

position of Pd(Et<sub>4</sub>dien)SO<sub>3</sub> are in good agreement with the results obtained under conditions where these reactions can be studied separately.

The kinetic data of this paper allow us to propose reaction mechanisms for the various steps that are in agreement with the observations of part 1 of this study and with our general understanding of such systems. The sulfite ligand exhibits a unique behavior, which can be related to the properties of S-bonded species. Similar dechelation reactions were also observed recently

in anation reactions of closely related complexes with thiosulfate, thiourea, and substituted thioureas.<sup>29</sup>

**Acknowledgment.** We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and a loan of PdCl<sub>2</sub> from Hereaus GmbH, Hanau, West Germany.

**Registry No.** Pd(Et<sub>4</sub>dien)OH<sub>2</sub><sup>2+</sup>, 20130-53-4; SO<sub>3</sub><sup>2-</sup>, 14265-45-3; Pd(Et<sub>4</sub>dien)SO<sub>3</sub>, 23151-69-1.

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## Kinetics and Mechanism of the Reduction of Nickel(III) Macrocyclic Complexes by Iodide Ion

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Received October 5, 1986

The kinetics of reduction of several nickel(III) tetraaza macrocyclic complexes by iodide ion have been measured in perchlorate media. Over a large range (up to 400-fold excess) of I<sup>-</sup> concentrations, the reaction order is unity with respect to both [Ni<sup>III</sup>L] and [I<sup>-</sup>]. For L = *C-rac*-5,12-dimethylcyclam, two processes are observed, complex formation,  $k_f = 2.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , followed by a redox step,  $k_4 = 5.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , both of which are iodide-dependent. In the reaction with Ni<sup>III</sup>tet-c<sup>3+</sup>, a redox equilibrium is again postulated. Differences in reactivity are attributed to varying stereochemistries of the substituents on the macrocyclic ring. Comparisons with other outer-sphere reactions of iodide indicate that the processes under investigation are inner sphere in nature. The mechanisms of iodide oxidation encountered in Ni(III)-peptide and Cu(III)-peptide complexes are compared with those observed in the present investigation, where axial ligand binding is stronger.

### Introduction

Redox reactions of nickel(II/III) macrocyclic complexes continue to be the subject of study.<sup>1-3</sup> Relatively few detailed investigations of oxidations by nickel(III) macrocycles have been made, since reactions may be either outer or inner sphere depending on the substitution lability of the axially coordinated solvent molecules on the metal center. Largely on the basis of a comparison of ligand-exchange rates and reaction rates, reductions of Ni(III) macrocycles by TiOH<sup>2+</sup>,<sup>4</sup> Fe<sup>2+</sup>, and VO<sup>2+</sup><sup>5</sup> have all been assigned as outer-sphere processes. For nickel(III) peptide complexes, which are more axially labile than the nickel(III) macrocycles,<sup>6</sup> an inner-sphere process has been postulated.<sup>7</sup>

Reduction of nickel(III) macrocycles by iodide ion was first described in 1979<sup>8</sup> in a pulse-radiolytic and flash-photolytic study of nickel(II/III) systems. Unfortunately, the kinetics of the process could not be investigated, owing to preferential oxidation of I<sup>-</sup> by the radicals used to generate the nickel(III) complexes. In the kinetics of reduction of Ni<sup>III</sup>cyclam<sup>3+</sup> by I<sup>-</sup>,<sup>9</sup> the reaction was found to be first order in both [I<sup>-</sup>] and [Ni(III)] and an outer-sphere mechanism was tentatively assigned. More recently<sup>10</sup>

similar concentration dependences have been observed in the oxidation with Ni(9-aneN<sub>3</sub>)<sub>2</sub><sup>3+</sup>, which is known to react as an outer-sphere reagent. In contrast, the kinetics of the reaction of I<sup>-</sup> with the nickel(III) complex of tri- $\alpha$ -aminoisobutyric acid Ni(H<sub>2</sub>Aib)<sub>3</sub> have been shown<sup>11</sup> to proceed via a major pathway second order in both [I<sup>-</sup>] and [Ni(III)]. This was attributed to the formation of a iodonickel(III) complex and subsequent rate-determining reaction of two such species to form I<sub>2</sub> and two Ni(II) peptide species directly in a concerted two-electron transfer. A second minor route, first order in [Ni(III)] and second order in [I<sup>-</sup>], involved reaction of the monoiodide species with I<sup>-</sup> to yield I<sub>2</sub><sup>-</sup>, which on further rapid oxidation with Ni(III) yielded I<sub>2</sub>.

Slightly different behavior was observed in the reaction of iodide with several copper(III) peptide complexes. At higher concentrations of I<sup>-</sup>, the behavior was similar to the minor [I<sup>-</sup>]<sup>2</sup> pathway of the nickel(III) systems. However, at lower [I<sup>-</sup>] the order of unity in both oxidant and reductant was consistent with a pathway in which I<sup>\*</sup> was produced, which reacted rapidly either with Cu(III) or with I<sup>\*</sup> to give I<sub>2</sub>. The differences in reaction behavior can be attributed<sup>11</sup> to the nature of the axial lability in the complexes. As has been shown, the peptide-iodonickel(III) species is formed readily, whereas for Cu(III) complexes, which are square planar, any association with the iodide may be an ion pair rather than an axially substituted (inner sphere) ion.

In this paper, the kinetics of reaction of several nickel(III) tetraaza macrocyclic complexes with I<sup>-</sup> are reported. Over the concentration ranges used (10-400-fold excess of reductant) there is evidence for only one pathway with a first-order dependence on both [Ni<sup>III</sup>L<sup>3+</sup>] and [I<sup>-</sup>].

### Experimental Section

The nickel(II) complexes [NiM<sub>n</sub>](ClO<sub>4</sub>)<sub>2</sub> (M<sub>n</sub> =  $\alpha$ -*C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane),<sup>12</sup> [NiM<sub>1</sub>](ClO<sub>4</sub>)<sub>2</sub> (M<sub>1</sub> = *C-*

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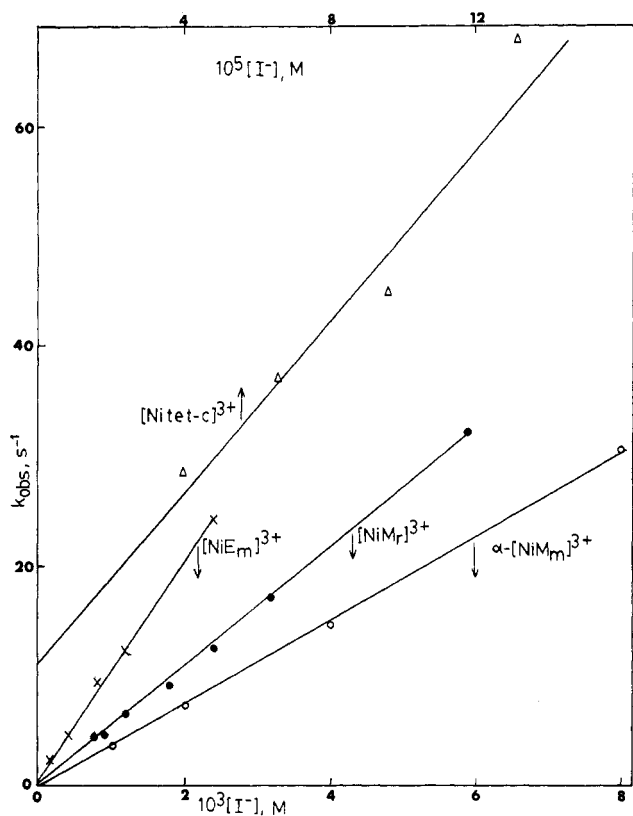


Figure 1. Plots of observed rate constants for reduction of Ni(III) macrocyclic complexes against [I<sup>-</sup>] at 25 °C.

*rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane,<sup>13</sup> [NiE<sub>m</sub>](ClO<sub>4</sub>)<sub>2</sub> (E<sub>m</sub> = *C-meso*-5,12-diethyl-1,4,8,11-tetraazacyclotetradecane),<sup>12</sup> and [Ni(tet-*c*)](ClO<sub>4</sub>)<sub>2</sub> (tet-*c* = *C-rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)<sup>14</sup> were prepared as described previously. Solutions of the diaquonickel(III) complexes were prepared by adding a stoichiometric deficiency of hexaaquacobalt(III) to an aqueous acidic solution of the Ni(II) complex.

The kinetics of the reaction were studied by using the stopped-flow method, under pseudo-first-order conditions of excess I<sup>-</sup>. The reactions were monitored at 320 nm for the disappearance of Ni(III) or at 350 nm for the appearance of I<sub>3</sub><sup>-</sup>, and plots of ln(A<sub>t</sub> - A<sub>∞</sub>) against time were found to be linear for 3 or more half-lives. Absorbance data were collected and processed by an IBM PC microcomputer interfaced to the spectrophotometer via a Techmar Inc. PC-Mate Lab Master Module.

## Results

The ionic strength of the solutions was maintained constant (*I* = 1.0 M) by using LiClO<sub>4</sub>/HClO<sub>4</sub> mixtures. The reactions of [NiM<sub>m</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup>, [NiM<sub>r</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup>, [NiE<sub>m</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup>, and [Ni(tet-*c*)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> with I<sup>-</sup> were studied. A spectrophotometric titration of the reaction of [NiM<sub>m</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> with I<sup>-</sup> showed the stoichiometry to be (1.09 ± 0.06):1, agreeing with the overall equation



Similar behavior was observed for the other complexes. The dependence of the observed first-order rate constant, *k*<sub>obsd</sub>, on [I<sup>-</sup>] was found to be linear, even at concentrations of I<sup>-</sup> up to 400 times in excess of [Ni(III)], leading to the rate law

$$\text{rate} = 2k[\text{Ni}^{\text{III}}\text{L}][\text{I}^{-}] \quad (2)$$

Table I lists the rate constants observed for the reactions at various temperatures, and Figure 1 shows the linear dependence of *k*<sub>obsd</sub> on [I<sup>-</sup>] for all the complexes at 25 °C. These plots all had a zero intercept, except in the case of the tet-*c* complex, where a small,

Table I. Observed Rate Constants for Iodide Reduction of Nickel(III) Macrocyclic Complexes, *I* = 1.0 M (LiClO<sub>4</sub>/HClO<sub>4</sub>)

		[NiM <sub>m</sub> ] <sup>3+</sup> + I <sup>-</sup>			
<i>T</i> , °C	9.9	15.0	20.1	25.0	
10 <sup>-3</sup> <i>k</i> <sub>3</sub> , M <sup>-1</sup> s <sup>-1</sup>	1.16 ± 0.04	1.69 ± 0.02	2.67 ± 0.02	4.03 ± 0.04	
		[NiM <sub>r</sub> ] <sup>3+</sup> + I <sup>-</sup>			
<i>T</i> , °C	11.3	15.0	20.0	25.0	
10 <sup>-3</sup> <i>k</i> <sub>3</sub> , M <sup>-1</sup> s <sup>-1</sup>	1.02 ± 0.06	1.65 ± 0.06	3.34 ± 0.08	5.46 ± 0.08	
		[NiE <sub>m</sub> ] <sup>3+</sup> + I <sup>-</sup>			
<i>T</i> , °C		15.0	20.0	25.0	
10 <sup>-3</sup> <i>k</i> <sub>3</sub> , M <sup>-1</sup> s <sup>-1</sup>		4.10 ± 0.03	7.7 ± 0.2	9.8 ± 0.3	
		[Ni(tet- <i>c</i> )] <sup>3+</sup> + I <sup>-</sup>			
<i>T</i> , °C		15.0	20.0	25.0	
10 <sup>-3</sup> <i>k</i> <sub>3</sub> , M <sup>-1</sup> s <sup>-1</sup>		1.2 ± 0.1	2.4 ± 0.1	3.9 ± 0.5	
<i>k</i> <sub>-3</sub> , s <sup>-1</sup>		6.4 ± 0.7	7.3 ± 0.4	11 ± 4	
		[NiM <sub>r</sub> ] <sup>3+</sup> + I <sup>-</sup> (Substitution Reaction)			
<i>T</i> , °C		15.0	20.0	25.0	
10 <sup>-4</sup> <i>k</i> <sub>3</sub> , M <sup>-1</sup> s <sup>-1</sup>		1.28 ± 0.02	1.9 ± 0.1	2.9 ± 0.1	
<i>k</i> <sub>-3</sub> , s <sup>-1</sup>		0.6 ± 0.3	0.6 ± 0.3	0.8 ± 0.3	

Table II. Observed Rate Constants for Reduction of [NiM<sub>m</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> by Iodide at Various Acid Concentrations, *I* = 3.0 M (LiClO<sub>4</sub>/HClO<sub>4</sub>)<sup>a</sup>

[H <sup>+</sup> ], M	10 <sup>-3</sup> <i>k</i> <sub>3,h</sub> (obsd), M <sup>-1</sup> s <sup>-1</sup>	[H <sup>+</sup> ], M	10 <sup>-3</sup> <i>k</i> <sub>3,h</sub> (obsd), M <sup>-1</sup> s <sup>-1</sup>
0.05	2.77	1.50	3.47
0.30	2.81	2.00	3.69
0.50	3.06 <sup>b</sup>	2.50	4.03
0.80	3.17	3.00	4.20

<sup>a</sup> Conditions: [I<sup>-</sup>] = 1.00 × 10<sup>-3</sup> M; [Ni(III)] = 4 × 10<sup>-5</sup> M; *T* = 20.9 °C. <sup>b</sup> *k*<sub>3,h</sub> = 494 M<sup>-2</sup> s<sup>-1</sup>.

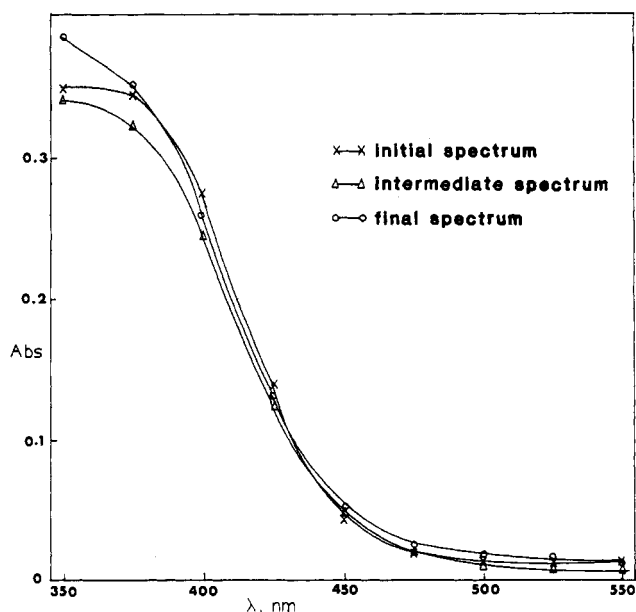


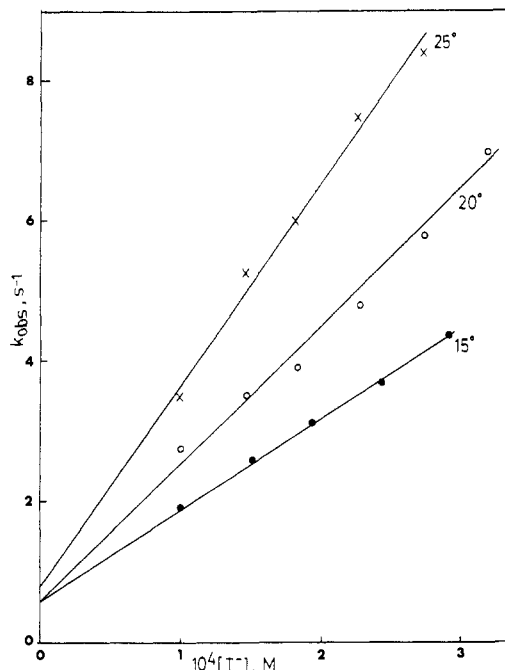
Figure 2. Initial, intermediate, and final spectra during the reaction of [NiM<sub>r</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> with I<sup>-</sup>.

positive intercept was observed.

With the M<sub>r</sub> complex, two separate reaction steps were observed. (There was also an indication of a second but less well defined step in the reaction of the E<sub>m</sub> complex.) Both reaction steps exhibited a first-order dependence on the iodide concentration. With use of the stopped-flow spectrometer between 350 and 650 nm, a point-by-point spectrum was obtained of the intermediate in the reaction of the M<sub>r</sub> complex with iodide as shown

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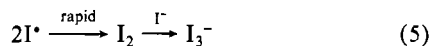
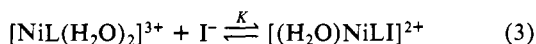
**Figure 3.** Plots of observed rate constants for the iodide substitution of  $[\text{NiM}_m(\text{H}_2\text{O})_2]^{3+}$ .

in Figure 2. It was found that the kinetics of the first step could be measured independently of the second step, at about 390 nm. The values of the rate constants for this first step are reported in Table I, and Figure 3 shows a plot of  $k_{\text{obsd}}$  vs.  $[\text{I}^-]$  at the three temperatures studied. The data give a linear relationship, with a positive intercept.

When the acid concentration was varied between 0.05 and 3.0 M at constant ionic strength  $I = 3$  M in the reaction of  $[\text{NiM}_m]^{3+}$  with iodide, a linear dependence on  $[\text{H}^+]$  was found (see Table II).

### Discussion

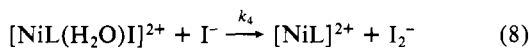
For the  $\text{M}_m$ ,  $\text{E}_m$ , and tet-*c* complexes two different mechanisms can be postulated that fit the data. Pathway A, given in eq 3–5,



followed by electron transfer to produce  $\text{I}^*$  and Ni(II) species. This pathway leads to the rate expression

$$d[\text{Ni(II)}]/dt = k_2 K [\text{NiL}^{3+}] [\text{I}^-] \quad (6)$$

An alternative mechanism, pathway B, is given in eq 7–9. With



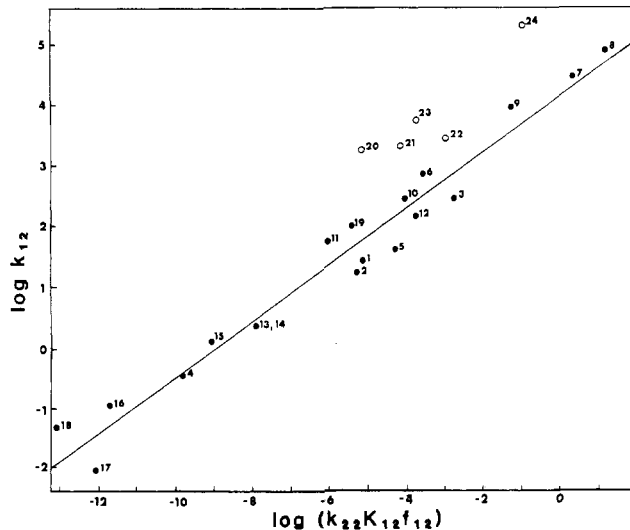
$$[\text{NiL}(\text{H}_2\text{O})\text{I}]^{2+} = k_3 [\text{NiL}^{3+}] [\text{I}^-] / (k_{-3} + k_4 [\text{I}^-]) \quad (10)$$

use of a steady-state approximation for the concentration of  $[(\text{H}_2\text{O})\text{NiLI}]^{2+}$  (eq 10), the rate law can be expressed as eq 11. If  $k_4 [\text{I}^-] \gg k_{-3}$ , this simplifies to the form given in eq 12.

$$\begin{aligned} d[\text{Ni(II)}]/dt &= k_4 k_3 [\text{NiL}(\text{H}_2\text{O})\text{I}]^{2+} [\text{I}^-] \\ &= k_4 k_3 [\text{NiL}^{3+}] [\text{I}^-]^2 / (k_{-3} + k_4 [\text{I}^-]) \quad (11) \end{aligned}$$

$$d[\text{Ni(II)}]/dt = k_3 [\text{NiL}^{3+}] [\text{I}^-] \quad (12)$$

The equilibrium constant  $K$ , in eq 3 and 7, involves the formation of either an inner-sphere complex with coordinated iodide,



**Figure 4.** Marcus free energy plot for iodide reductions. Outer-sphere processes yield  $k_{11} = (2 \pm 1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Labeling of the points in the figure corresponds to the entries in Table III.

as seen in the case of  $\text{Ni}(\text{H}_2\text{Aib}_3)$ , or an outer-sphere association complex, as suggested<sup>9</sup> for  $[\text{Ni}(\text{cyclam})]^{3+}$ . It has been observed that addition of  $\text{Cl}^-$  and  $\text{Br}^-$  to Ni(III) macrocyclic complexes gives axially coordinated monohalo complexes with equilibrium constants of  $10^2$ – $10^3 \text{ M}^{-1}$ .<sup>9,13</sup> Iodide could also coordinate axially to the Ni(III) center like the other halides, prior to the reduction step.

The Marcus theory<sup>15</sup> may be used to correlate free energy changes with observed kinetic data. In a recent modification of the equation,<sup>3,16</sup> the rate constant for the cross reaction,  $k_{12}$ , is related to the component exchange reactions,  $k_{11}$  and  $k_{22}$ , and to the equilibrium constant for the reaction,  $K_{12}$ , by the expression

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} W_{12} \quad (13)$$

In  $f_{12}$ ,  $W_{12}$ , and other terms used have been described.<sup>4</sup> Several studies have recently been performed on the reactions of  $\text{I}^-$  with outer-sphere systems such as  $\text{Fe(III)}$ –<sup>17,18</sup> and  $\text{Os(III)}$ –polypyridine<sup>19</sup> complexes and  $\text{Mo(CN)}_8^{3-}$ .<sup>20</sup> A self-exchange rate of  $7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  has been reported<sup>17,19</sup> for the  $\text{I}^*/\text{I}^-$  couple, and Marcus plots have been used confirming that the reactions are outer-sphere.

Table III shows the calculated values of  $\log k_{22} K_{12} f_{12}$  and  $\log k_{12}$ , where  $k_{12} = k_3/2$ , for 12 complexes whose reactions with  $\text{I}^-$  have been shown to be outer sphere<sup>17,19</sup> and 6 Cu(III) peptide complexes where the mechanism has not been definitely assigned<sup>12</sup> but whose self-exchange rates have recently been published,<sup>7</sup> as well as  $[\text{Ni}(\text{9}]\text{aneN}_3)_2]^{3+}$ ,<sup>21</sup> nickel(III) cyclam,<sup>4</sup> and the four complexes in the present study.<sup>14</sup> In Figure 4,  $\log k_{12}$  is plotted vs.  $\log k_{22} K_{12} f_{12}$ , and a line drawn through the points for the 12 complexes and for  $[\text{Ni}(\text{9}]\text{aneN}_3)_2]^{3+}$  has a least-squares slope of  $0.46 \pm 0.02$  and intercept of  $4.1 \pm 0.2$ . This is in excellent agreement with the Marcus equation, which predicts a slope of 0.5 and an intercept of  $\log k_{11}/2$ . The implied value of  $k_{11}$  from the intercept of Figure 4 is  $(2 \pm 1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which is in reasonable agreement with the previously reported value<sup>16</sup> of  $7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

The six Cu(III) peptide complexes also appear to lie on or near this line, implying that their reactions with  $\text{I}^-$  are outer sphere. However, the points for the nickel cyclam species and the four complexes in the present study all lie above the line in Figure 4; i.e., the rates are faster than predicted by the Marcus theory.

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Table III. Marcus Parameters for Reduction by Iodide

no.	complex	$E^\circ$ , V vs. NHE	$\log$ $k_{22}$	$\log$ $k_{11}K_{12}f_{12}$	$\log$ $k_{12}$	ref
1	Os(phen) <sub>3</sub> <sup>3+</sup>	0.84	8.49	-5.11	1.41	a
2	Os(bpy) <sub>3</sub> <sup>3+</sup>	0.837	8.25	-5.27	1.22	a
3	NpO <sub>2</sub> <sup>2+</sup>	1.14	2.02	-2.78	2.42	b
4	Mo(CN) <sub>3</sub> <sup>3-</sup>	0.75	4.48	-9.71	-0.47	c
5	IrBr <sub>6</sub> <sup>2-</sup>	0.866	8.21	-4.39	1.54	d
6	IrCl <sub>6</sub> <sup>2-</sup>	0.964	5.36	-3.60	2.84	d
7	Fe(bpy) <sub>3</sub> <sup>3+</sup>	1.035	8.52	0.58	4.44	a, f
8	Fe(phen) <sub>3</sub> <sup>3+</sup>	1.06	8.52	1.24	4.89	e, f
9	Fe(5,6-Me <sub>2</sub> phen) <sub>3</sub> <sup>3+</sup>	0.97	8.52	-1.20	3.95	g
10	Fe(4,7-Me <sub>2</sub> phen) <sub>3</sub> <sup>3+</sup>	0.87	8.52	-4.16	2.40	g
11	Fe(3,4,7,8-Me <sub>4</sub> phen) <sub>3</sub> <sup>3+</sup>	0.81	8.52	-6.07	1.76	g
12	Fe(4,4'-Me <sub>2</sub> bpy) <sub>3</sub> <sup>3+</sup>	0.88	8.52	-3.86	2.14	g
13	[Cu(H <sub>2</sub> A <sub>3</sub> )]	0.81	4.74	-7.94	0.35	7, 12
14	[Cu(H <sub>2</sub> DGEN)] <sup>+</sup>	0.81	4.74	-7.94	0.35	7, 12
15	[Cu(H <sub>2</sub> L <sub>3</sub> )]	0.77	4.74	-9.00	0.11	7, 12
16	[Cu(H <sub>3</sub> G <sub>4</sub> a)]	0.68	4.30	-11.72	-0.94	7, 12
17	[Cu(H <sub>2</sub> Aib <sub>3</sub> )]	0.66	4.74	-12.03	-2.0	7, 12
18	[Cu(H <sub>3</sub> G <sub>4</sub> ) <sup>-</sup> ]	0.63	4.30	-13.12	-1.30	7, 12
19	[Ni([9]aneN <sub>3</sub> ) <sub>2</sub> ] <sup>3+</sup>	0.947	3.78	-5.32	1.98	21
20	[Ni(cyclam)] <sup>3+</sup>	0.990	3.00	-5.03	3.19	9
21	[NiM <sub>m</sub> ] <sup>3+</sup>	0.995	3.85	-4.16	3.30	h
22	[NiM <sub>r</sub> ] <sup>3+</sup>	1.115	2.30	-3.02	3.44	h
23	[NiE <sub>m</sub> ] <sup>3+</sup>	0.990	4.38	-3.81	3.69	h
24	[Ni(tet-c)] <sup>3+</sup>	1.26	1.49	-0.99	5.29	h

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These five points are apparently linear with a slope of about 0.5, but the intercept of such a line would imply a self-exchange rate for I<sup>•</sup>/I<sup>-</sup> of >10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>, which exceeds the diffusion-controlled limit of 3 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>22</sup> Linear free energy relationships in inner-sphere reactions similar to those for outer-sphere relationships in inner-sphere reactions similar to those for outer-sphere processes have previously been observed.<sup>23-25</sup> These considerations strongly support the assignment of an inner-sphere mechanism to all five of the nickel(III) macrocyclic complexes.

In the case of the [NiM<sub>r</sub>]<sup>3+</sup> complex, two steps were observed. The first step in the reaction of [NiM<sub>r</sub>]<sup>3+</sup> is about 5 times faster than the second step ( $k_1 = 2.9 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> and  $k_2 = 5.5 \times 10^3$  M<sup>-1</sup> s<sup>-1</sup>). The spectrum of the intermediate (Figure 2) is consistent with a Ni(III) species and is similar to that of the Cl<sup>-</sup> and Br<sup>-</sup> adducts of [NiM<sub>r</sub>]<sup>3+</sup>. The value of  $2.9 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> for the forward rate is comparable to the value of  $4.2 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> found for the rate of substitution of Cl<sup>-</sup> in this complex.<sup>26</sup> Therefore, it seems reasonable to propose that this first reaction is the formation of an iodonickel(III) complex. There is no evidence for formation of a five-coordinate [NiLI]<sup>2+</sup> species as noted as rearrangement products in the Cl<sup>-</sup> and Br<sup>-</sup> substitutions of these Ni(III) species.<sup>26</sup> The redox step may be faster than such a rearrangement. The fact that both of the observed steps exhibit a first-order dependence on [I<sup>-</sup>] supports the assignment of pathway B (eq 7-9) for this reaction, i.e. the reaction of the iodonickel(III) complex with I<sup>-</sup> to form I<sub>2</sub><sup>-</sup>. Furthermore, from the data at 390 nm,  $k_3$  and  $k_{-3}$  are known, and  $k_4$ [I<sup>-</sup>] >  $k_{-3}$ , since  $k_{-3} = 0.8$  s<sup>-1</sup> and  $k_4 = 5.5 \times 10^3$  M<sup>-1</sup> s<sup>-1</sup>, so that, when [I<sup>-</sup>] > 10<sup>-3</sup> M,  $k_4$ [I<sup>-</sup>] > 5.5, leading to a first-order dependence on [I<sup>-</sup>] for the second step, as in eq 12.

In the cyclam, M<sub>m</sub>, E<sub>m</sub>, and tet-c complexes, there is no definitive evidence to distinguish between inner-sphere pathways A and B. However, in view of the similarity of these complexes to

Table IV. Rate Constants (10<sup>-3</sup>k, M<sup>-1</sup> s<sup>-1</sup>) of Halide Substitution of Ni(III) Macrocyclic Complexes

halide	Ni(III) complex				tet-c
	cyclam	M <sub>m</sub>	E <sub>m</sub>	M <sub>r</sub>	
Cl <sup>-</sup>	0.902	2.18	3.06	42	
Br <sup>-</sup>	0.207	0.89	2.75	≥10	
I <sup>-</sup>	3.08	4.03	9.80	29	390

[NiM<sub>r</sub>]<sup>3+</sup>, it would be reasonable to assume an identical mechanism for all of the Ni(III) macrocyclic complexes, i.e. pathway B. This is supported by the indication of two steps noted in the reaction with the [NiE<sub>m</sub>]<sup>3+</sup> complex, as well as by the presence of a reverse process in the case of [Ni(tet-c)]<sup>3+</sup>, which could be assigned to the reverse substitution step,  $k_{-3}$ .

The reason that the substitution step was more readily observed for [NiM<sub>r</sub>]<sup>3+</sup> than in the other complexes is probably its greater substitutional lability. In the M<sub>r</sub> complex, the rate of I<sup>-</sup> substitution is  $2.9 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>, comparable to the Cl<sup>-</sup> substitution rate of  $4.2 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>; both these rates are faster than the rate of the reduction step,  $5.5 \times 10^3$  M<sup>-1</sup> s<sup>-1</sup>, rendering the kinetics of the substitution step amenable to observation. Since the rate-determining step of the proposed mechanism is the substitution step, as shown by eq 12, the measured rate constant  $k_3$  for the cyclam, M<sub>m</sub>, E<sub>m</sub>, and tet-c complexes represents the rate of iodide substitution. In Table IV are listed for comparison the rates of halide substitution for four Ni(III) macrocycles. It can be seen that, for [Ni(cyclam)]<sup>3+</sup>, [NiM<sub>m</sub>]<sup>3+</sup>, and [NiE<sub>m</sub>]<sup>3+</sup>, these rate constants are in the order I<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup>, which may be due to two opposing effects. The trend in substitution rates on going from Cl<sup>-</sup> to Br<sup>-</sup> to I<sup>-</sup> should be expected to decrease, due to the decreasing electronegativity. But the nephelauxetic effect predicts the opposite trend: the rates should increase with increasing covalency of the Ni-X bond. Such reversals in stability trends for the halide series are often seen, especially in complexes of metals in unusual oxidation states.<sup>27</sup>

Calculation of equilibrium constants  $K_3$  for formation of the monoiodo complex yields values at 25 °C of  $3.6 \times 10^4$  M<sup>-1</sup> for

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$[\text{NiM}_r]^{3+}$  and  $3.5 \times 10^4 \text{ M}^{-1}$  for  $[\text{Ni}(\text{tet-c})]^{3+}$ . These values are very similar, as might be expected for complexes with related sterically crowded axial coordination sites. They also appear to be much larger than the  $K$  value for  $\text{Cl}^-$  and  $\text{Br}^-$  ( $K$  for  $[\text{NiM}_r]^{3+} + \text{Cl}^-$ ,  $640 \text{ M}^{-1}$ ). This implies that the thermodynamic stability of the iodonickel(III) complex is much greater than that of the chloronickel(III) complex. This can once again be attributed to the increased nephelauxetic effect of  $\text{I}^-$  over that of  $\text{Cl}^-$ , resulting in a more covalent Ni-X bond. Also, for the iodide reductions, the major component to the activation energy is due to the enthalpy term. The formation of the iodo complex is dominated by a large increase in entropy, consistent with reduced solvation on charge neutralization.

**Comparison with Cu(III) and Ni(III) Peptide Complexes.** It is of interest to compare the kinetics and mechanism of reactions under consideration with those for Ni(III)<sup>11</sup> and Cu(III)<sup>12</sup> peptide complexes. As discussed in the Introduction, in the case of  $\text{Ni}^{\text{III}}(\text{H}_2\text{Aib}_3)$ , the order is always second order in  $[\text{I}^-]$ , and there are two pathways, which are second order (major route) and first order (minor route) in  $[\text{Ni}(\text{III})]$ . These results are explained in terms of a mechanism wherein the iodonickel(III) complex reacts either with another iodonickel(III) species or with  $\text{I}^-$  to produce  $\text{I}_2$  or  $\text{I}_2^-$ , respectively. These oxidations are thermodynamically more favorable than the oxidation of  $\text{I}^-$  to  $\text{I}^*$ . The relevant  $E^\circ$  values have been estimated<sup>17</sup> at 0.620 V ( $2\text{I}^- \rightarrow \text{I}_2$ ), 1.08 V ( $2\text{I}^- \rightarrow \text{I}_2^-$ ), and 1.40 V ( $\text{I}^- \rightarrow \text{I}^*$ ). Thus, the  $\text{Ni}^{\text{III}}(\text{H}_2\text{Aib}_3)$  complex, which is very axially labile,<sup>10</sup> has as its major route for iodide oxidation the reaction of two iodonickel(III) complexes to produce  $\text{I}_2$  in a pathway with the lowest  $E^\circ$  or greatest thermodynamic ease. The minor route takes the next most thermodynamically feasible process, by oxidizing  $2\text{I}^-$  to  $\text{I}_2^-$ .

In the case of the Cu(III) peptides,<sup>12</sup> the complexes are axially inert, eliminating a bimolecular reaction of two complexes. At high concentrations of  $\text{I}^-$ , the mechanism appears to involve the reaction of an outer-sphere complex  $[\text{Cu}^{\text{III}}\text{H}_n\text{L}_n\text{I}^-]$  with  $\text{I}^-$  to produce  $\text{I}_2^-$ . At lower concentrations of iodide, the most thermodynamically unfavorable pathway, involving oxidation of  $\text{I}^*$  to  $\text{I}^-$ , becomes dominant.

In the Ni(III) macrocycles under study, the complexes are fairly labile, but not as labile as Ni(III) peptide complexes,<sup>6</sup> so that a reaction pathway involving two  $[\text{NiLI}]^{2+}$  species does not occur. However, the equilibrium constant for formation of the monoiodo complex is much larger (e.g.  $3.6 \times 10^4 \text{ M}^{-1}$  for  $[\text{NiM}_r]^{3+}$  compared with  $\leq 10 \text{ M}^{-1}$  for  $\text{Ni}(\text{H}_2\text{Aib}_3)$ ). The complex decomposition rate  $k_{-3}$  thus does not compete with the electron-transfer step in the case of the macrocyclic complexes, leading to a first-order, rather than a second-order, dependence on  $[\text{I}^-]$  (eq 12).

**Acid Dependence.** It can be seen (Table II) that the rate of iodide oxidation by  $[\text{NiM}_m]^{3+}$  increases slightly with  $[\text{H}^+]$ . The

derived dependence leads to eq 14, with a value of  $494 \text{ M}^{-2} \text{ s}^{-1}$

$$k_{3,\text{obsd}} = k_3 + k_{3,\text{h}}[\text{H}^+] \quad (14)$$

for  $k_{3,\text{h}}$  at 21 °C. It was previously reported<sup>9</sup> that there was no acid dependence in the case of the reaction with  $[\text{Ni}(\text{cyclam})]^{3+}$ , but this was based on only two measurements, at 0.1 and 1.0 M  $\text{H}^+$  and ionic strength 1.0 M. A more detailed study of the cyclam system over the range 0.05–3.0 M  $\text{H}^+$  at 3.0 M ionic strength revealed a similar linear dependence on  $[\text{H}^+]$ , with a third-order rate constant  $k_{3,\text{h}} = 280 \text{ M}^{-2} \text{ s}^{-1}$ .

An increase in rate with acid concentration was seen in the reaction of  $\text{I}^-$  with some of the Cu(III) peptide complexes and with  $\text{Ni}(\text{H}_2\text{Aib}_3)$ . This was attributed to the formation of an externally protonated species in which the peptide oxygen is protonated. In the case of the Ni(III) macrocycles, however, no such outside protonation can occur, since the nitrogens are already four-coordinate. Neither is the mechanism likely to involve a protonated  $\text{I}^-$  species, since the  $\text{p}K$  value for HI has been estimated at -11.<sup>28</sup> No first-order acid dependence was observed in the  $\text{Cl}^-$  and  $\text{Br}^-$  substitution reactions of these Ni(III) macrocycles. The mechanism of this acid-catalyzed pathway is thus unclear at present. However, the origins of the effect may lie in the fact that although the ionic strength is maintained constant, the ionic environment changes greatly for  $[\text{H}^+] = 0.05\text{--}3.0 \text{ M}$ .

### Conclusions

It has been shown, on the basis of spectroscopic and kinetic data, and by comparison with outer-sphere reactions via a Marcus correlation, that the oxidation of iodide ion by five Ni(III) macrocyclic complexes is inner sphere, proceeding by formation of an iodonickel(III) complex followed by reaction with another  $\text{I}^-$  ion to produce  $\text{I}_2^-$ . The predominance of this pathway over other possible routes has been rationalized by comparison of the redox and substitution properties of these complexes with those of similar species for which the oxidation of iodide has been studied.

**Acknowledgment.** Financial support from the Natural Sciences and Engineering Research Council (Canada) is gratefully acknowledged. M.G.F. thanks the University of Victoria for a Graduate Fellowship.

**Registry No.**  $[\text{NiM}_m](\text{ClO}_4)_2$ , 96947-08-9;  $[\text{NiE}_m](\text{ClO}_4)_2$ , 96866-27-2;  $[\text{Ni}(\text{tet-c})](\text{ClO}_4)_2$ , 16337-61-4;  $[\text{NiM}_r](\text{ClO}_4)_2$ , 96947-10-3;  $\text{I}^-$ , 20461-54-5.

**Supplementary Material Available:** A table of observed rate constants for iodide reduction of nickel(III) macrocyclic complexes (3 pages). Ordering information is given on any current masthead page.

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## Crystal Structures of Two $\text{MoOX}_2\text{L}_3$ Complexes, $\text{MoOCl}_2(\text{PMePh}_2)_3$ and $\text{MoO}(\text{NCO})_2(\text{PEt}_2\text{Ph})_3$ . Implications to Distortional Isomerism

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Received January 25, 1987

The molecular structures of two  $\text{MoOX}_2\text{L}_3$  complexes, green  $\text{MoOCl}_2(\text{PMePh}_2)_3$  (**1**) and blue  $\text{MoO}(\text{NCO})_2(\text{PEt}_2\text{Ph})_3$  (**2**), are reported. Compound **1** crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 10.433$  (3) Å,  $b = 18.871$  (5) Å,  $c = 9.981$  (3) Å,  $\alpha = 96.56$  (2)°,  $\beta = 107.02$  (2)°,  $\gamma = 77.83$  (2)°,  $V = 1834$  (2) Å<sup>3</sup>, and  $Z = 2$ . Compound **2** also crystallizes in space group  $P\bar{1}$  with  $a = 17.887$  (3) Å,  $b = 17.912$  (4) Å,  $c = 11.330$  (2) Å,  $\alpha = 94.78$  (2)°,  $\beta = 107.33$  (1)°,  $\gamma = 85.39$  (2)°,  $V = 3447$  (1) Å<sup>3</sup>, and  $Z = 4$ . Most notable is the Mo=O distance in **1** (1.669 Å), which is much shorter than the Mo=O distance in green  $\text{MoOCl}_2(\text{PEt}_2\text{Ph})_3$  (1.803 Å) and comparable to that in the blue isomer of  $\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$  (1.676 Å) and in blue **2** (average 1.684 Å). Implications of this short bond distance in **1** are discussed.

### Introduction

Coordination compounds that have the same ligands and the same overall geometry but differ in specific bond lengths and

angles are termed "distortional isomers". The first examples of such compounds were molecules of the type  $\text{MoOX}_2\text{L}_3$ , where X = halogen or pseudohalogen and L = phosphine or arsine.<sup>1,2</sup> Most