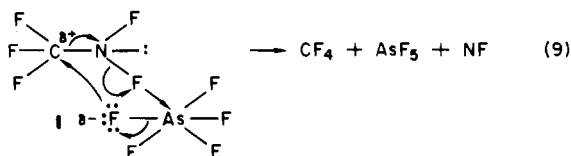the reaction analogous to (8) stops at the thermally unstable intermediate donor–acceptor stage, which on warm-up can decompose to the observed products by attack of a negatively polarized fluorine atom bound to As on the positively polarized central atom of the R group (eq 9). Such a mechanism, involving

$$\longrightarrow \quad CF_4 \; + \; AsF_5 \; + \; NF \qquad (9)$$

the formation of NF radicals, could explain the formation of both *cis-* and *trans*-N_2F_2 isomers and could also account for the observation of side reactions, as in the case of $ClNF_2$.

In summary, this study has shown that (i) strong Lewis acids, which are good fluoride acceptors, catalyze the decomposition of difluoramino compounds, (ii) the thermally unstable intermediates, which are initially formed, appear for RNF_2 compounds with highly electronegative R groups to be fluorine-bridged donor–acceptor complexes, and (iii) the exact nature of the final products is governed by their relative stabilities.

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Kinetics of Reduction of Nickel(III) Complexes by Iron(II) and Vanadium(IV) in Aqueous Acidic Perchlorate Media

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The kinetics of the reduction of a series of nickel(III) macrocycle complexes by $Fe(H_2O)_6{}^{2+}$ and VO^{2+}(aq) have been studied in acidic aqueous media. An inverse $[H^+]$ rate dependence observed in the reductions by VO^{2+}(aq) is attributed to a dominant $VO(OH)^+$ pathway. Applications of the Marcus theory relationship to the cross-reactions yield estimated self-exchange rate constants of 10^{-3}–10^{-2} M^{-1} s^{-1} for $Fe(H_2O)_6{}^{2+/3+}$ and 10–10^3 M^{-1} s^{-1} for $VO(OH)^{+/2+}$. These values are larger than the corresponding rate constants derived from metal polypyridine cross-reactions, and the differences are interpreted in terms of the structural and electronic properties of the oxidants. A comparison is made between the behavior of the $Fe(H_2O)_6{}^{2+}$ and $VO(OH)^+$ ions as reductants. Estimated self-exchange rate constants of $Fe(H_2O)_6{}^{2+/3+}$ and $VO(OH)^{+/2+}$ are compared with those of other transition-metal aquo ion couples.

Introduction

There has been considerable interest recently in the study of nickel complexes in the trivalent state.[1,2] Numerous nickel(III) complexes have been reported, the majority of these containing tetraaza macrocyclic[3,4] or polypyridine ligands.[5,6] The aqueous redox chemistry of these species is also of interest. While Ni(III) complexes display considerable stability in nonaqueous media, in aqueous solution these species are relatively unstable with respect to reduction. Kinetic studies of the oxidation of metal aquo ions by Ni(III) macrocyclic complexes in aqueous solution are limited to only a few examples.[7,8]

In this paper we report data on the kinetics of the oxidation of Fe^{2+} and VO^{2+} aquo ions by a series of Ni(III) macrocyclic complexes in acidic perchlorate media. The oxidants used in this study include both tetraaza macrocycle complexes, with labile axial coordination sites, and the substitution-inert, bis(triaza macrocycle) complexes of nickel(III). The results of these kinetic investigations are discussed in terms of outer-sphere vs. inner-sphere electron-transfer mechanisms, employing the Marcus theory relationships.[9] Also examined, with regard to the current investigation and others, is the parallel behavior of the Fe(II) and V(IV) aquo ions as reductants, a relationship first reported by Rosseinsky.[10]

Experimental Section

Stock solutions of iron(II) perchlorate were prepared by the oxidation of powdered iron metal (Fisher) in perchloric acid. The iron(II) concentration was determined by titration against standard $KMnO_4$ and by spectrophotometry as $Fe(phen)_3{}^{2+}$ (510 nm, $\epsilon = 11\,100$ M^{-1} cm^{-1}) following complexation with excess 1,10-phenanthroline. The acidity of the stock solution was determined by titration against standard NaOH using methyl orange as the indicator.

Stock solutions of vanadium(IV) perchlorate were prepared by the addition of a stoichiometric amount of barium perchlorate to a solution of vanadyl sulfate (Fisher), followed by removal of precipitated barium sulfate by decantation and filtration. The concentration of VO^{2+} was determined by titration against ammonium cerium(IV) nitrate in acetic acid using a ferroin indicator.

Ni(cyclam)$^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) (Chart I), Ni(Me$_2$cyclam)$^{2+}$ (Me$_2$cyclam = *C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), Ni(tet-c)$^{2+}$ (tet-c = *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), Ni(tet-d)$^{2+}$ (tet-d = *meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), Ni(Me$_2$diene)$^{2+}$ (Me$_2$diene = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), Ni(Me$_6$diene)$^{2+}$ (Me$_6$diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), Ni(non)$_2{}^{2+}$ (non = 1,4,7-triazacyclononane), and Ni(dec)$_2{}^{2+}$ (dec = 1,4,7-triazacyclodecane) were prepared as perchlorate salts as described previously.[11–14] The corresponding Ni(III) complexes were prepared in situ by the oxidation of the Ni(II) complex with a stoichiometric deficiency of Co(aq)$^{3+}$, just prior to their use in kinetic experiments.
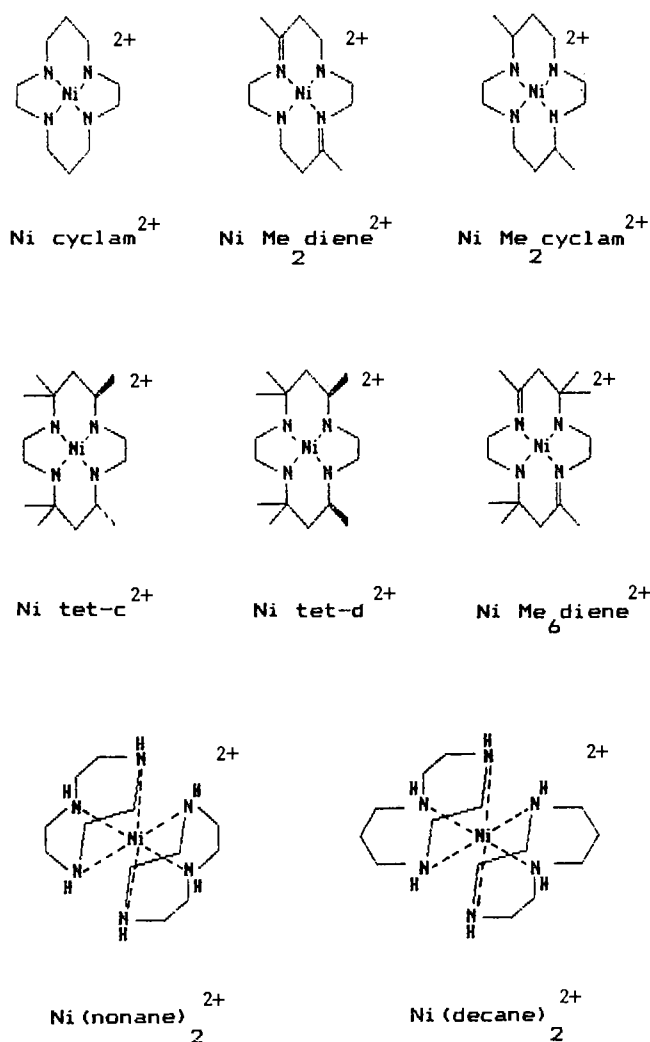
The stopped-flow apparatus and data acquisition system have been

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†Present address: Department of Chemistry, Queen's University, Kingston, Ontario, Canada.
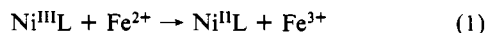‡Department of Chemistry, University of Ife, Ile-Ife, Oyo State, Nigeria.

Chart I

Table I. Rate Constants and Activation Parameters for the Oxidation of Fe^{2+} in 1.00 M $HClO_4$

oxidant	T, °C	$10^{-2}k_{obsd}$, $M^{-1} s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
$Ni(cyclam)^{3+}$	10.5	3.51 ± 0.04	5.3 ± 1.0	−28 ± 3
	14.2	3.81 ± 0.02		
	17.7	4.45 ± 0.01		
	21.3	4.94 ± 0.01		
	25.0	5.81 ± 0.04		
$Ni(Me_2cyclam)^{3+}$	10.0	5.79 ± 0.17	5.6 ± 1.0	−26 ± 3
	13.5	6.30 ± 0.02		
	16.7	6.94 ± 0.01		
	19.1	7.58 ± 0.08		
	25.0	9.24 ± 0.13		
$Ni(tet-c)^{3+}$	15.0	25.1 ± 0.8	2.3 ± 1.0	−35 ± 3
	19.6	27.6 ± 0.6		
	25.0	31.0 ± 1.4		
	28.1	32.0 ± 0.1		
$Ni(tet-d)^{3+}$	15.5	36.7 ± 0.1	0.9 ± 1.0	−39 ± 3
	20.1	38.0 ± 0.1		
	25.2	39.2 ± 1.4		
	28.0	41.1 ± 1.1		
$Ni(Me_2diene)^{3+}$	25.0	3.99 ± 0.17		
$Ni(non)_2^{3+}$	10.0	1.35 ± 0.06	0.4 ± 1.0	−47 ± 3
	15.0	1.45 ± 0.03		
	20.0	1.60 ± 0.01		
	25.0	1.70 ± 0.06		
$Ni(dec)_2^{3+}$	25.0	11.4 ± 0.2		

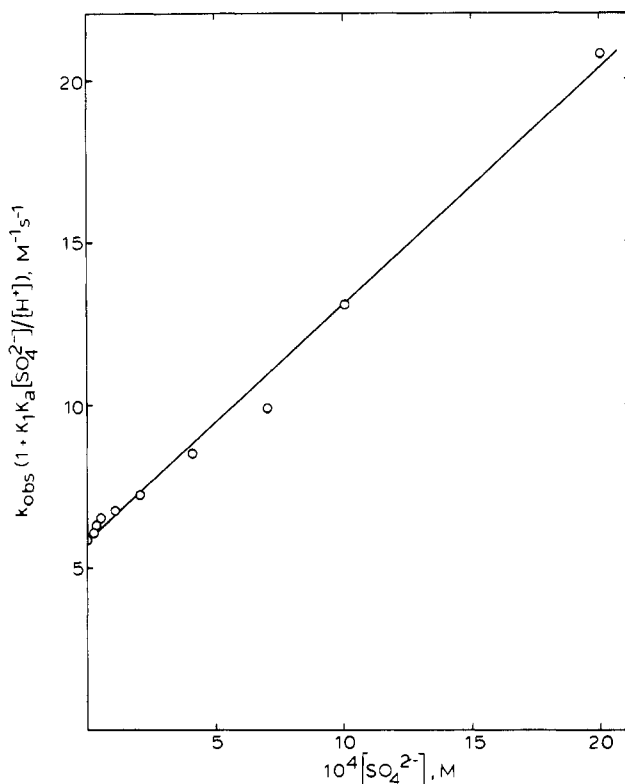**Figure 1.** Dependence of the observed rate constant on $[SO_4^{2-}]$ for the reduction of $Ni(cyclam)^{3+}$ by Fe^{2+} in 1.0 M $HClO_4$ at 25 °C.

described previously.[15] The slower oxidations of VO^{2+} were followed on a Beckmann DU-8 spectrophotometer equipped with a Kinetics II accessory. Thermostating was maintained at ±0.1 °C over the temperature range (8–30 °C) employed in the study. The ionic strength for all experiments was maintained at 1.00 M with $LiClO_4/HClO_4$ mixtures. $LiClO_4$ was prepared by the neutralization of Li_2CO_3 with moderately concentrated $HClO_4$ and thrice recrystallized from hot water.

The reactions were followed by monitoring the disappearance of the Ni(III) complexes between 350 and 410 nm. All measurements were made under pseudo-first-order conditions of excess reductant concentration. Plots of $\ln (A_t - A_\infty)$ against time, derived from the absorbance data, were linear for 3 or more half-lives.

Results

Kinetic measurements on the oxidation of $Fe(aq)^{2+}$ by $Ni^{III}L$ complexes were carried out in 1.00 M $HClO_4$, in both the absence and presence of sulfate ions. The stoichiometry of these reactions is represented (to ±2%) by

$$Ni^{III}L + Fe^{2+} \rightarrow Ni^{II}L + Fe^{3+} \qquad (1)$$

The pseudo-first-order rate constants displayed a first-order dependence on reductant concentration ((0.2–3.0) × 10^{-3} M)

$$-d[Ni(III)]/dt = k_{obsd}[Ni(III)][Fe^{2+}] \qquad (2)$$

and were independent of the hydrogen ion concentration over the range $[H^+]$ = 0.10–1.00 M. The second-order rate constants, k_{obsd}, determined at several temperatures are presented together with the corresponding activation parameters in Table I. Additional experiments were carried out on the reduction of $Ni(cyclam)^{3+}$ by $Fe(aq)^{2+}$ in 1.0 M $HClO_4$ in which the concentration of added

SO_4^{2-} ions varied over the range (2–200) × 10^{-5} M. A marked increase in k_{obsd} with increasing $[SO_4^{2-}]$ was observed for this reaction (Figure 1).

The oxidation of VO^{2+} by the nickel(III) macrocycle complexes followed the stoichiometry in eq 3, with the formation of a va-

$$Ni^{III}L + VO^{2+} + H_2O \rightarrow Ni^{II}L + VO_2^+ + 2H^+ \qquad (3)$$

nadium(V) species. This was confirmed by the addition of H_2O_2 to produce a solution exhibiting the characteristic red color of the V(V) peroxo complex.[16] Kinetic studies were made at 25 °C in

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Table II. Rate Constants at Various [H⁺] for the Reduction of Ni(III) Macrocycle Complexes by VO^{2+}(aq) ($\mu = 1.00$ M (LiClO₄))

oxidant	T, °C	10^2k_3, M⁻¹ s⁻¹ [H⁺] = 1.00 M	[H⁺] = 0.50 M	[H⁺] = 0.40 M	[H⁺] = 0.30 M	[H⁺] = 0.25 M	[H⁺] = 0.20 M	10^2k_b, s⁻¹
Ni(cyclam)³⁺	10.0	2.33	5.13	5.92	7.96		9.41	2.31 ± 0.26
	15.0	3.22	6.84		11.8		15.0	3.29 ± 0.24
	20.0	5.10	10.6		17.4		23.1	5.06 ± 0.30
	25.0	8.11	14.3	18.7		30.2ᵃ	38.5	7.51 ± 0.42ᵉ
Ni(Me₂cyclam)³⁺	25.0	9.34	19.6	22.7	30.1	34.6	43.6	8.36 ± 0.44
Ni(tet-c)³⁺	25.0	185	263	307	381		608	106 ± 13
Ni(tet-d)³⁺	25.0	262	452	578	707		928	166 ± 17
Ni(Me₂diene)³⁺	25.0		4.43 / 3.49ᵇ	5.15	6.17	9.37		2.10 ± 0.22
Ni(Me₆diene)³⁺	25.0	76.0	115	131			213	34.0 ± 1.8
Ni(non)₂³⁺	25.0	0.46	2.03			3.42	3.88 / 6.76ᶜ	0.78 ± 0.20
Ni(dec)₂³⁺	25.0	6.87 / 7.75ᵈ	13.6 / 9.97ᵇ	15.3				6.04 ± 0.38

ᵃ [H⁺] = 0.235 M. ᵇ [H⁺] = 0.60 M. ᶜ [H⁺] = 0.11 M. ᵈ [H⁺] = 0.80 M. ᵉ $\Delta H_b^{\ddagger} = 13 \pm 2$ kcal mol⁻¹, $\Delta S_b^{\ddagger} = -21 \pm 6$ cal deg⁻¹ mol⁻¹.

perchlorate media ($\mu = 1.00$ M (LiClO₄)) in the range [H⁺] = 0.11–1.00 M. The pseudo-first-order rate constants, k_3, displayed a first-order dependence on [VO²⁺] and a term inversely dependent on [H⁺] (Table II).

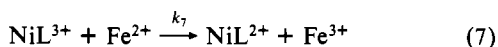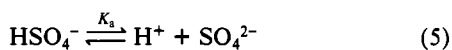$$-d[\text{Ni(III)}]/dt = (k_a + k_b/[\text{H}^+])[\text{Ni(III)}][\text{VO}^{2+}] \quad (4)$$

In most cases the intercept, k_a, was found to be small and subject to considerable experimental error. No calculations were based on these constants. The values of the slope, k_b, are presented in Table II. In other oxidations of VO²⁺, such as with Fe(bpy)₃³⁺,[17] similar rate behavior is observed.

Discussion

(a) Reduction of Ni(III) Macrocycles by Fe²⁺. The rate constants for the reduction of Ni^{III}L by Fe²⁺ in acidic perchlorate media (Table I) were found to be independent of [H⁺] over the range 0.10–1.00 M. Previous studies using Ni(oxime)²⁺ (H₂oxime = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime)[18] and Ni(bpy)₃³⁺ (bpy = 2,2′-bipyridine)[6], where there are no proton equilibria associated with the oxidants, have exhibited a similar lack of [H⁺] dependence, also conforming to eq 2. The small enthalpies of activation, coupled with large negative entropies of activation, are in the range observed previously for outer-sphere oxidation of Fe²⁺ by metal complexes.[19,20]

Several experiments on the reaction of Fe²⁺ with Ni(cyclam)³⁺ were carried out in the presence of sulfate ions ((2–200) × 10⁻⁵ M). Under these conditions only the monosulfato species, NiL(SO₄)⁺, is formed ($K_1 = 2 \times 10^3$ M⁻¹).[21] A marked increase in the rate was observed with increasing [SO₄²⁻], and Scheme I consistent with the data is represented in eq 5–8. The observed

Scheme I

$$\text{HSO}_4^- \underset{}{\overset{K_a}{\rightleftharpoons}} \text{H}^+ + \text{SO}_4^{2-} \quad (5)$$

$$\text{NiL}^{3+} + \text{SO}_4^{2-} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{NiL(SO}_4)^+ \quad (6)$$

$$\text{NiL}^{3+} + \text{Fe}^{2+} \xrightarrow{k_7} \text{NiL}^{2+} + \text{Fe}^{3+} \quad (7)$$

$$\text{NiL(SO}_4)^+ + \text{Fe}^{2+} \xrightarrow{k_8} \text{NiL}^{2+} + \text{Fe}^{3+} + \text{SO}_4^{2-} \quad (8)$$

rate constant may be expressed in the form

$$k_{\text{obsd}} = \frac{k_7 + k_8 K_1 K_a [\text{SO}_4^{2-}]/[\text{H}^+]}{1 + K_1 K_a [\text{SO}_4^{2-}]/[\text{H}^+]} \quad (9)$$

where $K_a = 7.9 \times 10^{-2}$ M ($\mu = 1.0$ M).[22] Figure 1 shows a plot of k_{obsd} (1 + $K_1 K_a$[SO₄²⁻]/[H⁺]) against [SO₄²⁻] for which the intercept corresponds to k_7 and the slope to $k_8 K_1 K_a$ (7.26 × 10⁵ M⁻¹ s⁻¹) at [H⁺] = 1.00 M. The calculated intercept (584 M⁻¹ s⁻¹) is almost identical with the rate constant observed in the absence of sulfate ions, 581 M⁻¹ s⁻¹. From the slope, a value of $k_8 = 4.6 \times 10^3$ M⁻¹ s⁻¹ was calculated for the oxidation of Fe²⁺ by NiL(SO₄)⁺. Previous studies of the oxidation of benzenediols[23] by NiL³⁺ and NiL(SO₄)⁺ have shown a 10–15-fold decrease in the rate constants for the sulfate complex, in keeping with the decrease in E^0 (~200 mV) observed on sulfate complexation. In the present case, the increased rate constant with NiL(SO₄)⁺ implies an electron-transfer mechanism involving a sulfate-bridged species. An alternative explanation, less favored, is that anion bridging may accelerate the reaction. Increases in rate derived from such sources are however much smaller than those observed here.

The electron-exchange rate for Fe(H₂O)₆²⁺/Fe(H₂O)₆³⁺ has been the subject of both experimental[24–26] and theoretical[19,20,26–29] investigation over several decades. The directly measured rate constant for this exchange ($k_{22} = 1.12$ M⁻¹ s⁻¹, $\mu = 0.10$ M)[26] shows a marked discrepancy from the values determined from cross-reaction data using the Marcus theory[19,29] ($k_{22} = 10^{-5}$–10⁻² M⁻¹ s⁻¹). Similar behavior has been observed for other metal aquo ions: for example, Co(H₂O)₆²⁺/Co(H₂O)₆³⁺, where direct exchange is envisaged as involving a water-bridged intermediate.[30] Cross-reaction kinetic studies involving the Fe²⁺/Fe³⁺ couple have been carried out with primarily, but not exclusively, metal tris-(polypyridine) complexes. In the present study the oxidants employed include Ni(non)₂³⁺ and Ni(dec)₂³⁺, which are unambiguously outer-sphere reagents[31,32] with no extensive electron delocalization on the ligand. (ESR spectra of Ni^{III}(9-aneN₃)₂³⁺ (10⁻⁵ M) show no change in the presence of SO₄²⁻ or Cl⁻ ions (0.1 M) consistent with the integrity of the NiN₆ chromophore.)

For the nickel(III) complexes investigated, the cross-reaction rate constants increase with the reduction potential of the oxidants,

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Table III. Cross-Reaction and Self-Exchange Rate Constants for the Oxidations of Fe(aq)$^{2+}$ and VO(OH)$^+$(aq) Ions ($\mu = 1.00$ M Unless Otherwise Indicated)

oxidant	E°, V	k_{11}, M^{-1} s^{-1}	$k_{Fe^{2+}}$(obsd), M^{-1} s^{-1}	$k_{Fe^{2+/3+}}$(calcd), M^{-1} s^{-1}	$k_{VO(OH)^+}$(obsd), M^{-1} s^{-1}	$k_{VO(OH)^{+/2+}}$(calcd), M^{-1} s^{-1}
Ni(cyclam)$^{3+}$	1.00	2.0×10^3 ^{a}	5.8×10^2	2.7×10^{-2}	8.8×10^4	2.0×10^3
Ni(Me$_2$cyclam)$^{3+}$	0.97	4.4×10^3 ^{b}	9.2×10^2	2.2×10^{-2}	9.8×10^4	7.9×10^2
Ni(tet-c)$^{3+}$	1.24	3.1×10^c	3.1×10^3	3.5×10^{-3}	1.2×10^6	1.2×10^3
Ni(tet-d)$^{3+}$	1.24	6.0×10^c	3.9×10^3	2.8×10^{-3}	2.0×10^6	1.8×10^3
Ni(Me$_2$diene)$^{3+}$	1.01	3.0×10^3 ^{b}	4.0×10^2	1.5×10^{-3}	2.3×10^4	1.5×10
Ni(Me$_6$diene)$^{3+}$	1.34	$6 (3.0)^d$	2.1×10^4 ^{e}	4.3×10^{-2}	4.0×10^5	3.4×10
Ni(non)$_2$$^{3+}$	0.95	6×10^3 ^{f}	1.7×10^2	7.5×10^{-4}	9.2×10^3	7.0
Ni(dec)$_2$$^{3+}$	0.99	3×10^4 ^{g}	1.1×10^3	9.1×10^{-3}	7.1×10^4	2.9×10
Ni(bpy)$_3$$^{3+}$	1.72	1.5×10^3 ^{h}	7.7×10^6 ^{h}	3.2×10^{-4}	3.8×10^6 ^{i}	3.3×10^{-4}
Fe(bpy)$_3$$^{3+}$	1.02	3×10^8 $(0.5)^j$	2.7×10^4 $(0.5)^k$	6.3×10^{-5}	6.3×10^4 $(0.5)^l$	1.1×10^{-3}

^{a} McAuley, A.; Macartney, D. H.; Oswald, T. *J. Chem. Soc., Chem. Commun.* **1982**, 274. ^{b} Fairbank, M.; McAuley, A., unpublished data. ^{c} Olubuyide, O., unpublished data. ^{d} Reference 30. ^{e} Reference 7. ^{f} Reference 31. ^{g} McAuley, A.; Olubuyide, O., to be submitted for publication. ^{h} Reference 6. ^{i} Macartney, D. H.; Sutin, N. to be published. ^{j} Ruff, I.; Zimmanyi, M. *Electrohchim. Acta* **1973**, *18*, 515. ^{k} Reference 34. ^{l} Reference 17. Self-exchange data for the Ni$^{II/III}$ couples were derived experimentally from cross-reactions using a Marcus treatment. Errors in k_{11} are generally not greater than 25%.

consistent with the Marcus relationship. In terms of a recent modification of the theory,[33] the rate constant for a cross-reaction k_{12} is related to the rate constants for the component exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross-reaction K_{12} by

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12}' \quad (10)$$

where

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

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

$$W_{ij} = \frac{Z_iZ_je^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}(\mu^{1/2}))} \quad (13)$$

$$A_{ii} = \left[\frac{4\pi N\sigma^2 vb\gamma r}{1000}\right]_{ii} \quad (14)$$

In these 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), $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, vb is the nuclear frequency that destroys an activated complex configuration, and γr is the thickness of the reaction layer (typically ~0.8 Å). For the Ni(III) macrocycles and Fe^{2+}, values of $\sigma \sim 12$ Å, and $vb = 8 \times 10^{12}$ s^{-1} and $\sigma = 6.5$ Å, $vb = 1 \times 10^{13}$ s^{-1}, respectively, were used. D_s is the dielectric constant of the medium.

Analysis of the cross-reaction data from this study using eq 10 leads to values of k_{11} for the Fe$^{2+/3+}$ couple in the range 7×10^{-4} to 5×10^{-2} M^{-1} s^{-1} (Table III). Representative data are presented in Figure 2, in a plot of 2 ln (k_{12}/W_{12}') − ln k_{11} against ln $(K_{12}f_{12})$. The intercept of this correlation, rearranged from eq 10, corresponds to the natural logarithm of the Fe$^{2+/3+}$ self-exchange rate constant. The value of k_{22} obtained (Figure 3) from reactions of the nickel(III) macrocyclic complexes is $\sim10^{-2}$ M^{-1} s^{-1} (dashed line). Figure 2 also contains several points for the reduction of Fe^{3+} by ruthenium(II) ammine complexes[36,37] that fall on the same
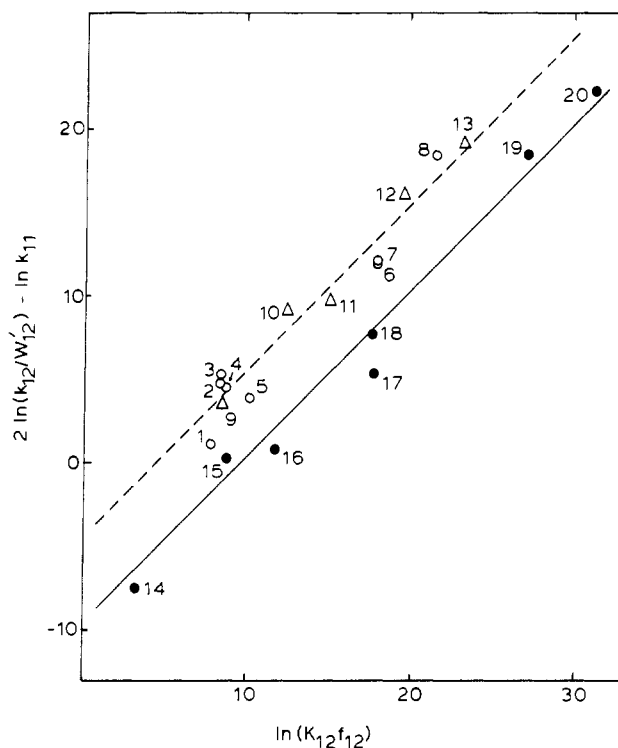
Figure 2. Plot of 2 ln (k_{12}/W_{12}') − ln k_{11} against ln $(K_{12}f_{12})$ for the oxidation of Fe^{2+} by Ni(III) macrocycles (O) and metal(III) tris(poly-pyridine) complexes[6,34,35] (●) and the reduction of Fe^{3+} by ruthenium(II) ammines[36,37] (△). Cross-reaction reagents:[38] (1) Ni(non)$_2$$^{3+}$; (2) Ni(cyclam)$^{3+}$; (3) Ni(dec)$_2$$^{3+}$; (4) Ni(Me$_2$cyclam)$^{3+}$; (5) Ni(Me$_2$diene)$^{3+}$; (6) Ni(tet-d)$^{3+}$; (7) Ni(tet-c)$^{3+}$; (8) Ni(Me$_2$diene)$^{3+}$; (9) Ru(NH$_3$)$_4(bpy)^{2+}$; (10) Ru(NH$_3$)$_5$isn^{2+}; (11) Ru(NH$_3$)$_5$py^{2+}; (12) Ru(en)$_3$$^{2+}$; (13) Ru(NH$_3$)$_6$$^{2+}$; (14) Os(bpy)$_3$$^{3+}$; (15) Fe(bpy)$_3$$^{3+}$; (16) Fe(phen)$_3$$^{3+}$; (17) Ru(bpy)$_3$$^{3+}$; (18) Fe(nphen)$_3$$^{3+}$; (19) Ni(dmbpy)$_3$$^{3+}$; (20) Ni(bpy)$_3$$^{3+}$.

line as those for the Ni(III) complexes in this study.

It is of interest to compare these rate constants with those derived from cross-reactions of Fe^{2+} with other metal complexes, including polypyridine systems.[6,34,35] In this case the cross-correlation leads to a self-exchange rate constant of $\sim10^{-4}$ M^{-1} s^{-1} (solid line in Figure 2). It appears that the Marcus model does not include completely the differing types of interaction involved in the electron-transfer processes of the two types of oxidant. The origin of the difference in behavior appears to lie in the electron distribution within the oxidants and the nature of the donor and acceptor orbitals of the cross-reactants. In the low-spin d^6 tris(polypyridine) complexes of iron, ruthenium, and osmium there is considerable mixing of the metal dπ and ligand π^* orbitals such that significant metal electron density resides on the ligand. Electron exchange in these couples takes place via a ligand π^*−π^*

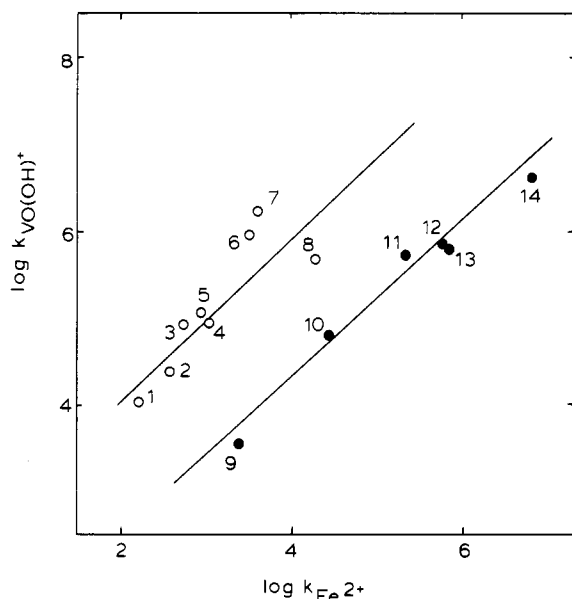(33) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275; *Prog. Inorg. Chem.* **1983**, *30*, 441.

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(38) Ligand abbreviations: py = pyridine; bpy = 2,2'-bypyridine; phen = 1,10-phenanthroline; nphen = 5-nitro-1,10-phenanthroline; dmbpy = 4,4'-dimethyl-2,2'-bipyridine; en = ethylenediamine; isn = isonicotinamide.

Figure 3. Plot of log $k_{VO(OH)^+}$ against log $k_{Fe^{2+}}$ for Ni(III) macrocycles and metal tris(polypyridine) complexes: (1) $Ni(non)_2^{3+}$; (2) $Ni(Me_2diene)^{3+}$; (3) Ni(cyclam)$^{3+}$; (4) $Ni(dec)_2^{3+}$; (5) $Ni(Me_2cyclam)^{3+}$; (6) Ni(tet-c)$^{3+}$; (7) Ni(tet-d)$^{3+}$; (8) $Ni(Me_6diene)^{3+}$ (9) $Os(bpy)_3^{3+}$; (10) $Fe(bpy)_3^{3+}$; (11) $Ru(dmbpy)_3^{3+}$; (12) $Ni(dmbpy)_3^{3+}$; (13) $Ru(bpy)_3^{3+}$; (14) $Ni(bpy)_3^{3+}$.
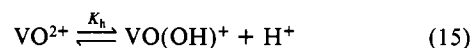
pathway, resulting from the stacked overlap of π^* lobes of the pyridines.[19] Direct d–d overlap in these complexes is considered highly nonadiabatic.[39] In their cross-reactions with iron aquo ions, for which d–d overlap provides the mode of $Fe^{2+/3+}$ electron exchange, there is a lack of pathway for electron transfer that is common to the exchange processes of both reagents. In the case of the low-spin d^7 nickel(III) complexes, which contain saturated nitrogen macrocycles, electron self-exchange with the corresponding d^8 nickel(II) species is considered to occur by overlap of metal-centered $d\sigma^*$ orbitals. The $Ni(non)_2^{3+}$ ion has been shown to exhibit considerable kinetic stability while resembling tris(ethylenediamine) complexes in its ligand coordination to the metal center.[14] In these saturated Ni(III) complexes, as well as in the simpler Ru(II) ammine systems, there would be less steric interference and greater ligand–ligand compatibility in the approach of the metal aquo ion for electron transfer by d–d overlap. It may be for this reason that the Fe^{2+}/Fe^{3+} electron exchange rate constant derived from the Ni(III) macrocycle and Ru(II) ammine cross-reactions is higher than those from the polypyridine complexes.

The self-exchange rate constants for $Fe(H_2O)_6^{2+/3+}$ derived from cross-reactions are in general significantly lower than the observed rate constant for the direct reaction. This difference has been interpreted in two ways. Hupp and Weaver[29] have proposed that the direct $Fe(H_2O)_6^{2+/3+}$ electron exchange occurs by a water-bridged inner-sphere pathway, a change in mechanism from the outer-sphere cross-reactions. They suggest that the effective self-exchange rate constant of $\sim 1 \times 10^{-3}$ M^{-1} s^{-1} obtained from the cross-reactions represents the value for an outer-sphere $Fe(H_2O)_6^{2+/3+}$ exchange pathway.
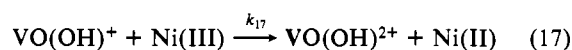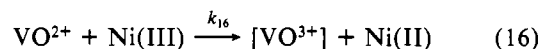
There is also support for the assignment of an outer-sphere mechanism to the $Fe(H_2O)_6^{2+/3+}$ exchange process. Swaddle[40] has recently demonstrated that the difference in the volumes of activation between the $Fe(H_2O)_6^{2+}-Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{2+}-Fe(H_2O)_5OH^{2+}$ reactions[41] is indicative of a change in mechanism, $Fe^{2+}-Fe(OH)^{2+}$ being a hydroxy-bridged process. The observed rate constant for the $Fe(H_2O)_6^{2+/3+}$ exchange (k_{22} = 1.1 M^{-1} s^{-1} at μ = 0.10 M)[26] is also in very good agreement with the semiclassical model for bimolecular electron transfer.

Sutin[6,19] has suggested that for reactions involving the iron aquo ions the exchange reactions tend to be more adiabatic than the cross reactions, as a result of the unique electronic and structural relationships in the exchange couple. This conclusion is supported by the results of the present study. The greater relative reactivity of the Ni(III) macrocycles toward Fe^{2+}, compared with the metal polypyridine complexes, can be related to structural and electronic effects. While the question of the $Fe(H_2O)_6^{2+/3+}$ exchange mechanism remains to be resolved, it is evident that the effective k_{22} value for $Fe(H_2O)_6^{2+/3+}$ for a given cross-reaction appears to depend on the nature of the cross-reactant. It is possible that the direct $Fe(H_2O)_6^{2+/3+}$ exchange process involves interpenetration of the aquo ligands beyond the point of close contact defined by the effective radius. Further kinetic studies on the electron-transfer reactions of iron aquo ions with other types of metal complexes would be valuable in refining the relationship between the cross- and self-exchange reactions of this system.

(b) Reduction of Ni(III) Macrocycles by VO^{2+}(aq). In the reductions of the Ni(III) macrocycles by VO^{2+}(aq), the observed inverse [H^+] dependence of the rate constant may be attributed to the acid dissociation equilibrium of the VO^{2+} ion

$$VO^{2+} \xrightarrow{K_h} VO(OH)^+ + H^+ \qquad (15)$$

where K_h = 8.5 × 10^{-7} M (25 °C, μ = 1.0 M).[42] The kinetic data are consistent with

$$VO^{2+} + Ni(III) \xrightarrow{k_{16}} [VO^{3+}] + Ni(II) \qquad (16)$$

$$VO(OH)^+ + Ni(III) \xrightarrow{k_{17}} VO(OH)^{2+} + Ni(II) \qquad (17)$$

leading to the expression for the observed rate constant (eq 18)

$$k_3 = k_{16} + k_{17}K_h/[H^+] \qquad (18)$$

Similar behavior has been observed previously for the outer-sphere oxidation of VO^{2+}(aq) by metal complexes.[17,43,44] As described earlier, k_{16} is negligible for the oxidants in this study so that k_3 = $k_{17}K_h/[H^+]$. The second-order rate constants, k_{17}, derived from the slopes of k_3 against [H^+]$^{-1}$, are presented in Table III.

In an application of the Marcus relationship similar to that above, the $VO(OH)^+/VO(OH)^{2+}$ self-exchange rate constant was estimated from the cross-reactions with the Ni(III) complexes. A value of $\sim$0.76 V for the reduction potential of the $VO(OH)^{2+/+}$ couple has recently been derived from kinetic studies of the reactions of $VO(OH)^+$ and $VO(OH)^{2+}$ with metal tris(polypyridine) complexes.[44] If we use this value, the calculated $VO(OH)^{+/2+}$ exchange rate constants (Table III) fall in the range $10-10^3$ M^{-1} s^{-1}. The limitations of the Marcus model are again evident when comparisons are made between the differing types of oxidant. The value derived from the Ni(III) systems differs significantly from that using polypyridine oxidants. Qualitative differences in the oxidizing species may account for the self-exchange rate derived (Ni(III) reactions) being substantially higher than the corresponding rate constants obtained from the cross-reactions with the polypyridine complexes ($\sim$5 × 10^{-4} M^{-1} s^{-1}). In this regard the behavior resembles that of the Fe^{2+} systems. The poor orbital overlap postulated above for the $Fe^{2+}/M(bpy)_3^{3+}$ reactions may also be occurring in the $VO(OH)^+/M(bpy)_3^{3+}$ reactions. Of interest is the finding that self-exchange rate constants for the $Fe^{2+/3+}$ and $VO(OH)^{+/2+}$ couples estimated from the metal polypyridine cross-reactions are very similar to each other. In both couples, an electron is exchanged between nonbonding t_{2g} orbitals and similar barriers to inner-sphere reorganization might be expected.

From the Ni(III) cross-reactions, however, the calculated $VO(OH)^{+/2+}$ rate constants are 10^4-10^5 greater than those for the $Fe^{2+/3+}$ couple. One explanation of this difference may reside in the nature of the geometry of the reducing ion. Unlike the

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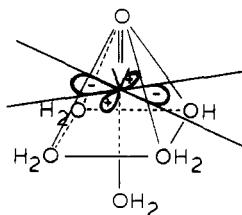(40) Swaddle, T. W. *Inorg. Chem.* **1983**, *22*, 2665.
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symmetrical octahedral $Fe(H_2O)_6{}^{2+}$ ion, deprotonation of an equatorial water in VO^{2+}(aq), cis to the oxo group, results in the asymmetric $VO(OH)^+$ ion as

A molecular orbital study carried out on the $VO(H_2O)_5{}^{2+}$ ion concluded[45] that the unpaired d electron resides in a nonbonding b_2 orbital. Rosseinsky[10] has suggested that this orbital is accessible to oxidants approaching the pyramidal face of VO^{2+}(aq). The resulting outer-sphere configuration would be favorable for cationic oxidants, with the neighboring V=O (and V—OH in the VO-(OH)$^+$ ion) helping to minimize the Coulombic repulsions. The geometric specificity of the interaction of this "region" and the cationic oxidant would (a) reduce electrostatic repulsions and (b) permit closer approach to the reactants, compared to the Fe^{2+} reaction. The former effect would result in a more stable precursor complex and the latter in better orbital overlap in a uniquely oriented donor–acceptor configuration. If this argument were to account for the greater reactivity of $VO(OH)^+$ over Fe^{2+} toward the Ni(III) macrocycles, then the similarities of their behavior with the metal polypyridine complexes imply that $M(bpy)_3{}^{3+}$ complexes do not differentiate between Fe^{2+} and $VO(OH)^+$ ions in terms of their molecular geometries, "regarding" both as spherical hydrophilic electron donors.

Direct electron exchange between VO^{2+}(aq) and $VO_2{}^+$(aq) in acidic aqueous solution is very rapid.[46] The substitution lability of these ions,[10] together with the recent observation of a mixed-valence $V_2O_3{}^{3+}$(aq) complex in equimolar $VO^{2+}/VO_2{}^+$ solutions,[47] suggests strongly that the direct electron exchange takes place by an inner-sphere mechanism. The outer-sphere rate constants calculated herein for the $VO(OH)^{+/2+}$ couple may be compared with values for other transition-metal aquo ion couples. The $VO(OH)^{+/2+}$ couple is isoelectronic with the $Ti(OH)^{2+/3+}$ couple (d^1/d^0), for which an electron exchange rate constant of $\sim 1 \times 10^{-2}$ M^{-1} s^{-1} has been determined from cross-reaction kinetic studies.[8,48] These couples, as well as $Fe^{2+/3+}$(aq) and $V^{2+/3+}$(aq) $(k_{22} = 1 \times 10^{-2}$ M),[49] involve the exchange of an electron between

nonbonding $d\pi$ orbitals. The observed rate constants are consistent with the moderate changes (0.10–0.15 Å)[26,50] in the metal–ligand bond distances between the oxidized and reduced species.

(c) Comparison of Fe^{2+} and $VO(OH)^+$ as Reductants. A comparison of this type has been explored in some detail by Rosseinsky, who found a correlation between the rate constants ([H⁺] = 1.0 M) for the redox reactions of VO^{2+} and Fe^{2+} with common cationic oxidants, principally other metal aquo ions. This correlation employed rate constants for VO^{2+} oxidations measured in 1.0 M acid solutions that were therefore composite rates comprising contributions from the acid-independent VO^{2+} and acid-dependent $VO(OH)^+$ pathways. With the subsequent availability of data on a wider variety of oxidants, it is now possible to extend the comparison of the rate constants for Fe^{2+} with those for $VO(OH)^+$. Figure 3 displays this relationship for the Ni(III) macrocycles and a series of metal tris(polypyridine) complexes. The two groups of oxidants form roughly parallel linear plots of log $k_{VO(OH)^+}$ against log $k_{Fe^{2+}}$, with the Ni(III) macrocycles at relatively larger values of $k_{VO(OH)^+}$. With the reduction potentials of Fe^{3+} and $VO(OH)^{2+}$ being similar, the separation between the points for the Ni(III) macrocycles and the metal polypyridine complexes represents enhanced reactivity of $VO(OH)^+$ toward the former oxidants, as discussed above. Rosseinsky[10] found a similar trend when comparing oxidants such as the cationic metal aquo ions, e.g. $Co(aq)^{3+}$ and $Mn(aq)^{3+}$, with anionic complexes such as $HCrO_4{}^-$. He proposed a mechanistic boundary between inner-sphere and outer-sphere processes based on a plot of log $k_{VO^{2+}}$ against log $k_{Fe^{2+}}$.

The oxidants considered to be inner sphere displayed greater reactivity toward VO^{2+} than the outer-sphere species, relative to their reduction by Fe^{2+}. In the present study the behavior of $VO(OH)^+$ may not necessarily represent a change in mechanism to a bridged inner-sphere process, but rather the formation of a uniquely oriented outer-sphere activated complex that enhances the electron transfer. Studies with other metal complexes are needed for a better understanding of the oxidation reactions of both VO^{2+} and $VO(OH)^+$.

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