 2 shows plots of the voltage trace at 500 nm during the reaction of $[NiM_r(H_2O)_2]^{3+}$ with Br^-, under conditions of excess bromide (Figure 2a) and excess Ni(III) (Figure 2b). It can be seen that the slow steps are virtually identical under both sets of conditions. The extent of absorbance change of this step varied relative to that of the first step, depending on the monitoring wavelength used and the complex being studied. The slow step was not reported in the halide complexations[5] of $[Ni(cyclam)(H_2O)_2]^{3+}$, but on reexamination of these reactions at several wavelengths, a second step was also seen, with a very small absorbance change compared to that of the first step.

In Table III are listed the observed first-order rate constants for this secondary process in several systems and under various conditions. It can be seen that the rate constants are very similar for all the complexes in the investigation.

A point-by-point wavelength study of the absorbance changes in each complexation reaction was made, enabling compilation of the spectra of both the intermediate and final species. Shown in Figure 3 are the spectra for the species formed in the chloride

Table II. Observed Values of k_1 and k_{-1} for Reactions of Nickel(III) Macrocycles ($[Ni^{III}L]^{3+}$) at 25 °C

L	$10^{-3}k_1$, M^{-1} s^{-1}	$\Delta H_1^{\ddagger}$, kcal mol^{-1}	$\Delta S_1^{\ddagger}$, cal mol^{-1} deg^{-1}	k_{-1}, s^{-1}	K, M^{-1}	ref
1. Chloride Substitution						
M_m	2.18 ± 0.07	18 ± 1	18 ± 4	9.4 ± 0.4	233 ± 17	this work
E_m	3.06 ± 0.37	15 ± 2	7 ± 6	22 ± 2	139 ± 30	this work
M_r	42 ± 13	16 ± 4	17 ± 13	66 ± 8	640 ± 280	this work
cyclam	0.9 ± 0.01	14.2 ± 0.3	−3 ± 3	4.3 ± 0.2	210 ± 11	5
CRH	0.42 ± 0.09			6.4 ± 0.1	66 ± 20	*a*
2. Bromide Substitution						
M_m	0.89 ± 0.03	10 ± 1	−10 ± 4	21.8 ± 0.3	41 ± 2	this work
E_m •	2.8 ± 0.2	22 ± 3	32 ± 4	25.6 ± 1.2	106 ± 11	this work
M_r	≥10			≥100		this work
cyclam	0.21 ± 0.2	11 ± 1	−12 ± 3	6.1 ± 0.2	34 ± 4	5
trans-Me_6diene	1.3 ± 0.3			120	11 ± 2	15

[a] Fairbank, M. G.; MacDonald, C. J., preliminary data (8.7 °C).

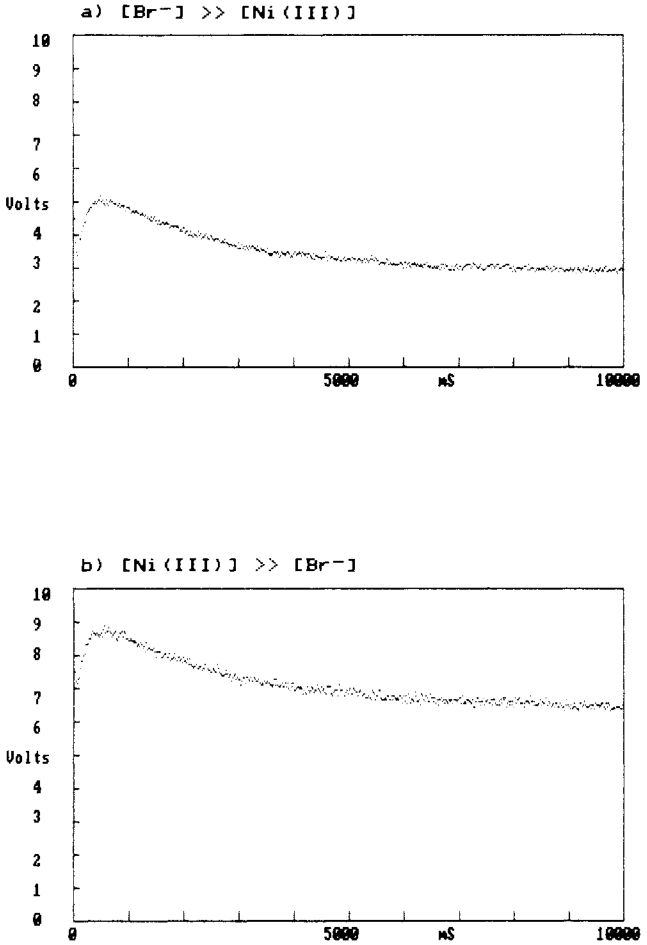

Figure 2. Stopped-flow voltage traces during the reaction of $[NiM_r(H_2O)_2]^{3+}$ with Br^- (λ = 500 nm, I = 1.0 M): (a) [Ni(III)] ≈ 5×10^{-5} M, [Br^-] = 5×10^{-4} M; (b) [Ni(III)] = 5×10^{-4} M, [Br^-] = 5×10^{-5} M.

Table III. Observed Rates of Rearrangement of Monohalo Complexes

Ni(III) complex	T, °C	k_2, s^{-1} [a]
$[Ni(cyclam)(H_2O)Cl]^{2+}$	10.9	0.39 ± 0.03
	15.0	0.41 ± 0.02
	25.1	0.37 ± 0.04
$[NiM_m(H_2O)Cl]^{2+}$	12.2	0.35 ± 0.03[b]
$[NiM_r(H_2O)Cl]^{2+}$	11.5	0.41 ± 0.03
$[NiM_r(H_2O)Br]^{2+}$	8.0	0.43 ± 0.02[b]
	10.0	0.48 ± 0.05
$[NiE_m(H_2O)Cl]^{2+}$	11.0	0.27 ± 0.09

[a] All measurement observed under conditions of excess halide concentration except where noted. [b] Using excess Ni(III) concentration.

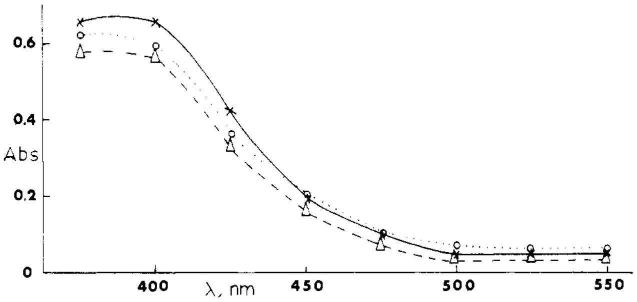

Figure 3. Initial (×) intermediate (△), and final (○) spectra during the chloride substitution of $[NiE_m(H_2O)_2]^{3+}$.

substitution reaction of $[NiE_m(H_2O)_2]^{3+}$. Similar spectra were obtained for the other reactions under study.

Discussion

Replacement of a solvent molecule by halide in an interchange mechanism is generally considered[5,8,9] to proceed via formation of an outer-sphere complex, followed by the replacement step (eq 4). The value of K_{os} for a complex of this charge type can be

$$[NiL(H_2O)_2]^{3+} + X^- \overset{K_{os}}{\rightleftharpoons} [NiL(H_2O)_2,X]^{2+} \xrightarrow{k} [NiL(H_2O)X]^{2+} + H_2O \quad (4)$$

calculated from the Eigen–Fuoss equation.[18] At 1.0 M ionic strength, the value of K_{os} is calculated[5] as 1.7–1.8 M^{-1}. Among the complexes studied here, the radius of the Ni(III) species should not change significantly, so the value of K_{os} may be considered constant. Thus, the derived k_1 and k_{-1} values for each complex can be compared directly.

As can be seen from Table II, the rates of both the forward and reverse substitution processes on Ni(III) macrocyclic complexes increase in the order cyclam < M_m < E_m << M_r. It has been shown[16] that all four of these complexes have identical chair conformations in the macrocyclic ring, the only differences being the presence at the asymmetric centers of two equatorial methyl groups in the M_m complex, two equatorial ethyl groups in the E_m complex, and one equatorial and one axial methyl group in the M_r complex.

It has also been shown[16] that there is little or no steric effect of equatorial methyl or ethyl groups on the redox chemistry of these species. The present results indicate a slight increase in the rate of substitution when equatorial groups are introduced into the macrocyclic ring. This is in agreement with studies on N-substituted Ni(II) macrocyclic complexes, where it was found that the $[Ni(N\text{-}Me_4cyclam)(H_2O)_2]^{2+}$ complex with the same ring conformation as the above complexes has a water exchange rate 8 times higher[19] than that of the cyclam complex.[20]

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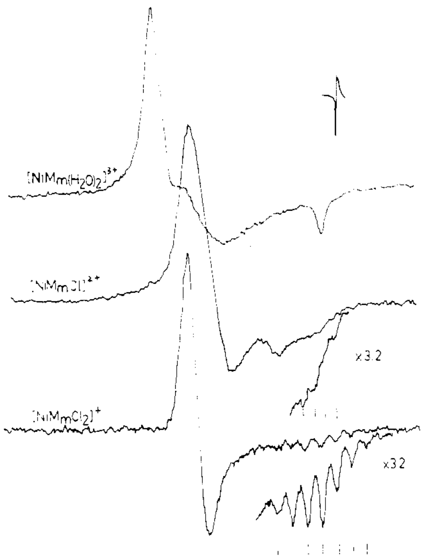
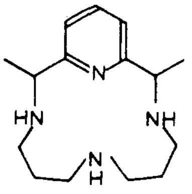


Figure 4. ESR spectra of $[NiM_m]^{3+}$ complexes.

When the rates of substitution of the M_m and M_r complexes are compared, it is evident that, as in the redox chemistry of these complexes, the change in orientation of the methyl group on the macrocyclic ring from equatorial to axial has a large effect, with an increase in the substitution rate of more than 1 order of magnitude.

Comparison of the present data with those for the reaction of $[NiCRH(H_2O)_2]^{3+}$ with Cl^- and of $[Ni(\textit{trans}\text{-}Me_6diene)(H_2O)_2]^{3+}$ with Br^- (see Table II) is more difficult. Both these complexes differ from the first four in ring configuration: the CRH macrocycle has different numbers of methylene carbons between the nitrogens (see diagram), while the latter ring contains an imine group and six methyl groups. Without further data from other similar Ni(III) complexes, the exact effect of these structural changes is unclear.



CRH

Equilibrium constants were calculated from the kinetic data (k_1/k_{-1}) and are listed in Table II. The errors quoted are the standard deviations at 25 °C, although actual errors may be greater than this, judging from the scatter in K values at different temperatures. However, it is probable that for the cyclam, M_m, and E_m complexes K differs little whereas for the M_r species the constant with Cl^- is significantly greater.

Mechanism of Complex Formation. It can be seen from the data in Table II that, when the forward and reverse rates of chloride substitution are compared to those of bromide substitution, the difference is never more than about 5-fold. This is typical of an I_d mechanism, which shows little sensitivity to the nature of the leaving or entering groups.

Of significant interest is the substantial rate increase on going from the unsubstituted and equatorially substituted cyclam rings to the axially substituted M_r complex. This observation can be used to discuss the activation process in the reactions. Work by Chau and Poon[21] showed that, in the rate of aquation of $[CoLCl_2]^+$, where L is tet-a and tet-b (*C-meso-* and *C-rac-*5,5,7,12,12,14-hexamethylcyclam), the two axial positions of the tet-b complex, where the ligand is in a boat form, are kinetically inequivalent (k_a and k_b) and the rates are in the order k_a(tet-b) > k_a(tet-a) > k_b(tet-b). In Co(III), the activation process is known to be dissociative, and thus the faster rate in tet-b refers to the sterically crowded side of the complex. If the mechanism were associative in nature, the faster of the two rates would be at the less sterically hindered side of the complex.

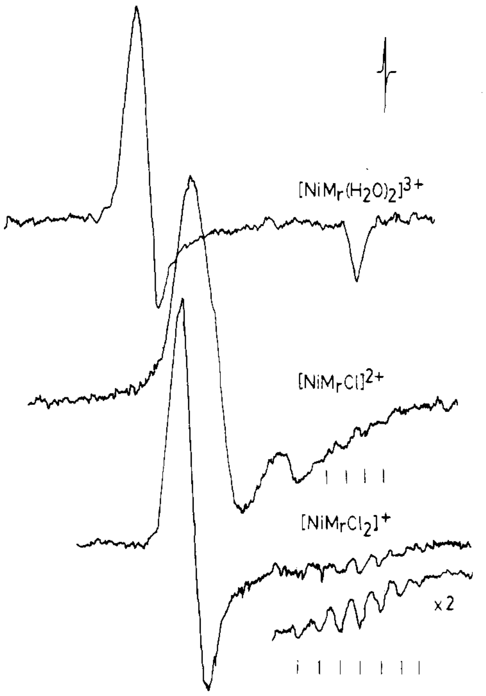


Figure 5. ESR spectra of $[NiM_r]^{3+}$ complexes.

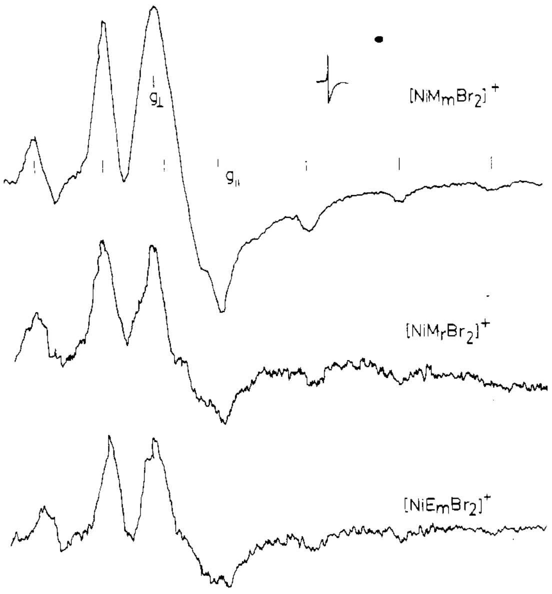


Figure 6. ESR spectra of $[NiLBr_2]^+$ complexes.

A similar activation process may be postulated in the reactions under consideration. One side of the M_r complex is sterically identical with both sides of the M_m complex (with an equatorial methyl group). The significantly faster rate of formation must be due to reaction on the other, more sterically crowded side. This implies dissociative character in the substitution mechanism, since such crowding would favor dissociation in the axial direction.

Electron Spin Resonance Studies. Nickel(III) is ESR-active owing to the one unpaired electron in the low-spin d^7 system. Spectra at 77 K of several of the Ni(III) chloro and bromo adducts are shown in Figures 4–6. The $[NiL(H_2O)_2]^{3+}$ and $[NiLX_2]^+$ complexes are consistent with tetragonally distorted octahedra (D_{4h} symmetry). Hyperfine splitting of the $g_\parallel$ signal is observed when Cl^- or Br^- ions are present. In Table IV are listed the values

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Table IV. *g* Values and Hyperfine Coupling Constants for Ni(III) Macrocyclic Complexes

	L^a		
type of complex	M_m	M_r	E_m
$[NiL(H_2O)_2]^{2+}$	2.197, 2.013	2.226, 2.022	2.220, 2.028
$[NiLCl]^{2+}$	2.142, 2.077, 2.011 (18)	2.136, 2.072, 2.013 (25)	
$[NiLCl_2]^+$	2.164, 2.012 (28)	2.161, 2.007 (28)	2.160, 2.012 (28)
$[NiLBr_2]^+$	2.141, 2.066 (115)	2.166, 2.063 (115)	2.170, 2.066 (117)

[a] $g_\perp$, $g_\parallel$ or g_x, g_y, g_z in the case of $[NiLCl]^{2+}$ (*A*, given in parentheses, in gauss).

of *g* and *A*, the hyperfine coupling constants. It may be seen that, for the dibromo species, the coupling constants are about 4 times as large as for the chloro ions, possibly due to the increased covalency of the Ni–Br bond. The Jahn–Teller distortion of the dichloro species has been confirmed in a crystal structure of $[Ni(cyclam)Cl_2]ClO_4$,[22] where the Ni–N bond distances are 1.97 Å compared to the average Ni–Cl distance of 2.45 Å.

In the ESR spectra of the monochloro complexes (Figures 4 and 5), the symmetry is less than D_{4h}, and separate signals are observed for g_x, g_y, and g_z. The g_z signal is in approximately the same position as $g_\parallel$ in the dichloro complexes, while the g_x and g_y signals have lower *g* values than the $g_\perp$ values. The signals are fairly broad, and only very weak hyperfine splitting of the g_z signal is observed. This is most likely due to the presence of some diaquo complex in the sample, since these two species are in equilibrium (eq 1). Attempts to observe the ESR spectrum of the monobromo complex were unsuccessful. This is presumably due to the lower value of *K* for the monobromo complex relative to that for the monochloro complex (see Table II), leading to a larger amount of diaquo complex in the sample.

Second Step of the Overall Reaction Scheme. The presence of a second step in these substitution reactions must be the result of a rearrangement in the complex. The rate is a unimolecular process, independent of both halide and Ni(III) concentrations, and shows the same absorbance change under conditions of excess $[NiL^{3+}]$ or excess $[X^-]$. Furthermore, the first-order rate constants appear to be very similar for all the complexes studied (0.3–0.6 s^{-1}) (Table III).

As noted, the ESR spectra of the monohalide complexes suggest a symmetry that is less than D_{4h}. This could result from the formation six-coordinate $NiL(OH_2)Cl^{2+}$ or from a rearrangement[23] of the complex after the addition of halide. The changes in absorbance in the rearrangement step between 375 and 425 nm seem in general to be larger for the monobromo complexes than for the monochloro complexes, which suggests that there is greater reorganization with the larger Br^- incoming ligand. It has been suggested[23] that these complexes are five-coordinate. Therefore, the rearrangement observed in the kinetic traces could be the removal of the water molecule from the complex ion to form a five-coordinate species:

$$[NiL(H_2O)X]^{2+} \xrightarrow{k_2} [NiLX]^{2+} + H_2O \qquad (5)$$

A similar small absorbance change was also observed in the oxidation of the Ni(II) complex of 1,4,7,10,13-pentaazacyclohexadecane[24] to Ni(III). The Ni(III) complex is believed to be a five-coordinate species, while the Ni(II) complex[25] is a distorted-octahedral complex with H_2O in the sixth position. An absorbance change observed subsequent to oxidation, again exhibiting first-order kinetics, is consistent with the rearrangement involving the removal of the water molecule to produce a more stable five-coordinate complex.

Five-coordinate Ni(III) species have also been proposed[14,15] for $NiLOH^{2+}$ complexes, where L = tet-a, tet-b, and trans-Me_6diene. The separate g_x and g_y signals in the ESR spectra of the monochloro complexes suggests that the symmetry is neither trigonal bipyramidal nor square pyramidal, as might be expected for a species where one of the five metal–ligand bonds is substantially different from the others.

The similarity of the spectra for $[NiM_mCl]^{2+}$ and $[NiM_rCl]^{2+}$ suggests that there is little difference in the geometries of these complexes, in spite of the presence of the axial methyl group in the latter complex. This is consistent with the formation of a five-coordinate species, which relieves steric strain in these systems.

Conclusions

It has been shown that substitution of diaquonickel(III) macrocyclic complexes by chloride and bromide ions to form $[NiL(H_2O)X]^{2+}$ is a reversible process. The rate is substantially increased when there is steric crowding of the axial site by an axial methyl group on the ligand. This has been interpreted in terms of an I_d mechanism for the substitution process. Such a mechanism is reasonable in light of the small diameter of the Ni^{3+} ion, which would hinder any associative activation process.

A rearrangement step is observed subsequent to the formation of the monohalide complex, believed to be the removal of an axial H_2O molecule to form a five-coordinate $[NiLX]^{2+}$ species. This is supported by kinetic, spectroscopic, and ESR evidence.

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Registry No. $[NiM_m(OH_2)_2]^{3+}$, 100761-77-1; $[NiM_r(OH_2)_2]^{3+}$, 100761-78-2; $[NiE_m(OH_2)_2]^{3+}$, 100681-56-9; $[NiM_m(OH_2)_2]^{2+}$, 96866-29-4; $[NiM_r(OH_2)_2]^{2+}$, 96947-15-8; $[NiE_m(OH_2)_2]^{2+}$, 96866-30-7; $[NiM_mCl]^{2+}$, 100681-57-0; $[NiM_rCl]^{2+}$, 100761-79-3; $[NiM_mCl_2]^+$, 100761-80-6; $[NiM_rCl_2]^+$, 100761-81-7; $[NiE_mCl_2]^+$, 100681-58-1; $[NiM_mBr_2]^+$, 100681-59-2; $[NiM_rBr_2]^+$, 100761-82-8; $[NiE_mBr_2]^+$, 100681-60-5; $[Ni(cyclam)(H_2O)Cl]^{2+}$, 100681-61-6; $[NiM_m(H_2O)Cl]^{2+}$, 100681-62-7; $[NiM_r(H_2O)Cl]^{2+}$, 100761-83-9; $[NiM_r(H_2O)Br]^{2+}$, 100681-63-8; $[NiE_m(H_2O)Cl]^{2+}$, 100681-64-9; Cl^-, 16887-00-6; Br^-, 24959-67-9.

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