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Electron-Exchange Rates of Polypyridine Complexes: Electron-Transfer Reactions Involving the Tris(polypyridine)nickel(II/III) Couple in Acidic Aqueous Media

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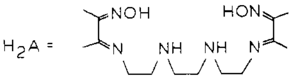
Received March 3, 1983

The kinetics of the reduction of NiL_3^{3+} by $NiL'_3{}^{2+}$ complexes (where L and L′ are substituted 2,2′-bipyridine or 1,10-phenanthroline derivatives) and by NiH_2A^{2+} (H_2A = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime), tris(5-nitro-1,10-phenanthroline)ruthenium(II), and $Fe(H_2O)_6^{2+}$ in acidic aqueous media have been studied by the stopped-flow technique. The kinetic data yield 1.5×10^3 M^{-1} s^{-1} for the NiL_3^{2+}–NiL_3^{3+} self-exchange rate constant at 25 °C and 1.00 M ionic strength. The $Fe(H_2O)_6^{2+}$ reduction of both $Ni(4,4'-(CH_3)_2bpy)_3^{3+}$ and $Ni(bpy)_3^{3+}$ is 10^2 times slower than predicted by the Marcus cross-relation, and reasons for this disagreement are discussed. The rate constant for the $Ni(bpy)_3^{2+}$–$Ni(bpy)_3^{3+}$ exchange is compared with other tris(2,2′-bipyridine) exchange rate constants, and the rate variations are discussed in terms of differences in the inner-shell reorganization barriers and electronic factors for the reactions.

Introduction

In recent years trivalent nickel complexes have been the object of considerable interest.[1,2] Numerous complexes containing nickel in this unusual oxidation state have been reported, the majority stabilized by nitrogen donor ligands such as the tetraaza macrocycles or polypyridine ligands. Tris(polypyridine)nickel(III) complexes, NiL_3^{3+}, where L is 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or a substituted bpy or phen derivative, have been prepared electrochemically in anhydrous acetonitrile[3] or in strongly acidic aqueous solutions.[4] Electron spin resonance studies of these species[3,5] have confirmed the presence of a low-spin d^7 nickel(III) center in a tetragonally distorted octahedral geometry. The NiL_3^{3+} complexes are strong one-electron oxidants ($E°$ = 1.6–1.9 V vs. NHE[3]), and the kinetics of the outer-sphere oxidation of H_2O_2, Br^-, and N_3^- by $Ni(bpy)_3^{3+}$ have been reported.[4,5]

In the present paper we report the kinetics of the oxidation of $Ni(4,4'-(CH_3)_2bpy)_3^{2+}$ and $Ni(phen)_3^{2+}$ by $Ni(bpy)_3^{3+}$ and the reduction of $Ni(4,4'-(CH_3)_2bpy)_3^{3+}$ and $Ni(bpy)_3^{3+}$ by NiH_2A^{2+} (H_2A = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime), RuL_3^{2+} (L = 5-nitro-1,10-phenanthroline), and $Fe(H_2O)_6^{2+}$ in acidic aqueous media. The self-exchange rate constant (k_{11}) for the $NiL_3^{2+/3+}$ couples have been estimated from the cross-reaction rate (k_{12}) and equilibrium (K_{12}) constants by employing modified Marcus theory equations.[6,7] The results obtained are compared with self-exchange rate constants determined for other Ni(II)/Ni(III) couples[8-11] and for tris(2,2′-bipyridine) complexes of other transition-metal ions.[12-15]



Experimental Section

Materials. Trifluoromethanesulfonic acid (CF_3SO_3H, 3M Co.) was distilled twice under reduced pressure. Lithium trifluoromethanesulfonate was prepared by the neutralization of CF_3SO_3H with recrystallized Li_2CO_3. Stock solutions of CF_3SO_3Li were analyzed by passing an aliquot through a Dowex 50W-X8 column in the H^+ form and titrating with standardized NaOH.

Tris(2,2′-bipyridine)nickel(II) perchlorate and tris(4,4′-dimethyl-2,2′-bipyridine)nickel(II) perchlorate were prepared by the addition of a slight stoichiometric excess of the ligand (G. F. Smith) to a solution of nickel perchlorate hexahydrate in methanol. The tris(bipyridine)nickel(III) perchlorate salts were prepared by electrochemical oxidation in anhydrous acetonitrile at 0 °C.[3] Acetonitrile was dried and distilled over calcium hydride under an argon atmosphere. The solid nickel(III) complexes were isolated by slow evaporation of the solvent, washed with a minimum of 0 °C CH_3CN (ice bath), and dried under vacuum.

Iron(II) perchlorate solutions were prepared by electrochemical reduction of iron(III) perchlorate in 1 M perchloric acid. Dilute solutions of ferrous ions in degassed 1.0 M CF_3SO_3H, prepared for kinetic experiments, were analyzed as $Fe(phen)_3^{2+}$ ion (510 nm, ϵ 11 100 M^{-1} cm^{-1}). The nickel(II) oxime complex, $[NiH_2A](ClO_4)_2$, was prepared as described previously.[16] The $[Ru(bpy)_3](ClO_4)_2$ and $[Ru(5\text{-}NO_2phen)_3](ClO_4)_2$ complexes were synthesized by methods described previously.[14]

Kinetic Measurements. Kinetic studies were performed on a Durrum D-110 stopped-flow spectrophotometer equipped with a 2-cm observation cuvette. All experiments were performed under pseudo-first-order conditions with excess reductant. Plots of ln ($A_t - A_\infty$) or ln ($A_\infty - A_t$) against time were linear for at least 3 half-lives, yielding pseudo-first-order rate constants that were reproducible to within 5%. Reactions involving $Fe(H_2O)_6^{2+}$, $Ru(5\text{-}NO_2phen)_3^{2+}$, and NiH_2A^{2+} as reductants were monitored at 400, 450, and 500 nm, respectively. These experiments were carried out in 1.00 M CF_3SO_3H except those involving NiH_2A^{2+}, for which the acid concentration was 0.50 M with the ionic strength maintained at 1.00 M with CF_3SO_3Li. The oxidations of $Ni(4,4'-(CH_3)_2bpy)_3^{2+}$ and $Ni(phen)_3^{2+}$ by $Ni(bpy)_3^{3+}$ were studied in 1.0 M H_2SO_4 at a wavelength of 450 nm. The reversible reaction of $Ni(bpy)_3^{3+}$ with $Ni(phen)_3^{2+}$ ($\Delta E° < 0.02$ V) was studied by measuring the rate of approach to equilibrium under pseudo-first-order conditions of excess $Ni(phen)_3^{2+}$ and $Ni(bpy)_3^{2+}$. The kinetic measurements were performed at several temperatures between 9 and 30 °C with thermostating provided by an external water bath.

Electrochemistry. The reduction potentials of the reactants used in this study were measured in 1.0 M CF_3SO_3H with use of cyclic voltammetry techniques. A Princeton Applied Research Model 173

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Table I. Rate Constants and Activation Parameters for Reactions at 25 °C and 1.00 M Ionic Strength

oxidant	reductant	$10^{-5}k$, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[b] cal deg^{-1} mol^{-1}
$Ni(bpy)_3^{3+}$	$Ni((CH_3)_2bpy)_3^{2+}$	0.21	8.0	−12
$Ni(bpy)_3^{3+}$	$Ni(phen)_3^{2+}$	0.011	8.9[c]	−15[d]
$Ni(phen)_3^{3+}$	$Ni(bpy)_3^{2+}$	0.020	5.2[c]	−26[d]
$Ni((CH_3)_2bpy)_3^{3+}$	$Fe(H_2O)_6^{2+}$	5.9	2.0	−25
$Ni(bpy)_3^{3+}$	$Fe(H_2O)_6^{2+}$	67	1.6	−22
$Ni((CH_3)_2bpy)_3^{3+}$	NiH_2A^{2+}	10.6	6.6	−9
$Ni(bpy)_3^{3+}$	NiH_2A^{2+}	62	3.5	−16
$Ru(bpy)_3^{3+}$	NiH_2A^{2+}	11.1		
$Ni((CH_3)_2bpy)_3^{3+}$	$Ru(NO_2phen)_3^{2+}$	41	2.4	−20

[a] Uncertainty is ±0.5 kcal mol^{-1}. [b] Uncertainty is ±2 cal deg^{-1} mol^{-1}. [c] Uncertainty is ±2 kcal mol^{-1}. [d] Uncertainty is ±5 cal deg^{-1} mol^{-1}.

potentiostat with a PAR Model 172 universal programmer were employed together with a Hewlett-Packard X-Y recorder. A glassy-carbon working electrode, platinum-wire counterelectrode, and saturated calomel reference electrode were used in a three-compartment cell.

Results

Kinetic Studies. The rate of the electron-transfer reaction

$$Ni(bpy)_3^{3+} + Ni(phen)_3^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ni(bpy)_3^{2+} + Ni(phen)_3^{3+} \quad (1)$$

was measured in both directions in 1.0 M H_2SO_4 solution. The equilibrium constant for eq 1 from potential measurements at 25 °C ($\Delta E° = 0.016$ V in acetonitrile)[3] is 0.54, and under pseudo-first-order conditions of excess $Ni(phen)_3^{2+}$ and $Ni(bpy)_3^{2+}$ concentrations, the rate constant for the approach to equilibrium is given by eq 2. Plots of k_{obsd} against $[Ni(phen)_3^{2+}]$ at constant $[Ni(bpy)_3^{2+}]$ and of k_{obsd} against $[Ni(bpy)_3^{2+}]$ at constant $[Ni(phen)_3^{2+}]$ yielded values for k_f and k_r, respectively. The kinetic data for this reaction (as well as for the other reactions studied) are given in the supplementary material, and the derived rate and activation parameters for the reactions are summarized in Table I. The relatively large errors in the activation parameters for reaction 1 are a consequence of the small absorbance changes associated with the electron transfer.

$$k_{obsd} = k_f[Ni(phen)_3^{2+}] + k_r[Ni(bpy)_3^{2+}] \quad (2)$$

The kinetic measurements on the other oxidation reactions of $Ni(4,4'-(CH_3)_2bpy)_3^{3+}$ and $Ni(bpy)_3^{3+}$ presented in Table I were carried out in 1.00 M sulfate or trifluoromethanesulfonate media with the reductant present in excess. The reactions of $Ni(4,4'-(CH_3)_2bpy)_3^{3+}$ and $Ni(bpy)_3^{3+}$ with $Fe(H_2O)_6^{2+}$ and $Ru(5-NO_2phen)_3^{2+}$ in 1.0 M CF_3SO_3H and of $Ni(bpy)_3^{3+}$ with $Ni(4,4'-(CH_3)_2bpy)_3^{2+}$ in 1.0 M H_2SO_4 followed the rate law in eq 3.

$$\frac{-d[NiL_3^{3+}]}{dt} = k_{12}[NiL_3^{3+}][\text{reductant}] \quad (3)$$

The pseudo-first-order rate constants displayed a first-order dependence on [reductant], as shown in Figure 1. The oxidation of $Ru(5-NO_2phen)_3^{2+}$ by $Ni(bpy)_3^{3+}$ was too fast for study at $[Ru(5-NO_2phen)_3^{2+}] = 5.0 \times 10^{-6}$ M, implying a second-order rate constant of $>10^7\ M^{-1}\ s^{-1}$.

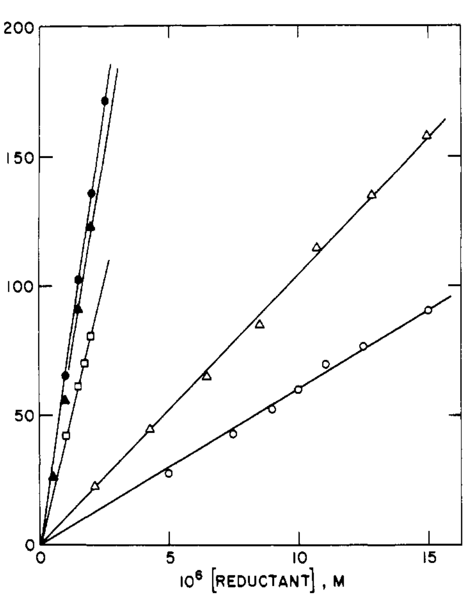

Figure 1. Dependence of k_{obsd} on reductant concentrations at 25 °C, $\mu = 1.00$ M (CF_3SO_3H/Li^+): (○) $Ni((CH_3)_2bpy)_3^{3+}/Fe^{2+}$; (●) $Ni(bpy)_3^{3+}/Fe^{2+}$; (△) $Ni((CH_3)_2bpy)_3^{3+}/NiH_2A^{2+}$; (▲) $Ni(bpy)_3^{3+}/NiH_2A^{2+}$; (□) $Ni((CH_3)_2bpy)_3^{3+}/Ru(NO_2phen)_3^{2+}$.

The oxidation of the nickel(II) oxime complex, NiH_2A^{2+}, in acidic solution yields a stable nickel(IV) species, NiA^{2+}.[16] Previous investigations of the oxidation of NiH_2A^{2+} by $Co^{3+}(aq)$[17] and tris(polypyridine)iron(III)[9] suggest a mechanism in which the one-electron oxidation of NiH_2A^{2+} ($E° = 1.25$ V) to a nickel(III) intermediate is the rate-determining step. It is likely that a similar mechanism obtains in the oxidation by $Ni(bpy)_3^{3+}$ and that the nickel(III) intermediate ($NiHA^{2+}$ at pH 0[10]) is rapidly oxidized ($E° = 0.65$ V) to NiA^{2+} by a second $Ni(bpy)_3^{3+}$ (eq 4 and 5).

$$Ni(bpy)_3^{3+} + NiH_2A^{2+} \xrightarrow{k_{12}} Ni(bpy)_3^{2+} + NiH_2A^{3+} \quad (4)$$

$$Ni(bpy)_3^{3+} + NiHA^{2+} \xrightarrow{\text{fast}} Ni(bpy)_3^{2+} + NiA^{2+} + H^+ \quad (5)$$

This mechanism is consistent with the rate law for the oxidation of NiH_2A^{2+} by $Ni(bpy)_3^{3+}$, $Ni(4,4'-(CH_3)_2bpy)_3^{3+}$, and $Ru(bpy)_3^{3+}$ in 0.50 M CF_3SO_3H ($\mu = 1.00$ M, CF_3SO_3Li) (eq 6).

$$\frac{-d[ML_3^{3+}]}{2dt} = \frac{d[NiA^{2+}]}{dt} = k_{12}[ML_3^{3+}][NiH_2A^{2+}] \quad (6)$$

The rate constants and activation parameters for the oxidation of NiH_2A^{2+} are included in Table I.

Cyclic Voltammetry. Reduction potentials of 1.58 V for $Ni(4,4'-(CH_3)_2bpy)_3^{3+}$ and 1.72 V for $Ni(bpy)_3^{3+}$ were determined from the cyclic voltammetry measurements in 1.0 M CF_3SO_3H. Reversible one-electron traces were observed for both complexes with 60–70-mV separations between cathodic and anodic peaks at scan rates of 5–50 mV s^{-1}. These potentials are in excellent agreement with the reported values extrapolated from cyclic voltammetry measurements on tris(polypyridine)nickel(III) complexes in acetonitrile ($E° = 1.73$ V for $Ni(phen)_3^{2+/3+}$).[3] The reduction potentials of the $Ru(bpy)_3^{3+}$ ($E° = 1.25$ V) and $Ru(5-NO_2phen)_3^{3+}$ ($E° = 1.51$ V) ions measured in 1.0 M CF_3SO_3H are similar to the values reported in 1.0 M H_2SO_4.[14]

The electrochemical behavior of NiH_2L^{2+} in aqueous solution has been reported previously.[18] Below pH 5 a single, reversible two-electron process is observed (eq 7) while above pH 5 two one-electron processes are found, corresponding to a pH-independent Ni(IV)/Ni(III) couple and a pH-dependent

$$NiA^{2+} + 2H^+ + 2e^- = NiH_2A^{2+} \quad (7)$$

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Table II. Observed and Calculated Rate Constants at 25 °C for Redox Cross-Reactions Involving Polypyridine Complexes

oxidant	reductant	$\log K_{12}$	k_{11},[i] $M^{-1}\ s^{-1}$	k_{22},[i] $M^{-1}\ s^{-1}$	k_{obsd}, $M^{-1}\ s^{-1}$	k_{calcd}, $M^{-1}\ s^{-1}$
$Ni(bpy)_3^{3+}$	$Ni((CH_3)_2bpy)_3^{2+}$	2.37	1.5×10^3 (1.0)	1.5×10^3 (1.0)	2.1×10^4	2.1×10^4
$Ni(bpy)_3^{3+}$	$Ni(phen)_3^{2+}$	−0.27	1.5×10^3 (1.0)	1.5×10^3 (1.0)	1.1×10^3	1.1×10^3
$Ni(phen)_3^{3+}$	$Ni(bpy)_3^{2+}$	0.27	1.5×10^3 (1.0)	1.5×10^3 (1.0)	2.0×10^3	2.0×10^3
$Ni(bpy)_3^{3+}$	$Fe(H_2O)_6^{2+}$	16.1	1.5×10^3 (1.0)	10 (1.0)[a]	6.7×10^6	4.4×10^8
$Ni((CH_3)_2bpy)_3^{3+}$	$Fe(H_2O)_6^{2+}$	13.7	1.5×10^3 (1.0)	10 (1.0)[a]	5.9×10^5	7.9×10^7
$Ru(bpy)_3^{3+}$	$Fe(H_2O)_6^{2+}$	8.81	4.2×10^8 (0.1)[b]	10 (1.0)[a]	7.2×10^5[c]	3.6×10^8
$Fe(bpy)_3^{3+}$	$Fe(H_2O)_6^{2+}$	3.90	3×10^8 (5.5)[d]	10 (1.0)[a]	2.7×10^4[e]	5.6×10^6
$Fe(H_2O)_6^{3+}$	$Co(phen)_3^{2+}$	6.27	10 (1.0)[a]	45 (1.0)[f]	5.3×10^2[g]	4.2×10^3
$Ni(bpy)_3^{3+}$	NiH_2A^{2+}	7.94	1.5×10^3 (1.0)	3×10^3 (1.0)[h]	6.2×10^6	8.5×10^6
$Ni((CH_3)_2bpy)_3^{3+}$	NiH_2A^{2+}	5.58	1.5×10^3 (1.0)	3×10^3 (1.0)[h]	1.1×10^6	1.0×10^6
$Ru(bpy)_3^{3+}$	NiH_2A^{2+}	0.00	4.2×10^8 (0.1)[b]	3×10^3 (1.0)[h]	1.1×10^6	1.6×10^6
$Fe(bpy)_3^{3+}$	NiH_2A^{2+}	−2.70	3×10^8 (5.5)[d]	3×10^3 (1.0)[h]	3.2×10^4[h]	3.2×10^4
$Ni(bpy)_3^{3+}$	$Ru(NO_2phen)_3^{2+}$	3.55	1.5×10^3 (1.0)	4.2×10^8 (0.1)[b]	$>10^7$	5.0×10^7
$Ni((CH_3)_2bpy)_3^{3+}$	$Ru(NO_2phen)_3^{2+}$	1.88	1.5×10^3 (1.0)	4.2×10^8 (0.1)[b]	4.1×10^6	4.3×10^6

[a] Interpolated from ref 12, 26, and 27. [b] Reference 22. [c] Reference 14. [d] Reference 25. [e] Reference 23. [f] Neumann, H. M., quoted in: Farina, R.; Wilkins, R. G. *Inorg. Chem.* 1968, *7*, 516. [g] Reference 24. [h] Reference 9. [i] Ionic strength given in parentheses (M).

Ni(III)/Ni(II) couple. The potentials, measured at several pH values between 0 and 8 (0.1 M acetate and phosphate buffers) at an ionic strength of 1.00 M (CF_3SO_3H/Li^+), agree (±10 mV) with the potentials measured previously at an ionic strength of 0.10 M (NaCl).[15] The reduction potential of the $NiH_2A^{2+/3+}$ couple was calculated to be 1.25 ± 0.01 V.

Discussion

The kinetic and thermodynamic data from the present and previous studies[3-5] suggest that redox reactions involving tris(polypyridine)nickel(III) complexes proceed by an outer-sphere mechanism (eq 8).

$$Ni(bpy)_3^{3+} + Red \xrightarrow{k_{12}} Ni(bpy)_3^{2+} + Ox \qquad (8)$$

The spectrum of $Ni(bpy)_3^{3+}$ decays slowly ($t_{1/2} \approx 4$ h at 25 °C) in 1.0 M CF_3SO_3H, likely due to reduction by water rather than ligand dissociation. The redox rates of the reactions under investigation are faster than the ligand substitution rates of the participating reactants. The low ΔH^* and negative ΔS^* parameters (Table I) for the NiL_3^{3+} reactions are not uncommon for outer-sphere reactions of this type.[13,19]

The self-exchange constants k_{11} for the $Ni(bpy)_3^{2+/3+}$ and $Ni(4,4'-(CH_3)_2bpy)_3^{2+/3+}$ couples can be estimated from the cross-reaction data by employing the Marcus cross-relations. In terms of a recent modification of the theory,[7] the rate constant for a cross-reaction k_{12} is related to the rate constants for the component self-exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross-reaction K_{12} by

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (9)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \frac{w_{11} + w_{22}}{RT}\right]} \qquad (10)$$

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

$$w_{ij} = \frac{z_i z_j e^2}{D_s \sigma_{ij}(1 + \beta\sigma_{ij}\mu^{1/2})} \qquad (12)$$

$$A_{ii} = \left[\frac{4\pi N\sigma^2\nu_n\delta r}{1000}\right]_{ii} \qquad (13)$$

and it has been assumed that the electronic factors $(\kappa_{el})_{ii}$ and nuclear tunneling factors $(\Gamma_n)_{ii}$ for all the reactions involved are either approximately unity or that their effects tend to cancel. In the above expressions w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken equal to the sum of a_i and a_j, the radii of ions i and j), D_s is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, ν_n is the nuclear vibration frequency that destroys the activated complex configuration, and δr is the thickness of the reaction layer. The value of A/σ^2 ranges from 10^{10} to 10^{11} M^{-1} Å^{-2} s^{-1}, the exact value depending on the particular reaction; a typical value is 3×10^{10} M^{-1} Å^{-2} s^{-1}, and this value will be used here. Radii of 6.8 Å for the tris(polypyridine) complexes,[20] 5.0 Å for NiH_2A^{2+},[21] and 3.3 Å for $Fe(H_2O)_6^{2+}$ [12] were used in evaluating σ_{ij}.

In the absence of a direct measurement of the $Ni(bpy)_3^{2+/3+}$ self-exchange rate constant, the best approximation of k_{11} is provided by a cross-reaction in which the two reactants are nickel complexes containing closely related polypyridine ligands.[20,22] In this regard the $Ni(bpy)_3/Ni(phen)_3$ system should be an excellent model because of the similarities in the sizes and free energies of the nickel complexes. At 25 °C the rate constants for the $Ni(bpy)_3^{3+}/Ni(phen)_3^{2+}$ and $Ni(phen)_3^{3+}/Ni(bpy)_3^{2+}$ reactions are 1.1×10^3 and 2.0×10^3 $M^{-1}\ s^{-1}$, respectively. With use of $k_{11} = (k_fk_r)^{1/2}$, a self-exchange rate constant of 1.5×10^3 $M^{-1}\ s^{-1}$ is calculated for the $NiL_3^{2+/3+}$ couples with $\Delta H_{11}^* = 6.7 \pm 2$ kcal mol^{-1} and $\Delta S_{11}^* = -22 \pm 5$ cal deg^{-1} mol^{-1}. This entropy of activation falls in the range found for other 2+/3+ couples at an ionic strength of 1.0 M.[12,20] The rate constant observed for the reaction of $Ni(bpy)_3^{3+}$ with $Ni(4,4'-(CH_3)_2bpy)_3^{2+}$ agrees with the value calculated from eq 9 with use of 1.5×10^3 $M^{-1}\ s^{-1}$ as a self-exchange rate constant common to the $NiL_3^{2+/3+}$ couples, providing further justification for the procedure used to estimate the exchange rate constants.

There are relatively few well-characterized (i.e. k_{22} and $E°$ known) outer-sphere reductants whose reactions with the NiL_3^{3+} complexes are slow enough to permit kinetic studies using stopped-flow techniques. For the $NiH_2A^{2+/3+}$ couple the self-exchange rate constant has been estimated as 3×10^3 $M^{-1}\ s^{-1}$ with use of kinetic data from the cross-reactions with a series of tris(polypyridine)iron(III) complexes.[9] The observed and calculated rate constants for the reaction of $Ru(bpy)_3^{3+}$ and NiH_2A^{2+} are also in good agreement (Table II) when this value is employed. From a potentially useful series of cross-

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reactions with the tris(polypyridine)iron(II) and ruthenium(II) ions ($k_{22} = 4 \times 10^8$ M^{-1} s^{-1}, $\mu = 0.10$ M),[22] only the reaction between $Ru(5\text{-}NO_2phen)_3^{2+}$ ($E° = 1.51$ V) and $Ni(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$ was accessible on the stopped-flow time scale. A fit of the cross-reaction data to the Marcus equations was made with 1.5×10^3 M^{-1} s^{-1} for the self-exchange rate constants of the $Ni(bpy)_3^{2+/3+}$ and $Ni(4,4'\text{-}(CH_3)_2bpy)_3^{2+/3+}$ couples. Excellent agreement between the observed and calculated rate constants (Table II) was achieved in all cases except for the reactions of $Ni(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$ and $Ni(bpy)_3^{3+}$ with $Fe(H_2O)_6^{2+}$. The $Fe(H_2O)_6^{2+/3+}$ self-exchange rate constant has been measured at several ionic strengths,[12,26,27] and a value of $k_{22} = 10$ M^{-1} s^{-1} at $\mu = 1.0$ M was interpolated from the reported rate constants. With use of this value of k_{22} the observed rates are about 100 times slower than the values predicted by the cross-relation. Similar deviations have been reported for the reactions of $Fe(H_2O)_6^{2+}$ with tris(polypyridine) complexes of other metal ions.[12-15,19]

Comment on the $Fe(H_2O)_6^{2+}$ Reactions. The reasons for the breakdown of eq 9 when it is applied to reactions of $Fe(H_2O)_6^{2+}$ with tris(polypyridine) complexes are not well understood. Various explanations have been advanced, including nonadiabaticity, anharmonicity, interpenetration of the ligands, and additional nonelectrostatic and electrostatic contributions to the work terms.[13-15,19,23,28] In this connection it should be noted that deviations for $Fe(H_2O)_6^{2+}$ reactions are not restricted to its oxidation by tris(polypyridine) complexes: reactions of $Fe(H_2O)_6^{2+}$ with a variety of oxidants including ammine complexes and other metal aquo ions are consistently slower than predicted by eq 9.[13,29] This disagreement can be circumvented by calculating cross-reaction rates that are based upon a lower $Fe(H_2O)_6^{2+/3+}$ exchange rate: in a recent application of this procedure[29] it was found that a large number of $Fe(H_2O)_6^{2+}$ reactions can be fit to eq 9 by using an effective $Fe(H_2O)_6^{2+/3+}$ exchange rate constant that corresponds to 5×10^{-4} M^{-1} s^{-1} at $\mu = 1$ M.[30] Substitution of this effective $Fe(H_2O)_6^{2+/3+}$ exchange rate into eq 9 yields 2×10^3 M^{-1} s^{-1} as the average rate constant for the $Ni(bpy)_3^{2+/3+}$ and $Ni(4,4'\text{-}(CH_3)_2bpy)_3^{2+/3+}$ exchanges, in excellent agreement with the exchange rate constant estimated from the other NiL_3^{3+} reactions.

The significance of the effective rate constant for the $Fe(H_2O)_6^{2+/3+}$ exchange merits some comment. Hupp and Weaver[29] propose that the $Fe(H_2O)_6^{2+/3+}$ exchange normally proceeds by a water-bridged pathway and that the experimental rate constant of 10 M^{-1} s^{-1} at $\mu = 1.0$ M is the rate constant for this inner-sphere reaction. The effective rate constant of 5×10^{-4} M^{-1} s^{-1} is then the rate constant for the (hypothetical) outer-sphere $Fe(H_2O)_6^{2+/3+}$ exchange. There is, however, an alternative explanation for the relatively slow rates of $Fe(H_2O)_6^{2+}$ reactions that does not invoke an inner-sphere $Fe(H_2O)_6^{2+/3+}$ exchange but that rests instead upon the postulate that $Fe(H_2O)_6^{2+}$ reactions are in general nonadiabatic. This hypothesis is supported by the results of recent calculations which indicate that κ_{el} for the $Fe(H_2O)_6^{2+/3+}$ exchange is $\sim 10^{-2}$ at the separation distance defined by first contact of the inner-coordination shells of the reactants (6.5 Å).[31] In order to correct for the effects of nonadiabaticity, two modifications to the classical cross-relation are necessary: (a) the right-hand side of eq 9 needs to be multiplied by $B_{12} = (\kappa_{el})_{12}/[(\kappa_{el})_{11}\,(\kappa_{el})_{22}]^{1/2}$; (b) the $A_{11}A_{22}$ term in the denominator of eq 10 needs to be multiplied by $[(\kappa_{el})_{11}\,(\kappa_{el})_{22}]$. The first correction is independent of driving force and may either decrease or increase the calculated rate constant, depending on whether $(\kappa_{el})_{12}$ is less or greater than $[(\kappa_{el})_{11}\,(\kappa_{el})_{22}]^{1/2}$. The second correction is independent of $(\kappa_{el})_{12}$: it is important only at large driving force and always decreases the calculated rate constant. In terms of this interpretation k_{eff} is related to k_{22}, the measured $Fe(H_2O)_6^{2+/3+}$ exchange rate constant, by

$$k_{\text{eff}} = \frac{(\kappa_{el})_{12}{}^2 k_{22}}{(\kappa_{el})_{11}(\kappa_{el})_{22}} \tag{14}$$

Substitution of $k_{\text{eff}} = 5 \times 10^{-4}$ and $k_{22} = 10$ M^{-1} s^{-1} gives $B_{12} \approx 10^{-2}$. The fact that $B_{12} < 1$ implies that the geometric mean of the electronic factors for the exchange reactions are, on the average, larger than the electronic factors for the cross-reactions.[32a] This, in turn, suggests that *for this series of reactions* the electronic coupling in the exchange reactions tends to be larger than the coupling in the cross-reactions, possibly because of the unique structural and electronic relationship of the reactants in the former class of reactions. This conclusion that exchange reactions tend to be more adiabatic than cross-reactions is very tentative,[32b] particularly since a limited set of data have been considered and alternative explanations (such as a change in mechanism) are possible. This question will be discussed in greater detail elsewhere.

Table III. Rate Constants for Electron-Exchange Reactions of Tris(bipyridine) or -(phenanthroline) Complexes at 25 °C

couple[a]	configns	Δd_0, Å	k_{11},[e] M^{-1} s^{-1}	ref
CrL_3^{2+}/CrL_3^{3+}	$(\pi d)^4/(\pi d)^3$	0[a]	10^9	*f*
FeL_3^{2+}/FeL_3^{3+}	$(\pi d)^6/(\pi d)^5$	0.00[b]	3×10^8 (5.5)	25
RuL_3^{2+}/RuL_3^{3+}	$(\pi d)^6/(\pi d)^5$	0[a]	4×10^8 (0.1)	22
CoL_3^{2+}/CoL_3^{3+}	$(\pi d)^5(\sigma^* d)^2/(\pi d)^6$	0.19[b]	18 (0.1)	*g*
CoL_3^{+}/CoL_3^{2+}	$(\pi d)^6(\sigma^* d)^2/$ $(\pi d)^5(\sigma^* d)^2$	−0.02[c]	$\geqslant 10^8$ (0.5)	12
NiL_3^{2+}/NiL_3^{3+}	$(\pi d)^6(\sigma^* d)^2/$ $(\pi d)^6(\sigma^* d)^1$	~0.12[d]	1.5×10^3 (1.0)	*h*

[a] Difference in the metal-nitrogen distances assumed to be the same as found for the $Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$ couple. [b] Reference 12. [c] Reference 38. [d] Preliminary result.[35] [e] Ionic strength given in parentheses (M). [f] Endicott, J. F., Brunschwig, B. S., quoted in ref 15. [g] Neumann, H. M., quoted in: Farina, R.; Wilkins, R. G. *Inorg. Chem.* 1968, *7*, 516. [h] This work.

Comparisons with Other Nickel(II)-Nickel(III) Exchanges. The value of 1.5×10^3 M^{-1} s^{-1} for the $Ni(bpy)_3^{2+/3+}$ exchange may be compared with exchange rate constants measured or estimated for other Ni(II)/Ni(III) couples. For a series of nickel(II)/nickel(III) oxime complexes $NiH_nA^{n+/(n+1)+}$ (n = 0-2) related by proton equilibria, the k_{11} values fall in the range (1-3) $\times 10^3$ M^{-1} s^{-1}.[9,10] Self-exchange rate constants have also been estimated for nickel(II)/nickel(III) complexes

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(30) Use of this approach carries the interesting implication that the cross-reactions and all the exchange reactions other than $Fe(H_2O)_6^{2+/3+}$ are "normal" (but not necessarily adiabatic) outer-sphere reactions and that the deviations from eq 9 arise from the use of an inappropriate $Fe(H_2O)_6^{2+/3+}$ exchange rate constant. In the present case the value of the effective $Fe(H_2O)_6^{2+/3+}$ rate constant is not very sensitive to the k_{22} value used in evaluating f_{12}.

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(32) (a) The value of B_{12} yields ~0.1 for $(H_{AB})_{12}/[(H_{AB})_{11}\,(H_{AB})_{22}]^{1/2}$, which may be compared with the value of unity predicted by the geometric mean approximation. It should be emphasized that the value of B_{12} estimated in the present work is an average value and that no allowance has been made for differences in the geometries of the ligands or in the orbital symmetries (π–π, σ–σ, or σ–π) of the reactions. (b) A similar view has also recently been expressed[32c] on the basis of the reactivity patterns exhibited by a different class of systems. (c) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

with tetraaza macrocyclic ligands. A rate constant of $\sim 10^3$ M^{-1} s^{-1} has been reported for the $Ni([14]aneN_4)^{2+/3+}$ couple,[8,11] while smaller values have been estimated for methyl-substituted derivatives: $k_{11} \simeq 2$ M^{-1} s^{-1} for *rac*- and *meso*-($Me_6[14]aneN_4$)nickel(II/III)[33] and $k_{11} \simeq 6$ M^{-1} s^{-1} for $Ni(Me_6[14]4,11\text{-dieneN}_4)^{2+/3+}$.[11] Steric and electronic effects of the methyl substituents and ring unsaturation on the NiN_4 bond configurations may be responsible for the relatively slow exchange rates of the latter couples.

While both $Ni(bpy)_3^{2+}$ and $Ni(phen)_3^{2+}$ possess fairly regular octahedral structures,[34,35] ESR studies[3] show evidence for Jahn–Teller distortions in $Ni(bpy)_3^{3+}$ and $Ni(phen)_3^{3+}$. Preliminary X-ray results are consistent with a tetragonally distorted $Ni(bpy)_3^{3+}$ structure and yield ~0.12 Å for the average difference Δd_0 in the Ni–N bond lengths in $Ni(bpy)_3^{2+}$ and $Ni(bpy)_3^{3+}$.[35] These estimates may be compared with Δd_0 values obtained from structural data for nickel(II) and -(III) complexes containing hexaaza oxime and tetraaza macrocyclic ligands. An average difference of ~0.07 Å in the Ni–N bonds exists between $[Ni^{II}H_2A](ClO_4)_2$[21] and $[Ni^{III}HA](ClO_4)_2$,[36] while for the $Ni([14]aneN_4)Cl_2^{0/+}$ couple Δd_0(Ni–N) is 0.088 Å and Δd_0(Ni–Cl) is 0.04 Å.[37]

Comparisons with the Exchange Rates of Other Tris(bipyridine) Complexes. The rate constant for the $Ni(bpy)_3^{2+/3+}$ exchange estimated in this work is compared with rate constants for exchange reactions of other tris(bipyridine) and -(phenanthroline) complexes in Table III. It will be seen that the exchange rates span more than 7 orders of magnitude. Since the solvent barrier is nearly constant for these systems $[(a_2 + a_3) >> \Delta d_0]$, the exchange rate differences must arise primarily from differences in the inner-shell barriers and electronic factors for the reactions. For purposes of the present discussion a relatively simple model will be used: changes in the intraligand bond lengths and angles will be neglected, and only differences in the metal–ligand bond distances in the two oxidation states will be considered. The metal–ligand bond length differences are included in Table III.

The nickel(II/III) electron-exchange reactions considered above involve the transfer of a σ^*d electron between a high-spin d^8 $[(\pi d)^6(\sigma^* d)^2]$ and a low-spin d^7 $[(\pi d)^6(\sigma^* d)^1]$ configuration.[1] The exchanges are relatively slow because transfer of a σ^*d electron is accompanied by sizable changes in the metal–ligand distances (Δd_0(Ni–N) ≈ 0.1 Å). For comparison, the $Co(bpy)_3^{+/2+}$ couple is also a d^8/d^7 system but the exchange involves instead transfer of a πd electron between a high-spin d^8 $[(\pi d)^6(\sigma^* d)^2]$ and a high-spin d^7 $[(\pi d)^5(\sigma^* d)^2]$ configuration. The transfer of a nonbonding electron in this process accounts for the small change in the Co–N bond lengths of <0.02 Å[38] and the large self-exchange rate constant of $\geq 10^8$ M^{-1} s^{-1}.[12] Table III contains other examples of $M(bpy)_3^{2+/3+}$ couples where transfer of a πd electron is associated with a large self-exchange rate. On the other hand, exchange in the $Co(bpy)_3^{2+/3+}$ couple formally involves electron transfer between a high-spin d^7 $[(\pi d)^5(\sigma^* d)^2]$ and a low-spin d^6 $[(\pi d)^6(\sigma^* d)^0]$ configuration. The large Co–N bond length change of 0.19 Å[11] accompanying σ^*d electron transfer and the change in spin multiplicity is primarily responsible for the smaller exchange rate (Table III). (Despite the spin change, the $Co(bpy)_3^{2+/3+}$ exchange does not seem to feature an especially large nonadiabaticity.[7,12]) The intermediate $Ni(bpy)_3^{2+/3+}$ exchange rate constant determined in this study is consistent with the intermediate Δd_0 value of ~0.12 Å determined for this couple.

In conclusion, the present study has demonstrated that the NiL_3^{3+} complexes behave as strong, one-electron outer-sphere oxidants and possess moderate self-exchange rate constants. The NiL_3^{3+} oxidant series could be very useful in investigating reactions of species with high redox potentials and may provide more information on the kinetic effects of large thermodynamic driving forces. Further studies with the NiL_3^{3+} complexes are in progress.[39]

Acknowledgment. The authors wish to acknowledge very helpful discussions with Dr. C. Creutz. This work was performed at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences. D.H.M. wishes to thank the Natural Sciences and Engineering Research Council of Canada for support in the form of a Postdoctoral Fellowship.

Registry No. $Ni(bpy)_3^{3+}$, 64592-13-8; $Ni(phen)_3^{3+}$, 78671-16-6; $Ni((CH_3)_2bpy)_3^{3+}$, 65336-48-3; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ni((CH_3)_2bpy)_3^{2+}$, 65437-85-6; $Ni(phen)_3^{2+}$, 17085-38-0; $Ni(bpy)_3^{2+}$, 21595-29-9; $Fe(H_2O)_6^{2+}$, 15365-81-8; NiH_2A^{2+}, 55758-44-6; $Ru(NO_2phen)_3^{2+}$, 54360-17-7.

Supplementary Material Available: Tables of kinetic data for the reactions (4 pages). Ordering information is given on any current masthead page.

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