

Kinetics and Mechanism of Reduction of Nickel(III) Complexes by Titanium(III) in Aqueous Media

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The kinetics of reduction by Ti(III) of several nickel(III) species and one Ni(IV) oxime complex have been measured in aqueous trifluoromethanesulfonate or chloride media. Over the range 0.1–1.0 M [H⁺] the principal reaction pathway involves the reaction $\text{TiOH}^{2+} + \text{Ni}^{\text{III}}\text{L} \xrightarrow{k_2} \text{Ti(IV)} + \text{Ni}^{\text{II}}\text{L}$ with $k_2 = 1.6 \times 10^6$, 1.65×10^6 , and $2.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the Ni(III) macrocycles L = cyclam, dimethylcyclam, and tet-*c*, respectively (see Chart I). For the octahedral species Ni(nonaneN₃)₂³⁺, $k_2 = 6.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, and with the Ni(IV)-oxime species, $k_2 = 2.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. In the case of the reaction with Ni(nonaneN₃)₂³⁺ a Cl⁻-promoted pathway is observed. The data have been combined to provide a Marcus correlation, and the outer-sphere character of these reactions is discussed.

Introduction

Although there has been considerable recent interest in the electron-transfer reactions of nickel(III)^{1–5} complexes, relatively few studies are available on the rates of reaction with aquo metal ion reductants.⁶ Over the last 10 years, continuing investigations have been made of the reactions of titanium(III). Many of these studies have centered on cobalt(III)⁷ and ruthenium(III)⁸ systems, but a variety of other oxidants including V(IV),⁹ Fe(III),¹⁰ V(V),¹¹ and Os(III)¹² complexes have been examined.

The kinetics of the Ti(III) reductions are dominated mainly by an inverse hydrogen ion dependence of the observed second-order rate constants, and in favorable cases, assignments of the reaction mechanism have been proposed. In some instances¹² the Marcus¹³ equation has been applied. There is interest in the analysis of outer-sphere reactions where the driving force is considerable. In the case of the reactions of Ti(III) with Os(LL)₃³⁺ species¹² (LL = bipyridine or phenanthroline) a good correlation was observed and estimates were made of the self-exchange rates for the $\text{TiOH}^{3+}/2+$ couple.

This paper reports on a study of the redox reactions between Ti(III) and nickel(III) macrocyclic complexes together with one hexadentate N₆ Ni(III) species and a hexadentate N₆ Ni(IV) oxime complex. For these systems, the variation of *E*^o values for the oxidants (~0.6–1.2 V) provides a wide range of driving force for the reactions. Earlier evidence from these laboratories suggests that the nickel(III) species oxidize benzenediols and ascorbic acid via the outer-sphere route, and it is of interest to compare these data with those involving a metal-ion reductant.

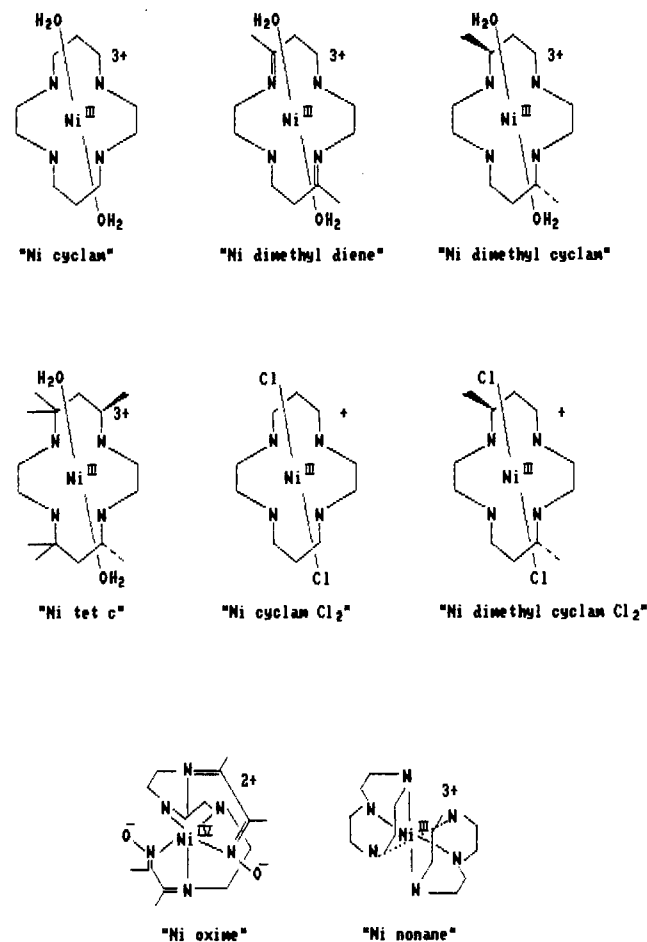
Experimental Section

Preparation of Ti(III) Solutions. All manipulations of Ti(III) were performed under an inert (N₂ or Ar) atmosphere, and where necessary platinum syringe needles were used for solution transfer. The solutions were prepared in trifluoromethanesulfonate (tfs) and chloride media by dissolution of titanium metal (Alfa Inorganics, M3N8 sponge) in the appropriate (~3 M) acid. Refluxing under argon for 24 h and filtration yielded solutions 0.6–0.8 M in Ti(III), which were stored under argon at 0 °C.

Stock solutions were standardized both by titration with Cr₂O₇²⁻ and by spectrophotometry ($\epsilon_{502} = 3.97 \text{ M}^{-1} \text{ cm}^{-1}$).⁹ The hydrogen ion concentration was determined with good agreement by two independent methods described by Earley.¹⁴

Nickel Complexes. The species used in this study are as shown in Chart I. Nickel(II) cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) and nickel(II) tet-*c* (tet-*c* = *C-rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) were prepared as perchlorates by the method of Curtis.¹⁵ For nickel(II) dimethylcyclam (*C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane) and

Chart I



nickel(II) dimethylcyclam-4,11-diene perchlorates, the preparation was as described by Kolinski.¹⁶ Nickel(II) bis(1,4,7-triazanonane-

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N,N',N'') was prepared by a modification¹⁷ of the published procedure.¹⁸ Analytical purity of all complexes was confirmed (Canadian Microanalytical Service, Vancouver).

In all cases the nickel(III) complexes were formed in situ by reaction with a stoichiometric deficiency of aquocobalt(III) as described previously.¹⁹ The $[\text{Ni}^{\text{III}}\text{LCl}_2]^+$ complexes (L = cyclam or dimethylcyclam) were prepared from the corresponding $\text{Ni}^{\text{III}}\text{L}(\text{OH}_2)_2^{3+}$ ion in chloride media. The presence of two axially coordinated chloride ions under the experimental conditions has been confirmed⁴ with use of ESR techniques, and hyperfine interaction of the chloride with the nickel(III) d^7 center is observed as a septet in the g_{\parallel} feature. The nickel(II)-oxime complex, $[\text{Ni}^{\text{II}}(\text{H}_2\text{L})](\text{ClO}_4)_2$, (H_2L = 3,14-dimethyl-4,7,10,13-tetraazaheptadeca-3,13-diene-2,15-dione dioxime) was prepared by addition of the ligand to a methanol solution of nickel(II) perchlorate. Dark violet crystals of the corresponding nickel(IV) complex, $\text{NiL}(\text{ClO}_4)_2$, were obtained by oxidation with concentrated nitric acid.²⁰

Solutions of aquocobalt(III) were prepared by electrolysis of Co(II) in perchloric acid (>4 M).¹⁹ Lithium trifluoromethanesulfonate was formed on neutralizing $\text{CF}_3\text{SO}_3\text{H}$ with Li_2CO_3 . Trifluoromethanesulfonic acid was either distilled or diluted and treated with activated carbon, followed by filtration through glass-fiber paper prior to use.

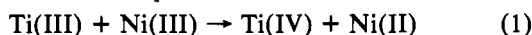
Kinetic Studies. Rate measurements were made with a stopped-flow apparatus described previously.²¹ Provision was made for the maintenance of a N_2 atmosphere, and freshly prepared reactant solutions were purged immediately prior to use. Solutions were thermostated to within ± 0.05 °C over the temperature range studied. The ionic strength was maintained at 1.0 M with use of $\text{CF}_3\text{SO}_3\text{H}/\text{LiSO}_3\text{CF}_3$ or HCl/LiCl mixtures. Experiments were carried out under pseudo-first-order conditions with excess reductant, the reactions being monitored by a decrease in absorbance (Ni(III) complexes, 350 nm; Ni(IV) oxime, 500 nm). Plots of $\ln(A_t - A_\infty)$ against time, derived from data collected on a PCM-12 minicomputer, were linear for 3 or more half-lives.

Electrode potentials of the $\text{NiL}^{3+/2+}$ and of the $\text{NiLCl}_2^{+/0}$ couples were measured with use of cyclic voltammetry in either 1.0 M $\text{CF}_3\text{SO}_3\text{H}$ or 1.0 M HCl. The relevant potentials of the Ni(IV) oxime species have been determined previously.²² A Princeton Applied Research Model 173 instrument with a PAR Model 175 universal programmer was employed in conjunction with a Pt working electrode and counterelectrodes and an SCE. With the exception of Ni(cyclam)²⁺ and Ni(Me_2cyclam)²⁺, which showed excellent reversibility, most systems were quasi-reversible (peak to peak separations of ~ 80 mV) as has been observed.

UV-visible spectra were recorded with a Beckman DU-8 spectrometer. ESR spectra were obtained at 77 K by use of a Varian E6 instrument with diphenylpicrylhydrazyl ($g = 2.0037$) as an internal reference standard.

Results

Reaction stoichiometries in acidic media were determined by spectrophotometric titration monitored between 350 and 380 nm. In all cases the nickel(III) complexes conformed to reaction 1 to within an experimental error of $\pm 3\%$. In the case



of the nickel(IV) oxime the determination at $\lambda = 500$ nm indicated the overall reaction given by eq 2 ($\pm 3\%$). Kinetic

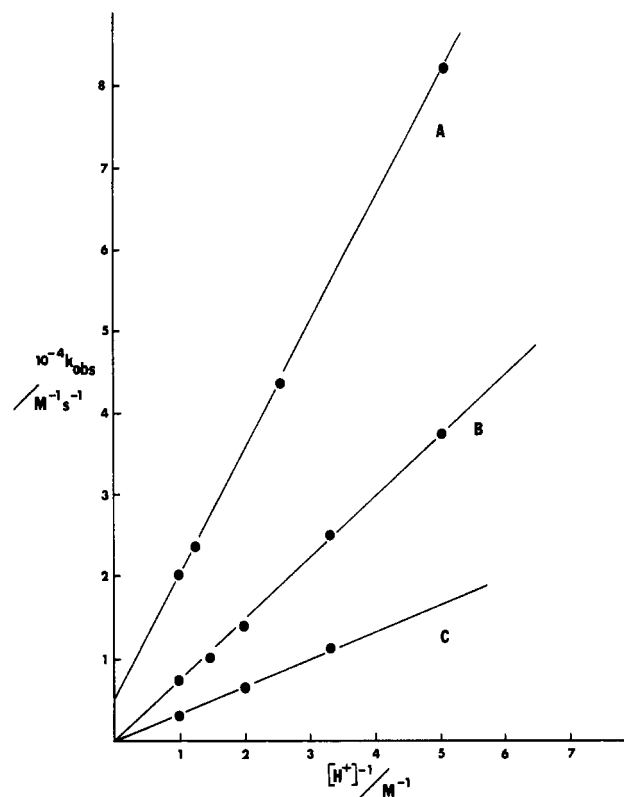
$$2\text{Ti(III)} + \text{Ni}^{\text{IV}}\text{L}^{2+} + 2\text{H}^+ \rightarrow 2\text{Ti(IV)} + \text{Ni}^{\text{II}}(\text{H}_2\text{L})^{2+} \quad (2)$$


Figure 1. Inverse hydrogen ion dependence of the second-order rate constant k_{obs} at an ionic strength of 1.0 M and 25 °C for reactions of Ti(III) with (A) Ni(triazanonane)₂³⁺ in chloride media, (B) Ni(cyclam)³⁺ in trifluoromethanesulfonate media, and (C) Ni(triazanonane)₂³⁺ in trifluoromethanesulfonate media.

data for the reactions studied are shown in Table I. The first-order dependence on [Ti(III)] at constant $[\text{H}^+]$ was confirmed over a wide range of reductant concentrations. Each second-order rate constant quoted in Table I is the average of at least three and usually four runs with various [Ti(III)] in the range $(0.6\text{--}20) \times 10^{-3}$ M. No dependence was observed on [Co(II)] or [Ni(II)] present although the rates increased with decreasing $[\text{H}^+]$. The dependences on $[\text{H}^+]$ and [Ti(III)], are described by eq 3. Typical hydrogen ion dependences of

$$\frac{-d[\text{Ni(III)}]}{dt} = \frac{k_1[\text{H}^+]^{-1}}{1 + K_a/[\text{H}^+]}\frac{[\text{Ti(III)}]_t[\text{Ni(III)}]_t}{[\text{Ti(III)}]_t[\text{Ni(III)}]_t} = k_{\text{obs}}[\text{Ti(III)}]_t[\text{Ni(III)}]_t \quad (3)$$

the observed second-order rate constant, k_{obs} , are shown in Figure 1, where it is seen that a linear variation with $[\text{H}^+]^{-1}$ is observed over the range of acid investigated. The lack of curvature in such a plot is consistent with the acid dissociation constant of $\text{Ti}_{\text{aq}}^{3+}$, K_a , being much smaller than the minimum $[\text{H}^+]$ used in this study (0.2 M). Previous studies in chloride media⁹ have yielded a value of $\sim 2 \times 10^{-3}$ M for K_a , and in trifluoromethanesulfonate solutions a good fit for many data is provided by using $K_a = 4.6 \times 10^{-3}$ M.⁸ For evaluation of rate constants, we have used this value. Unfortunately, for most of the nickel(III) species used as well as the Ti(III) reductant, instability at higher pHs eliminated the accessibility to a wider range of $[\text{H}^+]$.

Discussion

In the case of $[\text{Ni}^{\text{III}}(\text{nonane})_2]^{3+}$ and NiLCl_2^+ (L = cyclam or dimethylcyclam) under the acidity conditions prevailing, the observed hydrogen ion dependence must arise from the hydrolysis of the aquotitanium(III) ion. A similar situation obtains for the nickel(IV) oxime, where there are no proton-dependent equilibria in the range studied.²⁰ Also, hydrolysis

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Table I. Summary of Rate Constants for the Ti(III) Reductions of Ni(III) and Ni(IV) Complexes ($I = 1.0 \text{ mol dm}^{-3}$ (H(tfs)/Li(tfs)), [Ti(III)] = $(0.6\text{--}20) \times 10^{-3} \text{ M}$, [Ni(III)] or [Ni(IV)] $\approx 4 \times 10^{-5} \text{ M}$)

[H ⁺], M	k_{obsd} , $\text{M}^{-1} \text{ s}^{-1}$	T , °C	$k_1 \text{TiOH} = k_2 K_a$, s^{-1}	ΔH^\ddagger , kcal mol^{-1}	ΔS^\ddagger , $\text{cal mol}^{-1} \text{ deg}^{-1}$
Ni(cyclam) ³⁺					
0.2	3.6×10^4	25			
0.3	2.4×10^4	25	$(7.5 \pm 0.12) \times 10^3$		
0.5	1.42×10^4	25		9.8 ± 3.0	-7.6 ± 6.5
0.7	1.00×10^4	25			
1.0	7.4×10^3	25			
		35.3 ^a	1.2×10^4		
		18.8 ^a	4.1×10^3		
		8.4 ^a	2.8×10^3		
Ni ^{III} (Me ₂ cyclam) ³⁺					
0.4	1.8×10^4	25			
0.6	1.21×10^4	25	$(7.54 \pm 0.19) \times 10^3$		
0.8	9.3×10^3	25		6.3 ± 2.6	-19.6 ± 4.8
1.0	7.5×10^3	25			
		20.0 ^a	5.4×10^3		
		15.2 ^a	4.9×10^3		
		9.5 ^a	3.4×10^3		
Ni(IV) Oxime					
0.2 ^b	8.9×10^3 ^b	25.3			
0.3	4.0×10^3	25.3			
0.5	2.41×10^3	25.3	$(1.22 \pm 0.21) \times 10^3$		
0.7	1.73×10^3	25.3			
1.0	1.24×10^3	25.3			
		35.5	1.8×10^3	12.7 ± 4.9	-2.1 ± 6.5
		15.0	5.2×10^2		
		8.5	2.2×10^2		
Ni(triazanonane) ₂ ³⁺					
0.3	1.13×10^4	25			
0.5	6.28×10^3	25	$(3.14 \pm 0.20) \times 10^3$		
0.75	4.22×10^3	25		25.0 ± 2.0	41.3 ± 5.7
1.00	3.12×10^3	25			
		29.3 ^a	5.84×10^3		
		20.2 ^a	1.51×10^3		
Ni(tet-c) ³⁺					
0.3	4.2×10^4	25			
0.5	2.5×10^4	25	$(1.3 \pm 0.03) \times 10^4$		
0.75	1.6×10^4	25			
1.00	1.31×10^4	25			
Ni(Me ₂ diene) ³⁺					
0.3	1.21×10^4	25			
0.5	7.2×10^3	25	$(3.52 \pm 0.09) \times 10^3$		
0.75	5.21×10^3	25			
1.00	3.7×10^3	25			
Ni(cyclam)Cl ₂ ⁺ ^b					
0.2	5.4×10^3	25			
0.5	2.1×10^3	25	$(1.09 \pm 0.01) \times 10^3$		
0.7	1.5×10^3	25			
1.0	1.10×10^3	25			
Ni(Me ₂ cyclam)Cl ₂ ⁺ ^b					
0.4	6.6×10^3	25			
0.6	4.1×10^3	25	$(2.84 \pm 0.05) \times 10^3$		
0.8	2.9×10^3	25			
1.0	2.41×10^3	25			
		19.6 ^a	2.0×10^3		
		15.5 ^a	1.3×10^3	13.3 ± 4.7	2.0 ± 6.1
		8.9 ^a	5.7×10^2		
Ni(triazanonane) ₂ ³⁺ ^b					
0.2	8.1×10^4	25			
0.4	4.3×10^4	25	$(1.60 \pm 0.02) \times 10^4$		
0.8	2.4×10^4	25			
1.0	2.01×10^4	25			
		20.0 ^a	1.1×10^4		
		15.0 ^a	6.2×10^3		
		9.5 ^a	3.2×10^3	16.4 ± 4.0	15.7 ± 6.4
Ni(triazanonane) ₂ ³⁺ ^c					
1.0 (0) ^d	3.2×10^3				
1.0 (0.7) ^d	1.84×10^4				

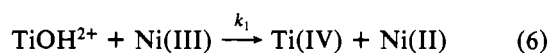
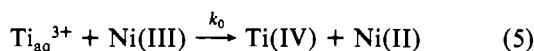
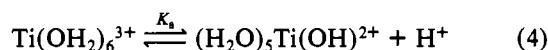
^a Rate constant assuming no temperature variation of K_a . ^b In Cl⁻ medium; $I = 1.0 \text{ mol dm}^{-3}$ (HCl/LiCl). ^c In Cl⁻/tfs media; $I = 1.0 \text{ M}$ (HCl, H(tfs)) at 25 °C. ^d Cl⁻ concentration (M) in parentheses.

Table II. Comparison of Calculated^a and Experimental Data ($T = 25^\circ\text{C}$) for the Cl^- -Assisted Pathways in the $\text{Ni}(\text{nonaneN}_3)_2^{3+}$ -Ti(III) Reaction ($I = 1.0\text{ M}$)

$[\text{H}^+]$, M	$[\text{Cl}^-]$, M	$10^3 k_2(\text{obsd})$, $\text{M}^{-1}\text{ s}^{-1}$	$10^3 k_2(\text{calcd})$, $\text{M}^{-1}\text{ s}^{-1}$
1.0	0.0	3.2	3.1
1.0	0.7	18.4	18.1
1.0	1.0	20.0	19.5
0.8	1.0	23.7	23.3
0.4	1.0	43.4	42.5
0.2	1.0	81.1	80.9

^a Using eq 2, $K_1 = 4\text{ M}^{-1}$, $k_a = 6.28 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$, $k_b = 3.69 \times 10^6\text{ M}^{-1}\text{ s}^{-1}$, $k_c = 5 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$.

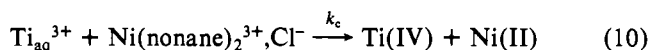
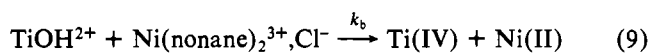
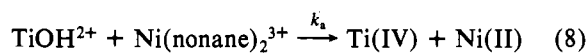
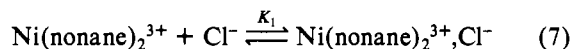
constants for the aquonickel(III) macrocyclic complexes^{2,23} are low ($\text{p}K_a \approx 4$). A mechanism consistent with the data may then be expressed as shown by eq 4–6, from which eq 3 may



be derived where $k_0 \approx 0$. Only in relatively few investigations^{7a,12,24} has the acid-independent path (k_0) been observed, and in such instances k_0 is usually about 2 orders of magnitude less than k_1 . In the present study only the reaction involving the bis(triazanonane) ligand in chloride media exhibits an acid-independent step. In all other cases the intercepts of plots of k_{obsd} against $[\text{H}^+]^{-1}$ do not vary statistically from zero. In this regard the reactions are similar to those involving ruthenium(III)¹⁴ and cobalt(III) ammine²⁴ complexes and those with poly(pyridine)cobalt(III) ions.^{7b,9b}

Reactions of Bis(triazanonane)nickel(3+). Over the range $[\text{H}^+] = 0.2\text{--}1.0\text{ M}$, the rate profile is consistent with the mechanism proposed (eq 3). In this system, where there is no dissociation of the metal–nitrogen bonds in either of the oxidation states, the electron transfer proceeds via an outer-sphere process and the inverse acid dependence may be ascribed directly to hydrolysis of the titanium(III). Previous studies²⁵ using this nickel(III) complex are consistent with a self-exchange rate of $\sim 6 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$, and this value has been used in the evaluation of a Marcus correlation.

Although in many instances chloride media have been used for Ti(III) studies owing to difficulties with perchlorate ion, in general, little difference in rate has been observed in comparison with similar investigations in trifluoromethanesulfonate (tfs^-) media. The stability constant for TiCl_2^{2+} formation is low ($\sim 0.07\text{ M}$).²⁶ We have carried out some reactions in a variety of tfs^-/Cl^- conditions ($I = 1.0\text{ M}$), and in contrast with the data in the absence of Cl^- , a positive intercept is observed in the k_{obsd} vs. $[\text{H}^+]^{-1}$ plot (Figure 1). This may be interpreted as arising from reaction of the ion pair $\text{Ni}(\text{nonane})_2^{3+}, \text{Cl}^-$ with the reductant (eq 7–10). With use of this reaction scheme,



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which includes a contribution from the oxidation via the unassociated cation, the second-order rate constant, k'_{obsd} , may be expressed as in eq 11. From a knowledge of k_a and K_a ,

$$k'_{\text{obsd}} = \{(K_a/[\text{H}^+])(k_a + k_b K_1[\text{Cl}^-]) + k_c K_1[\text{Cl}^-]\} / (1 + K_1[\text{Cl}^-]) \quad (11)$$

an iterative procedure was used to evaluate the rate constants k_b and k_c . The best fit of the data was achieved with $K_1 \approx 4\text{ M}^{-1}$. This value is close to that calculated²⁷ by using an ionic radius for the cation of $\sim 8\text{ \AA}$ and is similar to those derived previously from $\text{ML}_6^{3+}, \text{Cl}^-$ ion pairs. With use of eq 11 and the rate constants $k_a = 6.28 \times 10^5\text{ M}^{-1}\text{ s}^{-1}$, $k_b = 3.69 \times 10^6\text{ M}^{-1}\text{ s}^{-1}$, and $k_c = 5 \times 10^3\text{ M}^{-1}\text{ s}^{-1}$, calculated and experimental data for the chloride ion reactions are presented in Table II. Anion-assisted catalysis of some $\text{Co}^{\text{III}}\text{N}_6^{3+}$ outer-sphere reactions has been described.²⁸ In that report arguments were presented favoring symmetry considerations for the formation of precursor complexes, although the anion was coordinated to the reductant. In the present work an increase in rate of the same order of magnitude is reported for the chloride ion catalysis. Clearly a more extensive study is required before realistic discussion can take place. It is of interest, however, that the pathway (10) involving the ion pair with the titanium(III) aquo ion is now observed. Some enhancement of rate would also be expected if in the transition state the chloride ion is σ bonded to one $3+$ metal center and remotely associated with a second, although direct bonding as in an inner-sphere system would lead to even higher rates.

Reactions of Other Nickel(III) Complexes. In all cases, it is assumed that the predominant form of these species is a six-coordinate ion, with the axial sites occupied by water molecules. This d^7 ion is expected to show pseudooctahedral geometry, and in acetonitrile there is evidence of axially coordinated solvent in the Ni(III) macrocycles.⁴ Although studies on the rates of solvent exchange for Ni(III) species of this type are limited,²⁹ rate constants of $\sim 10^3\text{ M}^{-1}\text{ s}^{-1}$ have been obtained from studies of the substitution by halide ions. With use of $K_a \approx 5 \times 10^{-3}\text{ M}$ (eq 4), electron-transfer rate constants for all the macrocyclic ligand complexes in this study lie in the range $\sim 10^6\text{--}10^7\text{ M}^{-1}\text{ s}^{-1}$. It is thus assumed that these reactions are outer sphere and that the products are $\text{Ni}(\text{L})(\text{H}_2\text{O})_2^{2+}$, which then relax rapidly by loss of the axial solvent molecules to the familiar square-planar nickel(II) ions.

Marcus Theory Correlations. The Marcus theory¹³ affords the possibility of correlating free energy changes with kinetic data, and its applicability to a variety of bimolecular electron-transfer reactions has been well established.^{3,30,31} The general expression may be written as

$$\Delta G^*_{12} = \frac{\lambda}{4} \left(1 + \frac{\Delta G^\circ_{12}}{\lambda} \right)^2 \quad (12)$$

where λ represents the free energy required for solvent reorganization in the outer and inner coordination spheres of the reactants. It is known,³² however, that under very exothermic conditions ($-\Delta G^\circ_{12} \geq \lambda$) this equation loses its validity. Equation 12 does not include work terms. In a recent modification of the theory,³³ the rate constant for the cross-reaction, k_{12} , is related to the component exchange reactions

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Table III. Outer-Sphere Rate Data for Reactions of TiOH^{2+} with a Variety of Oxidants^b

no.		k_{22} , $\text{M}^{-1} \text{s}^{-1}$	E° , V	ΔG° , kcal mol^{-1}	\ln $(k_{22}K_{12}f_{12})^i$	$k_{12}(\text{exptl})$, $\text{M}^{-1} \text{s}^{-1}$	$k_{12}(\text{calcd})^j$, $\text{M}^{-1} \text{s}^{-1}$	$\ln k_{12} - \ln$ W_{12}
1	Ni(cyclam) ³⁺	2×10^3 ^a	0.960 ^a	-23.98	40.07	1.59×10^6	3.7×10^7	14.01
2	Ni(Me ₂ cyclam) ³⁺	4.4×10^3 ^a	0.970 ^a	-24.21	40.99	1.65×10^6	5.8×10^7	14.02
3	Ni ^{IV} oxime	6×10^4 ^f	0.660 ^a	-17.06	35.53	2.66×10^5	4.2×10^6	11.79
4	Ni(triazanonane) ₂ ³⁺	6×10^3 ^g	0.947 ^b	-23.68	40.73	6.74×10^5	5.1×10^7	12.96
5	Ni(tet-c) ³⁺	31 ^h	1.240 ^a	-30.44	42.90	2.74×10^6	6.5×10^7	14.52
6	Ni(Me ₂ diene) ³⁺	3×10^3 ^c	1.010 ^c	-25.14	41.56	7.40×10^5	2.0×10^8	13.23
	Ni(cyclam)Cl ₂ ⁺	6.5 ^b	0.740 ^b	-18.91		2.5×10^5		
	Ni(Me ₂ cyclam)Cl ₂ ⁺	4.2 ^b	0.795 ^b	-20.18		6.26×10^5		
7	Co(phen) ₃ ³⁺	40 ^d	0.370 ^d	-10.38	19.83	1.64×10^2	1.9×10^3	4.77
8	Ru(NH ₃) ₆ py ³⁺	4.3×10^5 ^e	0.305 ^e	-8.88	26.74	3.72×10^3	6.0×10^4	7.88
9	Ru(NH ₃) ₃ ³⁺	4.3×10^3 ^e	0.051 ^e	-3.02	13.34	3.72×10^1	7.8×10^1	3.29
10	Os(bpy) ₃ ³⁺	2×10^9 ^e	0.820 ^e	-20.75	48.35	1.95×10^7	1.9×10^9	16.40
11	Os[4,4'-(CH ₂) ₂ bpy] ₃ ³⁺	2×10^9 ^e	0.630 ^e	-16.37	43.96	3.72×10^6	2.7×10^8	14.74

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k_{11} and k_{22} and to the equilibrium constant for the reaction K_{12} by the expression

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

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4 \left[\ln \left(\frac{k_{11}k_{22}}{A_{11}A_{22}} \right) + \frac{w_{11} + w_{22}}{RT} \right]} \quad (14)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (15)$$

$$w_{ij} = Z_i Z_j e^2 / [D_s \sigma_{ij} (1 + \beta \sigma_{ij} l^{1/2})] \quad (16)$$

$$A_{ii} = \left[\frac{4\pi N \sigma^2 v_n \delta r}{1000} \right]_{ii} \quad (17)$$

w_{ij} represents the work required to bring together ions i and j (charges Z_i, Z_j) to the separation distance σ_{ij} ($=r_i + r_j$), and $\beta = (8\pi N e^2 / 1000 D_s k T)^{1/2}$. The nuclear vibration frequency which destroys the activated complex configuration³⁵ is designated ν_n , and δr is the thickness of the reaction layer. A value of $3 \times 10^{10} \text{ M}^{-1} \text{ \AA}^{-2} \text{ s}^{-1}$ has been used³³ for the value of A/σ^2 .

Many of the self-exchange parameters for systems under investigation are available. For the nickel(II/III) complexes with macrocyclic ligands, a rate constant of $\sim 1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ has been reported³⁴ for Ni(cyclam)^{2+/3+} exchange, and a similar value has been used for the dimethylcyclam complex. In the case of the *rac*-(Me₆[14]janeN₄) complex the value used is $31 \text{ M}^{-1} \text{ s}^{-1}$.³⁰ Endicott³ has also reported a value of $\sim 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for the Ni^{II/III}(Me₂diene) system. Details of other couples are provided in the footnotes to Table III. From a plot of $\log k_{12} - \log W_{12}$ against $\log k_{22}K_{12}f_{12}$ a line of slope 0.5 is anticipated with an intercept corresponding to $1/2 \log k_{11}$, the self-exchange rate for the $\text{TiOH}^{2+/3+}$ couple. With use of the data from the present investigation, together with those from other studies,¹² the plot shown in Figure 2 has been made. Good linearity with slope 0.39 ± 0.02 is observed over a very wide range of driving force. The interpolated value of k_{11} ($9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) is in excellent agreement with that obtained previously by Sutin.¹² Although many of these reactions are exothermic, they conform to the "normal" free energy region for electron transfer³¹ ($-\lambda < \Delta G^\circ_{12} < \lambda$). In the reaction with Ni^{III}(cyclam)³⁺, for example, using $k = 10^{11} e^{-\Delta G^\circ/RT}$ gives $\lambda = 65.5 \text{ kcal mol}^{-1}$, which may be compared

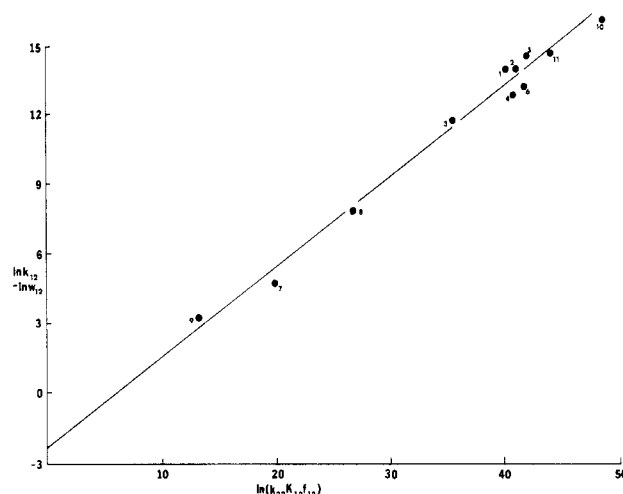


Figure 2. Plot of $\ln k_{12} - \ln W_{12}$ against $\ln (k_{22}K_{12}f_{12})$ (eq 13). Numbers refer to reactants in Table III.

with the overall free energy change of $\sim 24 \text{ kcal mol}^{-1}$.

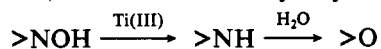
One feature of the Marcus relationship is that it enables estimates to be made of unknown self-exchange rate constants. Owing principally to the difficulty in defining accurately conditions where only Ni^{II}Cl₂ is present in solution, there is no value available for the self-exchange of the dichloro derivatives. Since the rates of substitution of Cl⁻ at Ni^{III}(cyclam)³⁺ and Ni^{III}(dimethylcyclam)³⁺³⁵ are $> 10^2$ less than the rates of reduction by TiOH^{2+} obtained in the present study, it may be assumed that the reactions proceed via an outer-sphere process. (In this regard it is perhaps interesting to note that the corresponding reaction with *trans*-Co(en)₂Cl₂⁺ has also been postulated as outer sphere.^{9b}) With use of the measured rates for the NiLCl₂⁺ + TiOH^{2+} reactions (Table I) and on the assumption that these nickel(III) complexes react in a manner similar to that for the others studied in that they fall close to the Marcus line in Figure 2, values of $k_{11} = 3.4 \times 10^4$ and $9.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ have been obtained for the cyclam and dimethylcyclam complexes, respectively. These constants are slightly greater than those obtained ($\sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$) for the diaquo complexes. X-ray crystallographic data are available for both the Ni(II)- and Ni(III)-dichloro(cyclam) species.³⁶ Different bond length changes are observed in the

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axial and equatorial positions: $\Delta d(\text{Ni}-\text{Cl}) = 0.04 \text{ \AA}$ and $\Delta d(\text{Ni}-\text{N}) = 0.088 \text{ \AA}$. The contribution of bond rearrangement to the intrinsic factors in electron transfer is well-known. The Ni(II/III) exchange involves the transfer of a $d\sigma^*$ electron between the high-spin d^8 Ni(II) and the low-spin d^7 Ni(III). The relatively small changes in the bond length, especially for the Ni-Cl bonds, may favor a more rapid electron transfer. Unfortunately there are at present very few well-characterized Ni(II/III) couples that retain octahedral symmetry. The exchange rate for Ni(nonaneN₃)₂^{3+/2+} has been determined¹⁷ as $6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. In the Ni(bpy)₃^{2+/3+} system, where bond extensions are believed to be of the order of $\sim 0.1 \text{ \AA}$, $k_{11} \approx 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. (In the hexadentate Ni(IV/III) oxime system, where $\Delta d(\text{Ni}-\text{N})$ values are similar, $k_{11} \approx 6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).

Although Ti(III) in chloride media is known to reduce oximes to imines,³⁷ which are further hydrolyzed to carbonyls



there is no evidence of any reaction of this type with the coordinated oxime.

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Conclusion

Evidence has been presented for an outer-sphere mechanism in the reduction of various nickel(III) (and one Ni(IV)) complexes by Ti(III). Estimates have been made of the self-exchange rates of NiLCl₂⁺⁰ couples (L = saturated macrocycle), and despite a large driving force for these reactions adherence is observed with the Marcus correlation.

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Registry No. Ti, 7440-32-6; Ni(cyclam)³⁺, 72360-42-0; Ni(Me₂cyclam)³⁺, 90413-06-2; Ni(oxime)²⁺, 55188-33-5; Ni(nonaneN₃)₂³⁺, 90413-07-3; Ni(tet-c)³⁺, 79329-59-2; Ni(Me₂diene)³⁺, 90413-08-4; Ni(cyclam)Cl₂⁺, 60105-34-2; Ni(Me₂cyclam)Cl₂⁺, 90413-09-5.

Supplementary Material Available: Tables of rate constants giving details of hydrogen ion and other concentration dependences (8 pages). Ordering information is given on any current masthead page.

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Reactions of Rhodium Trifluoroacetate with Various Lewis Bases. Formation of 4:1 Complexes with Pyridine and *tert*-Butyl Isocyanide and Rhodium-Rhodium Bond Cleavage with Phosphorus Donors

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The title compound was reacted with Lewis bases tetrahydrofuran (THF), dimethyl sulfoxide (Me₂SO), *N,N*-dimethylformamide (DMF), piperidine, pyridine, *N*-methylimidazole, acetonitrile, *tert*-butyl isocyanide, triphenylphosphine, triphenyl phosphite, dimethylphenylphosphine, and trimethyl phosphite. With THF, Me₂SO, acetonitrile, and P(OPh)₃, adducts were formed with axial ligands in analogy to previously reported Rh₂(O₂CR)₄L₂ complexes. However, for the other nitrogen donors and isocyanide, equatorial adduct formation occurred in solution followed in the case of piperidine and *N*-methylimidazole by decomposition. With pyridine and *t*-BuNC, 4:1 adducts were isolated constituting a new type of metal-metal bonded complex. Reaction with PMe₂Ph, PPh₃, and P(OMe)₃ resulted in dimer cleavage to give monomeric Rh(I) and Rh(III) products that were isolated for the latter two bases. IR and ¹⁹F, ¹H, and ³¹P NMR spectroscopies were used to characterize the complexes. These methods can distinguish between mono- and bidentate CF₃CO₂⁻ coordination. Comparison with earlier studies of the Mo₂(O₂CCF₃)₄ and Rh₂(O₂CCH₃)₄ systems shows the changes in reactivity that occur when the metals or carboxylate ligands are changed in these metal carboxylate dimers. Phosphorus donors do not cleave the Mo-Mo bond in Mo₂(O₂CCF₃)₄. Only 2:1 axial adducts with pyridine, *t*-BuNC, and P(OMe)₃ are formed with Rh₂(O₂CCH₃)₄.

Introduction

Metal carboxylate dimers have been widely studied.¹ These systems are of interest since they provide excellent models to study metal synergism. Because of the wide variety of metals that form metal carboxylate dimers, the chemistry of the metal-metal bond can be probed as a function of the d-electron population. One area in which a synergistic influence from metal-metal bonding has been established is in the affinity of the metal dimer for Lewis bases. In previous studies from this laboratory,² the coordination of ligands to the termini of the metal-metal axis in the Rh₂(O₂CR)₄ and Mo₂(O₂CR)₄ systems was studied. The metal-metal interaction in the dirhodium complex was found to lead to a very effective metal to ligand π -back-bonding interaction. Variation in the bridging carboxylate was also shown to have an effect on the metal-

ligand bond strength. The comparison of the rhodium to the molybdenum system is of particular interest since in Mo₂(O₂CR)₄ a quadruple bond exists while in Rh₂(O₂CR)₄ there is a single bond.³⁻⁵ In the rhodium system, the LUMO is the σ^* orbital and the filled π^* plays an important role in the chemistry of this system.² With a stronger metal-metal in-

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