Inorg. Chem. **1985**, *24*, 4187–4191

$\mathrm{(CO)_2L]PF_6}$ to yield the low-valent $\mathrm{Re_2^{3+}}$ core probably leads to increased π-back-donation from the metal centers to the carbonyl ligands and would be expected to result in a lowering in energy of the ν(CO) modes.

Acknowledgment. Support from the National Science Foundation (Grant No. CHE82-11407 to F.A.C. and Grant No. 82-06117 to R.A.W.) is gratefully acknowledged. We thank Stephen M. Tetrick for considerable help in the measurement of the NMR spectra and Edwar Shamshoum for assistance with crystal preparation.

Registry No. $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]PF_6{\cdot}CH_2Cl_2{\cdot}0.5Et_2O}$, 98919-87-0; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]PF_6}$, 98838-38-1; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]}$, 98838-46-1; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(CH_3CN)]PF_6}$, 98838-36-9; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(CH_3CN)]}$, 98838-45-0; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(C_6H_5CN)]PF_6}$, 98838-40-5; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(C_6H_5CN)]}$, 98838-47-2; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(Me_2CHNC)]PF_6}$, 98838-42-7; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(Me_2CHNC)]}$, 98838-48-3; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(Me_3CNC)]PF_6}$, 98838-44-9; $\mathrm{[Re_2Cl_3(dppm)_2(CO)_2(Me_3CNC)]}$, 98857-68-2; $\mathrm{Re_2Cl_4(dppm)_2(CO)_2}$, 96306-80-0; cobaltocene, 1277-43-6.

Supplementary Material Available: Full tables of bond distances and bond angles, anisotropic displacement parameters, and structure factors (30 pages). Ordering information is given on any current masthead page.

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Disproportionation of Nickel(III) Bis(oxime imine) Complexes

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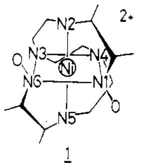
The kinetics of the redox equilibrium Ni(IV) + Ni(II) $\rightleftharpoons$ 2Ni(III) have been studied for nickel complexes of a bis(oxime imine) ligand system, $\mathrm{LH_2}$, as a function of pH. Above pH 5, reductions of $\mathrm{Ni^{IV}L^{2+}}$ by $\mathrm{Ni^{II}L}$, $\mathrm{Ni^{II}LH^+}$, and $\mathrm{Ni^{II}LH_2^{2+}}$ take place with second-order rate constants 1.24×10^6, 3.8×10^3, and 3.5×10^2 $\mathrm{M^{-1}\,s^{-1}}$, respectively. Below pH 5, disproportionation of nickel(III) is dominated by the reaction of $\mathrm{Ni^{III}L^+}$ with $\mathrm{Ni^{III}LH^{2+}}$, which has a second-order rate constant of 3.4×10^3 $\mathrm{M^{-1}\,s^{-1}}$. At very low pH, where the concentration of $\mathrm{Ni^{III}L^+}$ is very small, disproportionation of $\mathrm{Ni^{III}LH^{2+}}$, though thermodynamically favored, is slow. This reflects the inability of $\mathrm{Ni^{IV}L^{2+}}$ to support protonation. The electron-transfer reactions are outer-sphere in nature and are discussed in terms of Marcus theory.

Introduction

Over the past few years, interest has developed in the mechanistic chemistry of the nickel(IV) complexes[1,2] $\mathrm{Ni^{IV}L^{2+}}$ (**1**), where $\mathrm{LH_2}$ is the sexidentate ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (**2**). This complex is readily and reversibly reduced to the nickel(II) complex $\mathrm{Ni^{II}LH_2^{2+}}$, and the kinetics and mechanisms of reductions by a variety of one-[3-7] and two-electron[8-10] reagents have been examined. Oxidations of $\mathrm{Ni^{II}LH_2^{2+}}$ have also been reported.[11-13]



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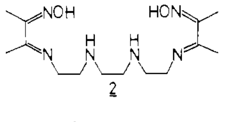

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A consistent feature of these studies is the participation of nickel(III) intermediates in the reactions. These intermediates are thermodynamically stable above pH 5 but below this value disproportionate to form nickel(IV) and nickel(II) complexes. A knowledge of the kinetics of these disproportionation–comproportionation processes is important in understanding the chemistry of the nickel(III) intermediates and their role in the nickel(IV)–nickel(II) redox interconversion.

In this paper, the kinetics and mechanisms of disproportionation of nickel(III) over the pH range 1–4 and the reduction of nickel(IV) by nickel(II) over the pH range 4–10 are investigated. The results are discussed in terms of Marcus theory,[14] and comparisons are made with other electron-transfer reactions of these nickel complexes.

Experimental Details

Materials. The compounds $\mathrm{Ni^{IV}L(ClO_4)_2}$ and $\mathrm{Ni^{II}LH_2(ClO_4)_2}$ were prepared as outlined previously.[1,3] Solutions of nickel(IV) were standardized spectrophotometrically with use of literature absorption coefficients (ϵ_{500} = 6300 $\mathrm{M^{-1}\,cm^{-1}}$) while nickel(II) solutions were prepared by dissolving accurately weighed amounts of the crystalline solid. The nickel(III) complex $\mathrm{Ni^{III}L^+}$ was generated by electrochemical means[3] or more simply by mixing equimolar amounts of $\mathrm{Ni^{IV}L^{2+}}$ and $\mathrm{Ni^{II}L}$ at pH >5. Samples of the complex $\mathrm{Ni^{II}((\mathit{S})\text{-}Me_2LH_2)(ClO_4)_2}$, where ($S$)-$\mathrm{Me_2LH_2}$ is (5S,12S)-4,7,10,13-tetraaza-3,5,12,14-tetramethylhexadeca-3,13-diene-2,15-dione dioxime, were prepared as outlined previously.[4] The nickel(IV) complex $\mathrm{Ni^{IV}((\mathit{S})\text{-}Me_2L)^{2+}}$ was obtained by oxidation of $\mathrm{Ni^{II}((\mathit{S})\text{-}Me_2LH_2)^{2+}}$ in aqueous solution with a stoichiometric amount of $\mathrm{Na_2IrCl_6}$ (Aldrich), followed by elution of the solution through an anion-exchange column (Amberlite CG-400, perchlorate form) to remove the $\mathrm{IrCl_6^{3-}}$ formed.

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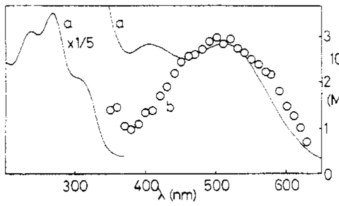

Figure 1. Absorption spectra of (a) $Ni^{III}L^+$ at pH 5.0 and (b) $Ni^{III}LH^{2+}$ at pH 1.0 in aqueous solution, 25 °C, and 0.1 M ionic strength.

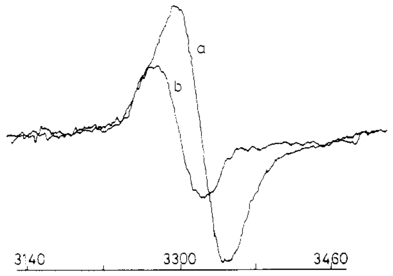

Figure 2. Electron paramagnetic resonance spectra of (a) $Ni^{III}L^+$ at pH 4.5 and (b) $Ni^{III}LH^{2+}$ at pH 1.0, 10 min after acid addition, in aqueous solution, 23 °C, and 0.1 M ionic strength. Spectra were run under comparable instrument settings with a microwave frequency of 9.159 GHz. Field settings are in gauss.

The buffers *N*-(2-hydroxyethyl)piperazine-*N'*-ethanesulfonic acid (hepes, Sigma), monochloroacetate, acetate, and borate (Baker Analyzed) were used without further purification. Sodium perchlorate was prepared by neutralizing sodium carbonate with perchloric acid (Baker Analyzed) and was recrystallized from water.

Methods. Kinetic measurements were made in 1.0×10^{-2} M buffer solutions at 0.10 M ionic strength with use of $NaClO_4$ as background electrolyte. Reactions were monitored with a Durrum D-110 stopped-flow spectrophotometer thermostated at 25.0 ± 0.1 °C. Data were collected with a Nicolet 3091 digital oscilloscope. The pH of solutions was monitored immediately after reaction with a Beckman SelectIon 2000 meter equipped with a Corning combination glass electrode with saturated calomel (NaCl) reference. Hydrogen ion concentrations were evaluated with use of the relationship $-\log [H^+] = pH - 0.02$, correcting for both hydrogen ion activity and liquid-junction potential.

Reduction of $Ni^{IV}L^{2+}$ by nickel(II) was monitored at 360 nm, where there is an increase in absorbance due to nickel(III). Under pseudo-first-order conditions with [nickel(II)] in excess, plots of log $(A - A_\infty)$ against time were linear for 3 or more half-lives and the observed rate constants, k_{obsd}, were evaluated from the slopes by least-squares analysis with an Apple II+ computer. Disproportionation of nickel(III) was monitored at 420 nm, where the extinction coefficient of $Ni^{III}LH^{2+}$ (1500 M^{-1} cm^{-1}) is significantly different from half the $Ni^{IV}L^{2+}$ value (5960 M^{-1} cm^{-1}). The complex $Ni^{II}LH_2^{2+}$ has negligible absorbance at this wavelength. Rate constants were obtained from initial rates, which were determined from linear plots of absorbance against time for the initial part of the reaction. The apparent change in molar extinction coefficient varies with pH due to deprotonation of the nickel(III) complex with $pK_H = 4.05$[3] and was calculated with use of $\epsilon_{420} = 2600$ M^{-1} cm^{-1} for $Ni^{III}L^+$. Solutions of $Ni^{III}L^+$, prepared unbuffered at pH 6-7, were reacted with buffered solutions in the pH range 1-4. Reduction of $Ni^{IV}((S)\text{-}Me_2L)^{2+}$ by $Ni^{III}L^+$ at pH ~7 was examined at 500 nm, where there is a significant difference in the extinction coefficients of the nickel(IV) and nickel(III) species.[4]

Electron paramagnetic resonance spectra were run in aqueous solutions at room temperature (23 °C) with a Varian E-102 spectrometer equipped with a 9-in. magnet. The spectrometer was calibrated with DPPH.

Results

(a) Disproportionation of Nickel(III), pH 1-4. Solutions of $Ni^{III}L^+$ are thermodynamically stable above pH 5 and are readily prepared by mixing equimolar amounts of $Ni^{IV}L^{2+}$ and $Ni^{II}L$. A visible spectrum of $Ni^{III}L^+$ is shown in Figure 1. An EPR spectrum of an aqueous solution of $Ni^{III}L^+$ is shown in Figure 2. The g_{av} value is 2.095 and is invariant with pH from 4.5 to 9.0.

When solutions of $Ni^{III}L^+$ are acidified below pH 4, the visible spectrum changes to that of $Ni^{III}LH^{2+}$ (Figure 1), and over a period of time, disproportionation giving $Ni^{IV}L^{2+}$ and $Ni^{II}LH_2^{2+}$ takes place. No further protonation of $Ni^{III}LH^{2+}$ is noted above pH 1.

Table I. Initial Rate Data for the Disproportionation of Nickel(III) at 25 °C and 0.1 M Ionic Strength

pH[a]	$10^4[Ni(III)]_0$, M	10^7k_{IR},[b] M s^{-1}	k_{so},[c] M^{-1} s^{-1}
1.10	1.73	3.3	11
1.13	0.23	0.12	23
1.16	0.93	1.8	21
1.17	2.33	9.8	18
1.20	2.24	9.3	19
1.26	1.92[d]	9.3	25
1.33	2.18[e]	13.3	28
1.47	1.92[d]	16.2	44
1.63[f]	1.73	9.2	31
1.68	2.11	19.2	43
1.68[g]	2.14	6.4	14
1.80[f]	1.73	9.8	33
1.87	1.92[d]	26	70
2.17	2.28	47	90
2.23	1.92[d]	54	150
2.29[f]	1.73	26	88
2.47	1.92[d]	87	240
2.57[f]	1.73	77	260
2.67[f]	2.28	155	300
2.74[f]	1.73	123	420
3.09[f]	1.73	211	700
3.10[f]	0.11	0.82	740
3.17[f]	0.42	12	680
3.19[f]	1.05	82	740
3.19[f]	1.73	244	810
3.41[f]	1.73	340	1140
3.42[f]	1.73	350	1170
3.58[f]	1.73	380	1020

[a] $HClO_4$. [b] Initial rate in concentration units. [c] Second-order rate constant evaluated from k_{IR} divided by $[Ni(III)]_0^2$ from column 2. [d] 2.0×10^{-4} M Ni(II) added. [e] 6.0×10^{-4} M Ni(II) added. [f] 0.01 M $[ClCH_2CO_2H]_T$. [g] 98% $DClO_4$ ($[D^+] = 0.022$ M).

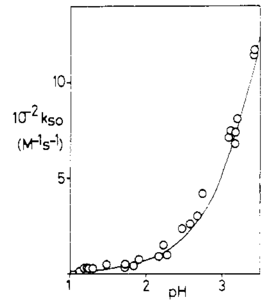

Figure 3. Plot of the second-order rate constant for disproportionation of nickel(III) as a function of pH at 25.0 °C and 0.1 M ionic strength. The solid line is calculated by using the rate law (5) and parameters given in the text.

Solution EPR data confirm a change in species. When a solution of $Ni^{III}L^+$ is made acidic (pH 1), a signal with $g_{av} = 2.112$ is detected (Figure 2). Initially this is comparable in intensity with the signal from $Ni^{III}L^+$ but disappears over a period of time as the disproportionation proceeds. These solution EPR studies confirm the nature of species detected in frozen-matrix[2,3] and single-crystal studies.[15]

The rate of the disproportionation reaction is dependent on pH. At low pH, where the reaction is most thermodynamically favored, the reaction is slow, and the latter stages are complicated by the decomposition of the nickel(IV) product in the presence of nickel(II). Initial rate studies were employed to circumvent this problem, and plots of initial rate, k_{IR}, against $[Ni(III)]_0$ at both pH 1.2 and pH 3.2 show a dependence that is second-order in the complex (Table I). The reaction is unaffected by added $Ni^{II}LH_2^{2+}$ but increases in rate with increasing pH. A plot of the second-order rate constant, obtained from initial rate data, as a function of pH is shown in Figure 3.

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Table II. Pseudo-First-Order Rate Constants for the Comproportionation Reactions of Ni(II) and Ni(IV) at 0.10 M Ionic Strength and 25 °C

pH	10^5[Ni(II)], M	10^5[Ni(IV)], M	k_{obsd}, s^{-1}	k_{so}, M^{-1} s^{-1}
4.66[a]	17.5	0.53	0.102 ± 0.013	5.83×10^2
4.67[a]	52.6	1.58	0.267 ± 0.003	5.08×10^2
4.86[a]	17.5	0.53	0.129 ± 0.002	7.34×10^2
5.02[a]	17.5	0.53	0.165 ± 0.005	9.43×10^2
5.32[a]	17.5	0.53	0.304 ± 0.003	1.74×10^3
5.32[a]	17.5	0.53	0.336 ± 0.009	1.92×10^3
5.76[a]	17.5	0.53	1.31 ± 0.02	7.49×10^3
6.15[a]	17.5	0.53	2.34 ± 0.02	1.34×10^4
6.18[b]	17.6	0.63	1.66 ± 0.04	9.49×10^3
6.23[a]	17.5	0.53	3.83 ± 0.09	2.19×10^4
6.39[b]	17.6	0.53	4.3 ± 0.2	2.43×10^4
6.85[b]	17.6	0.53	10.1 ± 0.3	5.78×10^4
7.18[b]	17.6	0.53	24.9 ± 0.1	1.43×10^5
7.38[b]	18.9	1.2	44.1 ± 1.4	2.34×10^5
7.73[b]	18.9	1.2	77 ± 1	4.06×10^5
7.91[b]	18.9	1.2	101 ± 1	5.33×10^5
7.98[b]	10.2	1.06	66 ± 1	6.47×10^5
8.00[b]	25.5	1.06	176 ± 5	6.90×10^5
8.01[b]	15.3	1.06	92 ± 2	6.05×10^5
8.21[b]	18.9	1.2	147 ± 3	7.77×10^5
8.47[b]	18.9	1.2	187 ± 3	9.92×10^5

[a] 10^{-2} M acetate buffer. [b] 10^{-2} M hepes buffer.

Analysis of the initial rate data is based on the distribution of nickel(III) species in solution. Protonation of $Ni^{III}L^+$ takes place around pH 4[3] (eq 1). Second-order pathways can result from

$$Ni^{III}LH^{2+} \rightleftharpoons Ni^{III}L^+ + H^+ \quad K_H \tag{1}$$

reactions of any two nickel(III) species (eq 2–4). The corresponding rate law, eq 5, provides a good fit to the experimental points with $k_1 = 4 \pm 4$ M^{-1} s^{-1}, $k_2 = (3.4 \pm 0.5) \times 10^3$ M^{-1} s^{-1}, k_3 small and indeterminate, and $K_H = 9.3 \times 10^{-5}$ M.

$$2Ni^{III}LH^{2+} \rightarrow Ni^{II}LH_2^{2+} + Ni^{IV}L^{2+} \quad k_1 \tag{2}$$

$$Ni^{III}LH^{2+} + Ni^{III}L^+ \rightarrow Ni^{II}LH^+ + Ni^{IV}L^{2+} \quad k_2 \tag{3}$$

$$2Ni^{III}L^+ \rightarrow Ni^{II}L + Ni^{IV}L^{2+} \quad k_3 \tag{4}$$

$$k_{IR} = 2\frac{k_1[H^+]^2 + k_2K_H[H^+] + k_3K_H^2}{([H^+] + K_H)^2}[Ni(III)]_0^2 \tag{5}$$

(b) Reaction of Nickel(IV) with Nickel(II), pH 5–9. The complex $Ni^{IV}L^{2+}$ is readily reduced by $Ni^{II}L$, giving 2 equiv of $Ni^{III}L^+$. Under pseudo-first-order conditions with nickel(II) in excess, reduction of $Ni^{IV}L^{2+}$ is first order, and the observed rate constants (Table II) reflect a first-order dependence on [nickel(II)]. The pH dependence of the second-order rate constant is complex and is shown in Figure 4. Two protonations of $Ni^{II}L$ take place at pH 7.80 and 5.90[2] (eq 6 and 7), giving three pathways for electron transfer (eq 8–10). No protonation of $Ni^{IV}L^{2+}$ has been reported above pH 0. The resulting rate expression (eq 11) gives an excellent fit to the experimental data with $k_{-1} = (3.5 \pm 0.7) \times 10^2$ M^{-1} s^{-1}, $k_{-2} = (3.8 \pm 0.5) \times 10^3$ M^{-1} s^{-1}, $k_{-3} = (1.24 \pm 0.04) \times 10^6$ M^{-1} s^{-1}, $K_{H1} = (1.00 \pm 0.05) \times 10^{-8}$ M, and $K_{H2} = (1.39 \pm 0.05) \times 10^{-6}$ M.

$$Ni^{II}LH^+ \rightleftharpoons Ni^{II}L + H^+ \quad K_{H1} \tag{6}$$

$$Ni^{II}LH_2^{2+} \rightleftharpoons Ni^{II}LH^+ + H^+ \quad K_{H2} \tag{7}$$

$$Ni^{IV}L^{2+} + Ni^{II}LH_2^{2+} \rightarrow 2Ni^{III}LH^{2+} \quad k_{-1} \tag{8}$$

$$Ni^{IV}L^{2+} + Ni^{II}LH^+ \rightarrow Ni^{III}LH^{2+} + Ni^{III}L^+ \quad k_{-2} \tag{9}$$

$$Ni^{IV}L^{2+} + Ni^{II}L \rightarrow 2Ni^{III}L^+ \quad k_{-3} \tag{10}$$

$$k_{so} = \frac{k_{-1}[H^+]^2 + k_{-2}K_{H2}[H^+] + k_{-3}K_{H1}K_{H2}}{[H^+]^2 + K_{H2}[H^+] + K_{H1}K_{H2}} \tag{11}$$

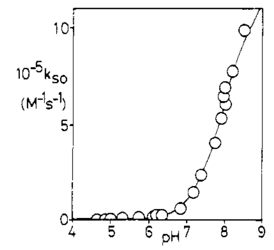

Figure 4. Plot of the second-order rate constant for reduction of nickel(IV) by nickel(II) as a function of pH at 25.0 °C and 0.1 M ionic strength. The solid line is calculated by using the rate law (11) and parameters given in the text.

Table III. Reduction Potentials of Nickel(IV) and Nickel(III) Complexes at 25 °C and 0.10 M Ionic Strength

	$E°$, V vs NHE
$Ni^{IV}L^{2+} + 2e^- + 2H^+ \rightleftharpoons 2Ni^{II}LH_2^{2+}$	0.94
$Ni^{IV}L^{2+} + e^- \rightleftharpoons Ni^{III}L^+$	0.65
$Ni^{III}L^+ + e^- \rightleftharpoons Ni^{II}L$	0.42
$Ni^{III}LH^{2+} + e^- \rightleftharpoons Ni^{II}LH^+$	0.64
$Ni^{III}LH_2^{3+} + e^- \rightleftharpoons Ni^{II}LH_2^{2+}$	1.07
$Ni^{III}LH^{2+} + e^- + H^+ \rightleftharpoons Ni^{II}LH_2^{2+}$	0.99
$Ni^{III}L^+ + e^- + 2H^+ \rightleftharpoons Ni^{II}LH_2^{2+}$	1.23

Discussion

(a) Disproportionation of Nickel(III). Between pH 1 and 4, disproportionation of nickel(III) is dominated by the reaction of $Ni^{III}L^+$ with $Ni^{III}LH^{2+}$. The rate of this process is 2 orders of magnitude faster than the rate of disproportionation of $Ni^{III}L^+$, k_3, determined in a previous study[4] to be 38 M^{-1} s^{-1}, and within the experimental uncertainty of the present work. This reactivity pattern has been observed in other reactions of nickel(III)[3,5] where $Ni^{III}LH^{2+}$ is reduced much faster than $Ni^{III}L^+$.

At low pH, disproportionation of the dominant nickel(III) species, $Ni^{III}LH^{2+}$, is slow with a second-order rate constant of 4 M^{-1} s^{-1}. Overall, the reaction (eq 2) is thermodynamically favored with a driving force around 0.06 V. However, electron transfer must be accompanied by a proton transfer; otherwise, the reaction products, $Ni^{II}LH^+$ and $Ni^{IV}LH^{3+}$, are thermodynamically disfavored. It seems likely that the low rate is related to the requirement for proton transfer; however, detailed studies are not possible as the faster reaction of $Ni^{III}L^+$ with $Ni^{III}LH^{2+}$ predominates even at pH 1.

Meyer and co-workers[16] have examined a similar proton-coupled electron transfer in the reaction of $[Ru(bpy)_2pyOH_2]^{2+}$ with $[Ru(bpy)_2pyO]^{2+}$. In this case second-order kinetics are obeyed and a large solvent isotope effect (k_{H_2O}/k_{D_2O}) of 16.1 indicates a possible limiting H atom transfer. The disproportionation reaction of $Ni^{III}LH^{2+}$ shows a small (<3) solvent isotope effect. An isotope effect of this magnitude might be expected if this were due to a shift in the acid dissociation constant, and while no conclusions can be drawn, a mechanism involving a contribution from H atom transfer seems unlikely in this instance.

(b) Reduction Potentials. A point worth noting is that the data at low pH reveal no evidence for the second protonation of nickel(III). Cyclic voltammetry studies indicate[2,3] that the reduction potentials of the nickel(IV) and nickel(III) complexes vary markedly with pH in accord with the values shown in Table III. The various pH-independent couples are dependent on a knowledge of the pK_H values of the metal ion complexes. Two protonations of $Ni^{II}L$ are detected in the pH range 0–14, at pH 5.90 and 7.80, while for $Ni^{III}L^+$, only one protonation has been recorded, pH 4.05, and for $Ni^{IV}L^{2+}$, no protonation takes place. However, McAuley and co-workers have estimated[12] a reduction potential for $Ni^{III}LH_2^{3+}$ based on the assumption that all Ni(III/II) self-exchange rates are of the order of 10^3 M^{-1} s^{-1}, and this leads to a

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Table IV. Evaluation of Self-Exchange Rates for Nickel Oxime Imine Complexes at 25.0 °C and 0.1 M Ionic Strength

	k_{12}, M^{-1} s^{-1}	k_{22}, M^{-1} s^{-1}	$E_2°$, V	ΔG_{11}^{**}, kcal mol^{-1}	k_{11}, M^{-1} s^{-1}
		(a) Reactions of $Ni^{IV}L^{2+}$			
$Ni(cyclam)^{2+}$	11.4[6]	1×10^{3}[18]	0.96[19]	8.5	6.2×10^{4}
$Co(edta)^{2-}$	36[4]	2×10^{-7}[20]	0.40[21]	8.8	3.5×10^{4}
$Co(5\text{-Cl-phen})_3^{2+}$	6.7×10^{4}[22]	1×10^{2}[23]	0.43[23]	9.4	1.4×10^{4}
$Co(phen)_3^{2+}$	3.2×10^{5}[3]	45[24]	0.37[25]	8.2	9.1×10^{4}
					av 4×10^{4}
		(b) Reactions of $Ni^{III/II}L^{+/0}$			
$Ni^{IV}L^{2+}$	1.24×10^{6}	4×10^{4}	0.65	9.8	6.8×10^{3}
$Cu(dpsmp)_2^{3-}$	3.8×10^{3}[5]	5×10^{6}[26]	0.62[5]	10.0	5.0×10^{3}
$Co(5\text{-Cl-phen})_3^{2+}$	1.67×10^{2}[27]	1×10^{2}[23]	0.43[23]	11.7	2.4×10^{2}
$Co(phen)_3^{2+}$	8.3×10^{2}[3]	45[24]	0.37[25]	10.9	1.0×10^{3}
					av 2×10^{3}
		(c) Reactions of $Ni^{III/II}LH^{2+/+}$			
$Ni^{IV}L^{2+}$	3.8×10^{3}	4×10^{4}	0.65	11.8	2.4×10^{2}
$Cu(dpsmp)_2^{3-}$	1.8×10^{5}[5]	5×10^{6}[26]	0.62[5]	11.6	3.3×10^{2}
$Co(5\text{-Cl-phen})_3^{2+}$	6.6×10^{3}[27]	1×10^{2}[23]	0.43	11.9	1.8×10^{2}
$Co(phen)_3^{2+}$	4.1×10^{4}[3]	45[24]	0.37[25]	10.5	1.9×10^{3}
					av 4×10^{2}
		(d) Reactions of $Ni^{II}LH_2^{2+}$[a]			
$Ni(bpy)_3^{3+}$	6.2×10^{6}[13]	1.5×10^{3}[13]	1.72[13]	13.4	15
$CoOH^{2+}$	1.8×10^{4}[11]	50[28]	1.44[28]	13.6	11
$Ru(bpy)_3^{3+}$	1.1×10^{6}[12]	4×10^{8}[29]	1.25[12]	14.1	4.1
$Fe(phen)_3^{3+}$	9.1×10^{4}[12]	3×10^{8}[30]	1.14[12]	14.6	1.9
$Fe(bpy)_3^{3+}$	3.2×10^{4}[12]	3×10^{8}[30]	1.09[12]	14.7	1.5
					av 4.5

[a] 1.0 M ionic strength.

second pK_H value for nickel(III) of −3 to −4.

This value seems rather extreme. Protonation is affected by external features such as charge and solvation and by internal features, the reorganization of bond lengths and angles. From the point of view of charge, addition of a proton to $Ni^{III}LH^{2+}$ relative to the neutral $Ni^{II}L$ is twice as difficult as the corresponding process with $Ni^{II}LH^{+}$ and consequently the second pK_H of nickel(III) should lie at least 2(7.80 − 5.90) = 3.80 pH units lower than the first nickel(III) pK_H. Protonation also weakens the Ni–N bonds in the complex, and hence, the pK_H depends on the strength of the Ni–N bond. This is apparent in the difference in pK_H values of $Ni^{III}LH^{2+}$ and $Ni^{II}LH_2^{2+}$, both similarly charged, which are 1.74 pH units apart. A reasonable estimate of the second pK_H of nickel(III) should be 3.80 + 1.74 pH units below the first as 4.05 and have a value around −1.50. This places the reduction potential of $Ni^{III}LH_2^{3+}$ as 1.07 V.

(c) Reduction of Nickel(IV) by Nickel(II). The reduction of $Ni^{IV}L^{2+}$ by nickel(II) is first-order in both reagents and shows a complex dependence on pH that is readily interpreted in terms of reactions of the different protonated forms of the reductant. Reactivity increases with the degree of nickel(II) deprotonation, in line with the thermodynamic driving force for the reactions. With use of the reduction potentials in Table III, values for the disproportionation rate constants k_2 and k_3 of 2.6×10^3 and 160 M^{-1} s^{-1} can be calculated. These are in reasonable agreement with the directly determined values.

Equation 8 is thermodynamically unfavorable and has a rate constant, k_{-1}, of 3.5×10^2 M^{-1} s^{-1}. The net reaction involves coupled proton and electron transfer. If the rate-limiting step in eq 8 is electron transfer, the immediate products are $Ni^{III}L^{+}$ and $Ni^{III}LH_2^{3+}$, and with use of the reduction potential of 1.07 V for the $Ni^{III/II}LH_2^{3+/2+}$ species, a rate constant of 4.5×10^9 M^{-1} s^{-1}, close to the diffusion limit (5×10^{10} M^{-1} s^{-1}) for reaction of $Ni^{III}LH_2^{3+}$ with $Ni^{III}L^{+}$, is evaluated. It should be noted that use of a potential of 1.23 V[12] for the couple leads to a rate in excess of the diffusion limit for the disproportionation reaction.

The higher valent nickel oxime imine complexes are relatively inert to substitution. For example, $Ni^{IV}L^{2+}$ will not dissociate even in concentrated HNO_3 and $Ni^{III}LH^{2+}$ disproportionates faster than the ligand dissociates in 1.0 M acid. It is likely that the electron-transfer reactions are outer-sphere in nature. Previous work from this and other laboratories[3-13] has attempted to rationalize electron-transfer rate data for those complexes with use of Marcus theory. Adherence to the Marcus equations provides not only evidence that the reactions are outer-sphere in nature but also a reasonable framework for discussion of the energetics of electron transfer.

(d) Marcus Considerations. Marcus theory[14] relates the rate of a cross reaction between two complexes, k_{12}, to the driving force for the reaction and the self-exchange rates for the individual reagents, k_{11} and k_{22}. It is conveniently expressed in free energy terms as eq 12 and 13, where ΔG^{**} represents an electrostatically

$$\Delta G_{12}^{**} = \tfrac{1}{2}(\Delta G_{11}^{**} + \Delta G_{22}^{**} + \Delta G_r^{0}(1 + \alpha^{**})) \quad (12)$$

$$\alpha^{**} = \Delta G_r^{0}/4(\Delta G_{11}^{**} + \Delta G_{22}^{**}) \quad (13)$$

corrected free energy of activation and ΔG_r is the electrostatically corrected free energy change. The electrostatic correction involves evaluation of work functions for the approach of charged reagents in the reaction medium.[17]

In Table IV are presented rate and thermodynamic data for various outer-sphere electron-transfer reactions of nickel(IV), -(III), and -(II) oxime imine complexes, together with the self-exchange rates for the nickel systems evaluated with use of eq 12 and 13. For each nickel system there is reasonable consistency

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Table V. Trans-N–N Distances (Å) for Nickel Oxime Imine Complexes

	$Ni^{IV}L^{2+}$	$Ni^{III}LH^{2+}$	$Ni^{II}LH_2^{2+}$
N(1)–N(3)	3.91	4.11	4.14
N(4)–N(6)	3.93	4.06	4.15
N(2)–N(5)	3.74	3.96	4.01

between the self-exchange rates calculated from different cross reactions.

The $Ni^{IV/III}L^{2+/+}$ self-exchange rate is 4×10^4 M^{-1} s^{-1}, which is in good agreement with previous estimates[3,4,12] and is 1 order of magnitude greater than the fastest of the nickel(III/II) self-exchange rates, that of $Ni^{III/II}L^{+/0}$. In an attempt to obtain an independent measure of the nickel(IV/III) self-exchange rate, the reduction of $Ni^{IV}((S)\text{-}Me_2L)^{2+}$ by $Ni^{III}L^+$ was examined at pH 7. The reaction is complicated because the oxidant is optically active and need not react with both optical isomers of the reductant at the same rate. Nevertheless, $Ni^{IV}((S)\text{-}Me_2L)^{2+}$ and $Ni^{IV}L^{2+}$ have similar reduction potentials and similar reactivities with other reagents. For example, the respective reduction rates by $Co(phen)_3^{2+}$ are 8.9×10^5 [31] and 3.2×10^5 M^{-1} s^{-1} [3] at 25 °C and 0.10 M ionic strength. The data[32] allow evaluation of the second-order rate constant for this pseudo-self-exchange process as $(6 \pm 1) \times 10^4$ M^{-1} s^{-1}, in remarkably good agreement with the calculated value.

All three of the complexes $Ni^{IV}L^{2+}$, $Ni^{III}L^+$, and $Ni^{II}L$ have similar structures, and comparisons of the nickel(IV/III) and -(III/II) self-exchange behavior are of interest. The effect of electrostatic repulsion between the reagents can be accounted for in the work terms and should enhance the (III/II) rate over that of (IV/III). It is not dominant in this comparison. More important may be the differences in electronic structure with a t_{2g}^6–$t_{2g}^6e_g^1$ change for $Ni^{IV/III}L^{2+/+}$ and a $t_2^6e_g^1$–$t_{2g}^6e_g^2$ change for $Ni^{III/II}L^{+/0}$, with use of, for simplicity, the nomenclature of an octahedral complex. Changes in electronic structure are frequently manifest in metal–ligand bond distances.[33] Accurate structural data are available for $Ni^{IV}L^{2+}$ and $Ni^{II}LH_2^{2+}$,[34] and limited data, trans-N–N bond distances, for $Ni^{III}LH^{2+}$ have also been reported.[15] To facilitate comparison, the trans-N–N bond distances for all three complexes have been calculated and are presented in Table V.

The complexes are related by changes in oxidation state and protonation, but it seems clear[35] that the structural rearrangement in the metal-bound nitrogen framework is greater in the case of Ni(IV/III) than in Ni(III/II). From these arguments it would appear that the order of the self-exchange rates is anomalous. However, other factors require consideration. Complexes where the metal ion is in a high oxidation state may possess some "noninnocent", ligand character where part of the metal ion charge is delocalized over the ligand chromophore. Thus changes in the ligand backbone that occur during the redox process may be important. No data on nickel(III) species are available, but there are significant differences in C–C and C–N bond lengths between $Ni^{IV}L^{2+}$ and $Ni^{II}LH_2^{2+}$.[34]

The nickel(III/II) self-exchange rates show a trend, decreasing with increasing protonation. In part, this is due to the increase in charge on protonation. Indeed, the electrostatics-corrected self-exchange rates of $Ni^{III/II}L^{+/0}$ and $Ni^{III/II}LH^{2+/+}$ are identical. However, self-exchange in the doubly protonated complex appears considerably slower and may reflect a change in electronic structure of the nickel(III) species compared with that for $Ni^{III}L^+$ and $Ni^{III}LH^{2+}$, where the EPR parameters suggest predominantly metal-centered oxidation.

Finally, the complexes $Ni^{IV}L^{2+}$ and $Ni^{III}LH^{2+}$ are comparable in structure, charge, and reduction potential but differ in self-exchange rate. Marcus theory predicts that the ratio of reaction rates of these two complexes $k(Ni^{IV}L^{2+})/k(Ni^{III}LH^{2+})$ by a common reductant should be independent of the reductant and equal to the square root of the ratio of the respective self-exchange rates, $4 \times 10^4/4 \times 10^2 = 10$. From the data in Table IV experimentally derived values for this ratio vary between 7.8 and 10.1, providing good evidence and a sensitive criterion for an outer-sphere mechanism.

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Registry No. **2**, 55188-33-5; $Ni^{II}L$, 59980-38-0; $Ni^{III}L^+$, 59980-37-9.

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(32) Reduction of $Ni^{IV}((S)\text{-}Me_2L)^{2+}$ (1×10^{-5} M) by $Ni^{III}L^+$ was examined briefly at pH 7. Complications from the competition for nickel(IV) by small amounts of nickel(II) in the nickel(III) solution were avoided by preparing the latter reagent with a slight (10^{-6} M) excess of $Ni^{IV}L^{2+}$. First-order rate constants of 13 ± 2 and 2.7 ± 0.2 s^{-1} were obtained for $[Ni^{III}L^+] = 2.5 \times 10^{-4}$ and 4.5×10^{-5} M, respectively, at 25 °C and 0.1 M ionic strength ($NaClO_4$).

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(35) The effects of protonation can be accounted for in the nickel(II) species since Ni(II)–N(oximato) bond lengths for deprotonated complexes are around 0.09 Å shorter than protonated bond lengths.[34] Similarly for nickel(III) the deprotonated Ni(III)–N bond corresponds to N(4)–N(6). Hence, estimates for Ni(1)–N(3) and N(4)–N(6) for deprotonated complexes of nickel(III) and -(II) are both around 4.06 Å.