Inorg. Chem. **1988**, *27*, 1863-1868

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Stereoselectivity in the Outer-Sphere Reduction of Nickel(IV) Bis(oxime-imine) Complexes by $[Co(phen)_3]^{2+}$

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Received January 20, 1988

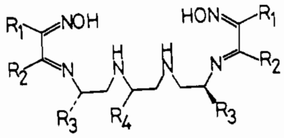
The kinetics and mechanisms of oxidation of $[Co(phen)_3]^{2+}$, $[Co(bpy)_3]^{2+}$, $[Co(4,7\text{-}Me_2phen)_3]^{2+}$, and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ (phen = 1,10-phenanthroline, bpy = 2,2′-bipyridyl) by seven bis(oxime–imine) nickel(IV) complexes have been examined at 25.0 °C and 0.10 M ionic strength by stopped flow spectrophotometry. The nickel(IV) species are substituted methyl and benzyl derivatives of $[Ni^{IV}Me_2L(1)]^{2+}$, $[Ni^{IV}MePhL(1)]^{2+}$, and $[Ni^{IV}PhMeL(1)]^{2+}$ ($Me_2L(1)H_2$ = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime; $MePhL(1)H_2$ and $PhMeL(1)H_2$ have methyl groups on the oxime–imine chromophore replaced by phenyl groups). Reactions are biphasic with an initial, rapid, pH-independent reduction of nickel(IV) to give nickel(III) species that are subsequently reduced to nickel(II) in the pH-dependent second reaction. Consideration of the reaction rates and comparisons with rates calculated by using Marcus theory lead to the conclusion that the electron transfers are outer sphere in nature. Stereoselectivities in the oxidations of $[Co(phen)_3]^{2+}$ have been investigated with a series of chiral nickel(IV) derivatives formed stereospecifically with the Λ configuration from optically active ligands, $Me_2L(2)H_2$ and $Me_2L(3)H_2$, which have respectively (*S*)-methyl and (*S*)-benzyl groups attached to the 5- and 12-positions of the amine backbone. Except for the reaction with $[\Lambda\text{-}Ni^{IV}PhMeL(2)]^{2+}$, the preferred product is $[\Lambda\text{-}Co(phen)_3]^{3+}$ with optical purities ranging from 19% to 36%. For $[\Lambda\text{-}Ni^{IV}PhMeL(2)]^{2+}$, the preferred product is 9% $[\Delta\text{-}Co(phen)_3]^{3+}$. It is argued that the magnitude of the stereoselectivities indicates an intimate interaction between the reactants, which are both cationic species. The dependence on structure can be explained by considering hydrophobic interactions and reflects precursor ion pair structure rather than a stereoelectronic effect associated with the electron-transfer act.

Introduction

Although chiral induction in electron-transfer reactions is now well documented,[1-7] the majority of reports deal with reactions between oppositely charged reagents where strong precursor ion pair formation is possible as a result of electrostatic interactions. These electrostatic interactions, as well as others such as hydrogen bonding,[4,6] have been shown to influence the course and extent of stereoselectivity. There are few reports[8] of chiral induction in direct reactions between similarly charged reagents although the presence of chiral catalysts, especially DNA,[9] produces significant effects. The study of reactions between like charged complexes affords an opportunity for examination of stereoelectronic effects in the absence of a dominant ion pairing interaction,[10,11] although it must be emphasized that stereoselectivity depends not on the absolute magnitude of the precursor complexation constant or of the electron-transfer rate constant, but on the relative magnitudes of the constants for enantiomeric species.

Recently, stereoselectivities in the reductions of a series of nickel(IV) complexes by $[Co(edta)]^{2-}$ to give the corresponding nickel(II) complexes and $[Co(edta)]^-$ have been used to define a detailed picture of the electron-transfer precursor.[5] The nickel(IV) complexes are moderately potent oxidants, and the kinetics and mechanisms of reactions with a number of well-characterized reductants have been examined.[3,12-15] Of particular interest[12] is the reaction with $[Co(phen)_3]^{2+}$, a labile, racemic, cationic reductant that forms a substitution-inert product, $[Co(phen)_3]^{3+}$. The reaction is biphasic and involves an initial rapid pH-independent reduction of nickel(IV) to give a nickel(III) intermediate and 1 equiv of $[Co(phen)_3]^{3+}$ followed by the slower, pH-dependent reduction of the nickel(III) to give nickel(II) and a second equivalent of the $[Co(phen)_3]^{3+}$ product. Both steps in the reaction are outer sphere in nature and should be amenable to stereoselectivity investigations. However, when compared with the corresponding reactions with $[Co(edta)]^{2-}$, detection of stereoselectivity in reactions with $[Co(phen)_3]^{2+}$ presents additional problems. In the presence of cobalt(II), $[Co(phen)_3]^{3+}$ racemizes rapidly by a self-exchange electron-transfer pathway,[16] a feature that has confounded previous studies.[10,17] The self-exchange rate of the $[Co(phen)_3]^{3+/2+}$ system is 8 orders of magnitude faster than the value for $[Co(edta)]^{-/2-}$.[18]

Chart I



$R_1R_2L(1)H_2$ (R_3 = H, R_4 = H)
$R_1R_2L(2)H_2$ ($R_3 = CH_3$, R_4 = H)
$R_1R_2L(3)H_2$ ($R_3 = CH_2C_6H_5$, R_4 = H)
$R_1R_2L(4)H_2$ (R_3 = H, $R_4 = CH_3$)

Table I. Stepwise Stability Constants for Cobalt(II) Complexes with 1,10-Phenanthroline and Its Substituted Derivatives at 25 °C and 0.1 M Ionic Strength

ligand	log K_1	log K_2	log K_3	pK_{a1}	ref
phen	6.96	6.73	6.08	4.98	20
4,7Me_2phen	8.08	8.00	8.43	5.95	20
5,6-Me_2phen	7.47	8.00	8.14	5.60	20
bpy	5.65	5.60	4.80	4.47	20

In this paper, the kinetics and mechanisms of oxidation of $[Co(phen)_3]^{2+}$ by a series of nickel(IV) complexes are reported.

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Stereoselectivity is used as an extrakinetic probe of the mechanism. Reactions of $[Co(bpy)_3]^{2+}$ and two derivatives of $[Co(phen)_3]^{2+}$ are also reported.

Experimental Section

(a) Materials. The preparations of the nickel(II) complexes $[Ni^{II}Me_2L(1)H_2](ClO_4)_2$, $[Ni^{II}MePhL(1)H_2](ClO_4)_2$, $[Ni^{II}PhMeL(1)H_2](ClO_4)_2$, $[\Lambda\text{-}Ni^{II}Me_2L(2)H_2](ClO_4)_2$, $[\Lambda\text{-}Ni^{II}MePhL(2)H_2](ClO_4)_2$, $[\Lambda\text{-}Ni^{II}PhMeL(2)H_2](ClO_4)_2$, and $[\Lambda\text{-}Ni^{II}Me_2L(3)H_2](ClO_4)_2$ used in this study have been outlined previously.[5,19] Ligand structures are summarized in Chart I. Oxidation to the corresponding nickel(IV) species was achieved by the addition of a few drops of cold concentrated HNO_3 to approximately 10 mg of the nickel(II) complex followed by dilution with an equal volume of cold water. In most instances, dark needles of the perchlorate salts of the doubly deprotonated nickel(IV) complexes are obtained by the dropwise addition of saturated $NaClO_4$. Solutions of the nickel(IV) complexes were prepared by dissolution of the salts or by appropriate dilution of nitric acid solutions and were standardized spectrophotometrically.[5] Solutions of the corresponding nickel(III) complexes were prepared by the addition of an equivalent amount of the nickel(II) salt to solutions of the nickel(IV) complexes at pH 7 (10^{-4} M phosphate buffer).

The ligands, 1,10-phenanthroline (phen, Aldrich), 2,2′-bipyridyl (bpy, Aldrich) and 2,2′:6′,2″-terpyridine (terpy, Aldrich) were used as received. The ligands 4,7-dimethyl-1,10-phenanthroline (4,7-Me_2phen, G. F. Smith) and 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen, G. F. Smith) were twice recrystallized from hot water to give white needles. Solutions of the cobalt(II) reductants were prepared from $Co(NO_3)_2 \cdot 6H_2O$ (Baker, Analysed) and the appropriate ligand added in sufficient excess to ensure >98% formation of the tris complexes in accord with the stability and acidity constants given in Table I.[20] As noted previously,[21] solutions of the $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ complex and to a lesser extent those of the $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ complex were found to be sensitive to aerial oxidation. Precautions were taken to prepare and use these solutions under an atmosphere of nitrogen gas. All solutions were prepared immediately before use. The complex $[Co(terpy)_2]^{3+}$ was prepared as the perchlorate salt by literature methods.[22]

(b) Methods. Kinetic measurements were made in 1.0×10^{-2} M acetate or phosphate buffer at an ionic strength of 0.10 M ($NaNO_3$). Experiments were run under pseudo-first-order conditions with an excess of the cobalt(II) reductant over the pH range 3.5–9.0. The pH was measured immediately after reaction by using a Beckman SelectIon 2000 meter equipped with a Corning combination glass electrode with a saturated calomel (NaCl) reference. Reactions were monitored close to the absorption maxima of the nickel(IV) complexes at 500 nm wtih a Durrum D-110 stopped-flow spectrophotometer thermostated at 25.0 ± 0.1 °C. Data were collected with a Nicolet 3091 digital oscilloscope. The reactions between the nickel(IV) complexes and the cobalt(II) reductants are biphasic with each phase accounting for approximately half of the total absorbance change. At higher pH, the two reactions, are well-separated (×100) and can be treated as two individual pseudo-first-order reactions. The faster process, which corresponds to reduction of nickel(IV) to nickel(III), is independent of pH but the slower reaction, reduction of nickel(III) to nickel(II), is greatly accelerated with decreasing pH such that, at lower pH, the reactions are kinetically complex since rates for the two consecutive processes differ by approximately a factor of 10. Under these conditions, the slower nickel(III) reduction was studied by using the nickel(III) form of the oxidant as starting material. Plots of log $(A - A_\infty)$ against time are generally linear for at least 3 half-lives, and the observed pseudo-first-order rate constants, k_{obsd}, were evaluated from the slopes by least-squares analysis with an Apple II$^+$ computer. In a number of instances the reaction rates under pseudo-first-order conditions exceeded the range accessible by the stopped-flow technique, and rates were measured under second-order conditions. The oxidations of $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ and $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ by $[Co(terpy)_2]^{3+}$ were examined at pH 7.5 in a 1×10^{-2} Tris buffer at an ionic strength of 0.10 M ($NaNO_3$) and at 25.0 °C by monitoring the absorbance change due to $[Co(terpy)_2]^{3+}$ at 505 nm.

Stereoselectivities in the reductions of the nickel(IV) complexes by $[Co(phen)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$ were determined by measuring the circular dichroism in the cobalt(III) product formed when an excess of the cobalt(II) reductant in 0.10 M $NaNO_3$ is mixed with a solution of the optically active nickel(IV) complex in 0.10 M HNO_3. The activity, monitored at 487 nm for $[Co(phen)_3]^{3+}$ and 449 nm for $[Co(bpy)_3]^{3+}$, decays as a function of time due to self-exchange racemization and was extrapolated to the time of mixing. In general, the results quoted are the averages of duplicate experiments.

Table II. Second-Order Rate Constants for Reduction of Nickel(IV) and Nickel(III) Complexes by $[Co(phen)_3]^{2+}$ and Its Derivatives at 25.0 °C and 0.10 M Ionic Strength

oxidant	$10^{-5}k_{IV}$, $M^{-1}\,s^{-1}$	$10^{-4}k_{IIIa}$, $M^{-1}\,s^{-1}$	$10^{-2}k_{IIIb}$, $M^{-1}\,s^{-1}$	10^5K_h, M
	Reductant = $[Co(phen)_3]^{2+}$			
$[Ni^{IV}Me_2L(1)]^{2+}$	3.2 ± 0.5	4.1 ± 0.1	8.3 ± 1.1	8.91 ± 1.5
$[Ni^{IV}MePhL(1)]^{2+}$	35 ± 6	34 ± 1	3.9 ± 0.1	37.1 ± 5.0
$[Ni^{IV}PhMeL(1)]^{2+}$	300 ± 200	140 ± 5	110 ± 5	23.0 ± 6.0
$[\Lambda\text{-}Ni^{IV}Me_2L(2)]^{2+}$	8.5 ± 1.0	6.4 ± 0.3	8.7 ± 0.1	6.86 ± 0.52
$[\Lambda\text{-}Ni^{IV}PhMeL(2)]^{2+}$	150 ± 60			
$[\Lambda\text{-}Ni^{IV}Me_2L(3)]^{2+}$	40 ± 10	130 ± 5	130 ± 8	29.9 ± 6.2
$[Ni^{IV}Me_2L(4)]^{2+}$	6.1 ± 0.6	4.0 ± 0.2	6.7 ± 0.3	9.58 ± 0.80
	Reductant = $[Co(4,7\text{-}Me_2phen)_3]^{2+}$			
$[Ni^{IV}Me_2L(1)]^{2+}$	32 ± 10	51 ± 1	110 ± 5	8.91 ± 1.5
$[Ni^{IV}MePhL(1)]^{2+}$	70 ± 30	130 ± 9	1400 ± 200	37.1 ± 5.0
	Reductant = $[Co(5,6\text{-}Me_2phen)_3]^{2+}$			
$[Ni^{IV}Me_2L(1)]^{2+}$	36 ± 3	59 ± 2	110 ± 10	8.9 ± 1.51
$[Ni^{IV}MePhL(1)]^{2+}$	200 ± 100	990 ± 10	1100 ± 30	37.1 ± 5.0
	Reductant = $[Co(bpy)_3]^{2+}$			
$[Ni^{IV}Me_2L(1)]^{2+}$	6.5 ± 0.3	6.2 ± 0.1	19 ± 1	8.91 ± 1.5

Results and Discussion

(a) Overall Reaction. The prototypical reaction between $[Ni^{IV}Me_2L(1)]^{2+}$ and $[Co(phen)_3]^{2+}$ has been reported previously.[12] As expected from the relevant reduction potentials, 2 equiv of $[Co(phen)_3]^{2+}$ are required to reduce the nickel(IV) complex to nickel(II) (eq 1), giving rise to biphasic kinetic behavior. The faster reaction corresponds to the rapid reduction of nickel(IV) to give a nickel(III) intermediate that is subsequently and more slowly reduced to nickel(II). Spectroscopic characteristics of both the nickel(IV) and the nickel(III) complexes have been reported previously[5] for all of the species used in this work. As a general rule, the nickel(IV) complexes have extinction coefficients at 500 nm that are approximately twice those of the corresponding trivalent species so that the two reaction phases each account for around 50% of the absorbance change at this wavelength. Both reactions can be examined in some kinetic detail. At higher pH, the nickel(III) intermediate is in its less reactive unprotonated form, $[Ni^{III}Me_2L(1)]^+$, and, under pseudo-first order conditions, the time scales of the two phases are well separated, allowing treatment as independent reactions. However, at lower pH, protonation of the intermediate occurs with a resulting increase in reduction potential and reactivity, such that the time scales of the consecutive reaction steps are much closer together. To facilitate data treatment, the nickel(IV) reaction was examined exclusively at higher pH and the reactions of the intermediates were examined by using nickel(III) generated independently at pH >5 where it is thermodynamically stable with respect to disproportionation. When such nickel(III) solutions are mixed with cobalt(II) solutions at pH <5, conditions can be chosen such that disproportionation[23] is much slower than reduction, allowing examination over an extensive pH range.

$$[Ni^{IV}Me_2L(1)]^{2+} + 2[Co(phen)_3]^{2+} \rightarrow [Ni^{II}Me_2L(1)] + 2[Co(phen)_3]^{3+} \quad (1)$$

(b) Nickel(IV) Reductions. Pseudo-first-order rate constants for the nickel(IV) reduction reactions are presented in Table SI, available as supplementary material. The reactions are first order in both oxidant and reductant. In a number of cases, the nickel(IV) reduction steps were too fast for convenient study under pseudo-first-order conditions and second-order conditions over a very limited concentration range were employed. With a stopped-flow instrument of the design used, this creastes considerable errors[24] and these values must be considered rather approximate.

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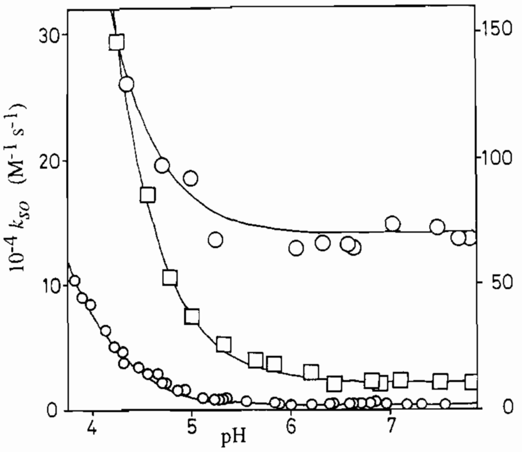

Figure 1. Plots of the second-order rate constant for reduction of $[Ni^{III}MePhL(1)]^+$ by (∘) $[Co(phen)_3]^{2+}$, (○) $[Co(4,7\text{-}Me_2phen)_3]^{2+}$, both left-hand ordinate, and (□) $[Co(5,6\text{-}Me_2phen)_3]^{2+}$, right-hand ordinate, as a function of pH at 25.0 °C and 0.10 M ionic strength. The solid curves are drawn by using eq 3 and the data in Table II.

Second-order rate constants, k_{IV}, for all the nickel(IV) reductions are presented in Table II and are pH-independent processes consistent with the mechanism in eq 2. It seems likely that they

$$[Ni^{IV}Me_2L(1)]^{2+} + [Co(phen)_3]^{2+} \xrightarrow{k_{IV}} [Ni^{III}Me_2L(1)]^+ + [Co(phen)_3]^{3+} \quad (2)$$

are outer sphere in nature since the nickel(IV) complexes are very inert to substitution to the extent that ligand dissociation is slow even in concentrated HNO_3. Ligand dissociation in the cobalt(II) complexes is also generally slower than the pseudo-first-order rate constants for the electron-transfer reactions. Blinn and Wilkins[25] report a value of 0.16 s^{-1} at 25 °C for $[Co(phen)_3]^{2+}$. Formation constants for the dimethyl-substituted complexes are somewhat higher[20] than for $[Co(phen)_3]^{2+}$ with the implication that ligand dissociation is even slower.

The trends in the rates of reduction of the nickel(IV) complexes show a number of features. Complexes $[Ni^{IV}Me_2L(1)]^{2+}$, $[Ni^{IV}Me_2L(4)]^{2+}$, and $[\Lambda\text{-}Ni^{IV}Me_2L(2)]^{2+}$ show slightly increased reactivity as the number of methyl groups on the amine backbone increases. However, this increase is not large, less than a factor of 3. All three species have similar reduction potentials. The increase is readily explained by the modest increase in steric bulk that results in reduced electrostatic repulsions and a small increase in the self-exchange rates of the complexes.[26] Substitution of the methyl groups on the oxime–imine chromophores by phenyl groups also enhances electron-transfer reactivity. Again this reflects the increased steric bulk of the complexes, and while reduced electrostatic interactions play a role, the dominant feature is an increase in the reduction potential of the complexes.[5] Similar comments can be made for the addition of methyl groups to the phenanthroline reductants.

(c) Nickel(III) Reductions. Pseudo-first-order rate constants for the nickel(III) reduction reactions are presented in Table SII, also available as supplementary material. The reductions of the nickel(III) complexes by $[Co(phen)_3]^{2+}$ and its derivatives show a first-order dependence on the concentrations of both [nickel(III)] and [cobalt(II)], but the second-order rate constants are strongly dependent on pH (Figure 1). This dependence is ascribed to a protic equilibrium involving one of the oxime oxygens of the oxidant and can be described by eq 3, which is consistent with

$$-d[Ni(III)]/dt = (k_{IIIa}[H^+] + k_{IIIb}K_h)/([H^+] + K_h)[Co(II)][Ni(III)] \quad (3)$$

the mechanism in eq 4–6. Best fit values of the rate constants

$$[Ni^{III}Me_2L(1)H]^{2+} \overset{K_h}{\rightleftharpoons} [Ni^{III}Me_2L(1)]^+ + H^+ \quad (4)$$

$$[Ni^{III}Me_2L(1)H]^{2+} + [Co(phen)_3]^{2+} \xrightarrow{k_{IIIa}} [Ni^{II}Me_2L(1)H]^+ + [Co(phen)_3]^{3+} \quad (5)$$

$$[Ni^{III}Me_2L(1)]^+ + [Co(phen)_3]^{2+} \xrightarrow{k_{IIIb}} [Ni^{II}Me_2L(1)] + [Co(phen)_3]^{3+} \quad (6)$$

for the protonated reactants, k_{IIIa}, and the unprotonated complexes, k_{IIIb}, together with the protonation constants, K_h, are presented in Table II. The protonated form has a higher reduction potential and shows substantially enhanced redox reactivity. The reductions of the nickel(III) complexes, particularly those that are unprotonated, are slower than the corresponding reactions of nickel(IV). Data on the substitution lability of the complexes are not available, but they are substantially more labile than the nickel(IV) complexes. In some instances ligand exchange at the cobalt(II) center exceeds the rates of electron transfer, opening the possibility of inner-sphere mechanisms. However, trends in the reaction rates closely parallel those observed with the nickel(IV) series, which are unambiguously outer sphere, and this suggests that these nickel(III) reactions are outer sphere also.

Values for the protonation constants show two features. The first is that methyl substitution on the amine carbon framework of the ligand has very little effect since the pK_h values for $[Ni^{III}Me_2L(1)H]^{2+}$, $[Ni^{III}Me_2L(2)H]^{2+}$, and $[Ni^{III}Me_2L(4)H]^{2+}$ are 4.05, 4.16, and 4.02, respectively. On the other hand, substitution of a phenyl group for a methyl group on the oxime–imine framework or of a benzyl group on the amine–carbon backbone leads to a reduction in the pK_h. It is not readily apparent why the presence of bulky substituents should increase the acidity of the nickel(III) protons, but it may well be related to the overall solvation of the complexes. It is noteworthy that the trend can be correlated with the trend in reduction potentials[5] where phenyl substituents again destabilize the higher charged species.

(d) Marcus Treatment. The trends in the rates of outer-sphere reactions of this type can be discussed fruitfully with the aid of relative Marcus theory,[26,27] which relates the cross-reaction rate constants to the self-exchange rate constants for the reactants. It is conveniently expressed in free energy terms as eq 7 and 8,

$$\Delta G_{12}^* = \tfrac{1}{2}(\Delta G_{11}^* + \Delta G_{22}^* + \Delta G^\circ(1 + \alpha^*)) \quad (7)$$

$$\alpha^* = \Delta G^\circ / 4(\Delta G_{11}^* + \Delta G_{22}^*) \quad (8)$$

where ΔG_{12}^* represents the free energy of activation for the cross-reaction, ΔG_{11}^* and ΔG_{22}^* are the corresponding terms for the self-exchange reactions, and ΔG° is the free energy change for the cross-reaction. It is customary to correct these parameters for electrostatic work involved in the approach of charged reagents in the reaction medium as in eq 9, where ω_{12} is the work term,

$$\omega_{12} = z_{11}z_{22}e^2/D_s r_{12}(1 + \beta\mu^{1/2}r_{12}) \quad (9)$$

D_s is the static dielectric constant for the medium, $\beta = (8\pi Ne^2/1000D_s kT)^{1/2}$, z_{11} and z_{22} are the charges on the two reactants, and r_{12} is the apparent reaction distance, generally approximated by the sum of the reactant radii, $a_{11} + a_{22}$, given by eq 10, where d_x, d_y, and d_z are orthogonal diameters of the

$$a_{11} = \tfrac{1}{2}(d_x d_y d_z)^{1/3} \quad (10)$$

metal complex.[26] Recent discussion[28] of the use of this approximation for like-charged reactants supports close contact between the complexes.

The Marcus analysis depends on the availability of self-exchange rate data for the reagents used in these studies. Good estimates for the reduction potentials and self-exchange rates of the nickel(IV) complexes have been reported,[5,29] and these are summarized in Table III. The self-exchange rates for the nickel(IV)/nick-

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Table III. Summary of Reduction Potential and Self-Exchange Rate Data for the Complexes

complex	$E°$, V	k_{11}, $M^{-1}\ s^{-1}$	ref
$[Ni^{IV}Me_2L(1)]^{2+}$	0.66	6×10^4	23
$[Ni^{IV}MePhL(1)]^{2+}$	0.69	8×10^5	5
$[Ni^{IV}PhMeL(1)]^{2+}$	0.71	4×10^6	5
$[Co(phen)_3]^{3+}$	0.37	45	16, 22, 35
$[Co(bpy)_3]^{3+}$	0.32	20	16, 22, 35
$[Co(terpy)_2]^{3+}$	0.31	400	16, 22, 35
$[Co(4,7\text{-}Me_2phen)_3]^{3+}$	0.16	7	*a*
$[Co(5,6\text{-}Me_2phen)_3]^{3+}$	0.23	26	*a*

[a] This work.

el(III) systems have been estimated from the rates of the pseudo-self-exchange processes between the complexes $[Ni^{III}Me_2L(1)]^+$, $[Ni^{III}MePhL(1)]^+$, and $[Ni^{III}PhMeL(1)]^+$ and their chiral dimethyl analogues $[\Lambda\text{-}Ni^{IV}Me_2L(2)]^{2+}$, $[\Lambda\text{-}Ni^{IV}MePhL(2)]^{2+}$, and $[\Lambda\text{-}Ni^{IV}PhMeL(2)]^{2+}$, respectively. As noted above, reduction potentials are comparable for each pair of complexes, and in all cases examined, the reactivity of the chiral dimethyl derivative is comparable with the reactivity of the parent complex. Where comparisons have been made,[23] the values of these pseudo-self-exchange rates are close to those calculated from Marcus theory, serving to justify their use as independent measures of the rate. For the nickel(III) complexes, independent estimates of the self-exchange rates are not available, and while reduction potential data are available for the unprotonated complexes, values for the protonated complexes are much less certain, although, in two cases examined,[30] there is an increase in the potential of 0.22 V on protonation. In the light of these deficiencies, discussion of the Marcus treatment will be restricted to the nickel(IV) reactions.

For the reductants, values for the reduction potentials and self-exchange rates are well established[16,22] for $[Co(phen)_3]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$; however, there is some disagreement in appropriate values for reduction potentials for the substituted phenanthroline complexes. The reduction potential of $[Co(4,7\text{-}Me_2phen)_3]^{3+}$ is variously reported as 0.34,[31] 0.26,[32] 0.155,[21] and 0.16 V[33] for roughly comparable conditions. The two former values appear to reflect experiments in which the cobalt(II) complex dissociates and are likely to be less reliable. It is noteworthy that the single value reported[31] for $[Co(5,6\text{-}Me_2phen)_3]^{3+}$, 0.42 V, refers to comparable conditions and must also be considered as inaccurate. A cyclic voltammetric examination of both these complexes was undertaken to establish reduction potentials relevant to the conditions of the present study:[34] pH 7.5, 1.0×10^{-2} M Tris buffer, 0.10 M ionic strength ($NaNO_3$) and 25.0 °C. Both couples are quasi-reversible with peak–peak separations increasing from ~80 mV at a scan rate of 10 mV s^{-1} to ~130 mV at 100 mV s^{-1}. The midpoint potentials give reduction potentials of 0.16 ± 0.01 and 0.23 ± 0.01 V (vs NHE) for the complexes $[Co(4,7\text{-}Me_2phen)_3]^{3+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{3+}$, respectively. The former value is in good agreement with more recent literature determinations.[21,33]

Most existing estimates[31,35] of the self-exchange rates for the two dimethyl-substituted phenanthroline complexes are based on Marcus calculations for reactions that are thermodynamically unfavorable, a consequence of the erroneous determination of the reduction potentials. Koval and co-workers[21] report a more reliable estimate for the self-exchange rate for $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ between 4 and 10 $M^{-1}\ s^{-1}$ at 0.20 M ionic strength and 25.0 °C based on cross-reaction rate data with a number of ruthenium(III) pentaamine and copper(III) peptide complexes. In the present work, the cross-reactions between $[Co(terpy)_2]^{3+}$ and $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ were examined at 25.0 °C and 0.10 M ionic strength to obtain independent estimates. Reactions are first-order in both oxidant and reductant, (Figure 2, Table SIII), and the second-order rate constants are 867 ± 16 $M^{-1}\ s^{-1}$ and 478 ± 8 $M^{-1}\ s^{-1}$, respectively. These data give Marcus calculated self-exchange rates of 7 $M^{-1}\ s^{-1}$ for $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ and 26 $M^{-1}\ s^{-1}$ for $[Co(5,6\text{-}Me_2phen)_3]^{3+/2+}$ in good agreement with the results of Koval and co-workers.[21] The reduction potential and self-exchange rate data for the reductants are summarized in Table III.

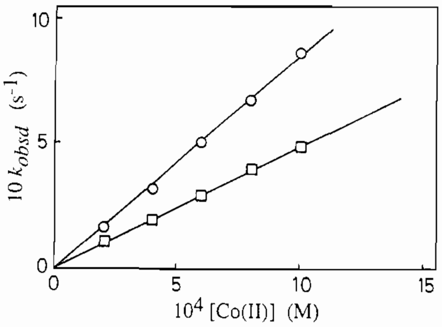

Figure 2. Plot of k_{obsd} against cobalt(II) concentration for the reduction of $[Co(terpy)_2]^{3+}$ by (□) $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and (○) $[Co(5,6\text{-}Me_2phen)_3]^{2+}$ at pH 7.5, 25.0 °C, and 0.10 M ionic strength.

Table IV. Details of Marcus Calculations and Comparisons with Observed Rate Constants[a]

reaction	a_{11}, Å	a_{22}, Å	$10^{-5}k_{12}$(calcd), $M^{-1}\ s^{-1}$	$10^{-5}k_{12}$(obsd), $M^{-1}\ s^{-1}$
$[Ni^{IV}Me_2L(1)]^{2+}$ + $[Co(phen)_3]^{2+}$	5.4	7	3.0	3.2
$[Ni^{IV}Me_2L(1)]^{2+}$ + $[Co(bpy)_3]^{2+}$	5.4	7	5.0	6.5
$[Ni^{IV}Me_2L(1)]^{2+}$ + $[Co(4,7\text{-}Me_2phen)_3]^{2+}$	5.4	8	30	32
$[Ni^{IV}Me_2L(1)]^{2+}$ + $[Co(5,6\text{-}Me_2phen)_3]^{2+}$	5.4	8	20	36
$[Ni^{IV}MePhL(1)]^{2+}$ + $[Co(phen)_3]^{2+}$	6.4	7	17	35
$[Ni^{IV}MePhL(1)]^{2+}$ + $[Co(4,7\text{-}Me_2phen)_3]^{2+}$	6.4	8	150	100
$[Ni^{IV}MePhL(1)]^{2+}$ + $[Co(5,6\text{-}Me_2phen)_3]^{2+}$	6.4	8	100	200
$[Ni^{IV}PhMeL(1)]^{2+}$ + $[Co(phen)_3]^{2+}$	6.9	7	52	300

[a] 25.0 °C, 0.10 M ionic strength.

The Marcus analysis of the rate data is presented in Table IV where the observed second-order rate constants are compared with those calculated from eq 7 and the parameters in Table III. In general, agreement is excellent, within a factor of 2, and is consistent with adiabatic outer-sphere electron transfer. However, for the reduction of $[Ni^{IV}PhMeL(1)]^{2+}$ by $[Co(phen)_3]^{2+}$, the observed rate is an order of magnitude faster than calculated. While this discrepancy is not substantially outwith the range of experimental error, it may be an indication that the interactions between the complexes in the cross-reaction are different from those in the corresponding self-exchange reactions. It is noteworthy that no comparable discrepancy between observed and calculated rate constants is detected in the corresponding reductions[5] by $[Co(edta)]^{2-}$.

In this series of reactions, there are a number of trends in varying structure: the substitution and position of methyl groups on the periphery of the phenanthroline rings of the reductants and the substitution and position of phenyl rings on the oxime–imine chromophore of the oxidant. Both structural variations have a minor effect beyond that expected on the basis of reduction potentials and self-exchange rates.

It has been pointed out that despite the bulk of phenanthroline ligands, self-exchange electron transfer between metal–phenanthroline complexes is substantially adiabatic.[36] Overlap between

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(34) [Cobalt(II)] = 1.0×10^{-3} M, [Me_2phen] = 4.0×10^{-3} M.

(35) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 151.

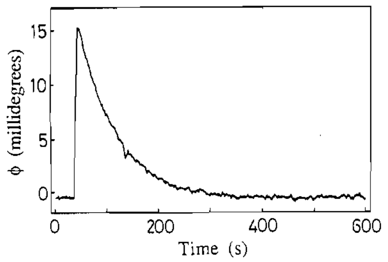

Figure 3. Decay of the circular dichroism signal at 487 nm for $[\Lambda\text{-Co(phen)}_3]^{3+}$ formed in the oxidation of $[\text{Co(phen)}_3]^{2+}$ by $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ at pH 1.83 and 0.10 M ionic strength. Time is recorded from initiation of the reaction.

donor and acceptor orbitals is sufficient to allow an electronic transmission coefficient κ close to unity, implying that there is delocalization over the ligand chromophore. Koval and coworkers[21] have examined the effects of steric bulk on the periphery of the phenanthroline rings on the electron-transfer reactivity of a number of cobalt complexes and conclude that, with large substituents, the steric repulsion is sufficient to prevent good orbital overlap between the complexes, leading to nonadiabatic behavior. In the present case, the substituents on the phenanthroline rings have moderate bulk and no deviations suggestive of significant nonadiabatic behavior are noted. The distribution of the methyl substituents also appears unimportant, consistent with the relatively high symmetry of the complexes.

Space-filling models reveal that the phenyl substituents on the oxime–imine chromophores of the nickel(IV) complexes are not in conjugation with the oxime–imine π-system as a result of steric interactions with the adjacent methyl groups. However, it would appear that this does not markedly affect orbital overlap between the complexes. Distribution of the substituents in this case appears more important, suggesting that the orientation of these lower symmetry complexes with respect to the reductant may be significant.

(e) Stereoselectivity Experiments. Detection of stereoselectivity in the oxidation of $[\text{Co(phen)}_3]^{2+}$ and its derivatives by the optically active nickel(IV) complexes presents some experimental difficulties because the racemization of $[\text{Co(phen)}_3]^{3+}$ in the presence of an excess of $[\text{Co(phen)}_3]^{2+}$ is relatively rapid. An excess of $[\text{Co(phen)}_3]^{2+}$ is required since the rate of racemization of the reductant is much slower ($6.9\ \text{s}^{-1}$)[25] than the rate of the electron-transfer process. Hence if a stoichiometric amount of reductant is used, the $[\text{Co(phen)}_3]^{3+}$ product must be racemic. In order to study the stereoselectivity, advantage is taken of a number of favorable circumstances. The nickel(IV) complexes are very stable in acidic media (0.10 M HNO_3), and the rates of oxidation of $[\text{Co(phen)}_3]^{2+}$ by both nickel(IV) and nickel(III) ($\sim 10^{-4}$ M) under these conditions with an excess ($\sim 10^{-3}$ M) of $[\text{Co(phen)}_3]^{2+}$ are rapid ($t_{1/2} < 10$ ms) when compared with the rate of ligand dissociation of $[\text{Co(phen)}_3]^{2+}$ ($t_{1/2} = 4.3$ s).[25] Thus when the optically active nickel(IV) complex in acidic solution is added to an unbuffered solution containing excess $[\text{Co(phen)}_3]^{2+}$, 2 equiv of $[\text{Co(phen)}_3]^{3+}$ are formed rapidly while the excess $[\text{Co(phen)}_3]^{2+}$ is substantially destroyed by the slower ligand dissociation. The specific rate of ligand dissociation exceeds the rate of racemization of $[\text{Co(phen)}_3]^{3+}$ by the self-exchange pathway. Hence any optical activity in the $[\text{Co(phen)}_3]^{3+}$ product will be preserved. In fact the conditions chosen for the study are a compromise, and slow racemization of the $[\text{Co(phen)}_3]^{3+}$ is observed (Figure 3). Optical activity in the product was monitored at 487 nm for $[\text{Co(phen)}_3]^{3+}$ and 449 nm for $[\text{Co(bpy)}_3]^{3+}$. A further complication arises since the nickel(II) oxime–imine complex formed in the reaction is also optically active and has a circular dichroism signal at these wavelengths. However, under the conditions of the study, the complex is hydrolyzed. To ensure that interference from nickel(II) could be neglected, an experiment was run with $[\text{Fe(CN)}_6]^{4-}$ as reductant. In this case, no optical activity was detected.

Table V. Electron-Transfer Stereoselectivity for Oxidations of $[\text{Co(phen)}_3]^{2+}$ by Optically Active Nickel(IV) Derivatives at 22 °C and 0.1 M Ionic Strength

oxidant	$10^4[\text{Ni}^{IV}]$, M	$10^3[[\text{Co(phen)}_3]^{2+}]$, M	pH	stereo-selectivity
$[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$	1.11	1.68	1.49[a]	21% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$	1.79	1.26	1.40	14% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$	1.13	1.68	1.39	18% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$	0.56	1.68	1.42	19% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$	1.05	1.68	*b*	16% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$	1.62	1.68	1.83	25% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$	0.51	1.68	1.86	24% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$	0.80	1.68	1.80	9% ΛΔ
$[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(3)}]^{2+}$	0.29	1.68	1.82	36% ΛΛ
$[\Lambda\text{-Ni}^{IV}\text{Me}_2\text{L(2)}]^{2+}$	1.07	1.68[c]	1.50	3.5% ΛΛ

[a] 6 °C. [b] 25% aqueous ethanol. [c] $[\text{Co(bpy)}_3]^{2+}$.

The results of the stereoselectivity experiments are presented in Table V. At low [Co(II)]:[Ni(IV)] ratios there is a dependence of the stereoselectivity on $[\text{Co(phen)}_3]^{2+}$ concentration, consistent with slow racemization of the reductant. However, for the modest stereoselectivities observed in these studies, the concentration dependence is negligible when the ratio exceeds 15:1. A number of other experiments using $[\text{Co(5,6-Me}_2\text{phen)}_3]^{2+}$ and $[\text{Co(4,7-Me}_2\text{phen)}_3]^{2+}$ as reductants were also attempted, but these were unsuccessful. It seems likely that ligand dissociation in these complexes is slower due to their higher thermodynamic stability and that this results in an increase in the self-exchange racemization rate.

Interpretation of the results is complicated by the fact that the stereoselectivities are the sum for two distinct reactions, nickel(IV) reduction and nickel(III) reduction, each with their own stereoselective requirements. However, both processes are mechanistically similar and will be treated as a single reaction. The stereoselectivities in the oxidations of $[\text{Co(phen)}_3]^{2+}$ are large compared with stereoselectivities in other outer-sphere reactions, suggesting that there is a fairly intimate interaction between the reactant complexes. For reactions between similarly charged complexes, this is an important revelation in that it indicates that the energetic requirements for adiabatic electron transfer are sufficient to overcome electrostatic repulsions. Similar conclusions based on Marcus analysis of rate data have been reached[28] in reactions between metal phenanthroline complexes in nonaqueous media.

As a corollary to this intimate interaction, the stereoselectivities are found to be markedly dependent on the structures of the nickel(IV) complexes. This is particularly apparent in comparing the results for the isomeric pair $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ and $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$ where the stereoselectivities are 23% ΛΛ and 9% ΔΛ, respectively. Current understanding of this modest but highly structure sensitive behavior is that electron transfer in the metal ion complexes is not strongly orientation dependent, and hence subtle steric factors have an effect on the balance of one arrangement of the reactants over another. Stereoselectivity, on the other hand, is dependent on orientation and reflects this balance. Thus the complexes $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ and $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$ interact quite differently with the reductant.

Reasons for these differences in interaction can be understood by examining space-filling models of the complexes involved. The phenyl groups in $[\Lambda\text{-Ni}^{IV}\text{PhMeL(2)}]^{2+}$ are directed along the C_2 axis emanating from the dioxime face of the complex, while those for $[\Lambda\text{-Ni}^{IV}\text{MePhL(2)}]^{2+}$ are almost perpendicular to this axis (Figure 4). For adiabatic electron transfer between two cationic reactants, the former complex will experience a greater proportion of electron transfer through a microstate in which $[\text{Co(phen)}_3]^{2+}$ approaches the C_2 axis since the effective reaction distance is longer, and consequently, electrostatic repulsions are smaller. However, simple calculations[37] indicate that this electrostatic

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(36) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275–282.

(37) For a model in which the electron-transfer rate is calculated for orthogonal axes, including the C_2 axis containing the oxime face. See ref 5 for details.

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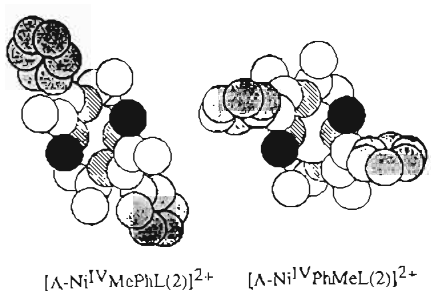

Figure 4. View along the C_2 axes of space-filling representations of [Λ-Ni^{IV}MePhL(2)]$^{2+}$ and [Λ-Ni^{IV}PhMeL(2)]$^{2+}$. Data were taken from ref 4 and 5. Oxygen atoms are shown in black, nitrogen atoms are shown as striped, and the shaded areas indicate the positions of the phenyl rings of interest.

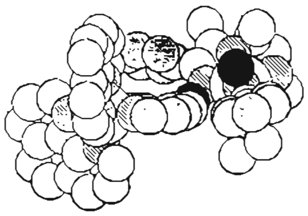

Figure 5. Possible stacking type interaction (shaded) between a 1,10-phenanthroline ring on [Co(phen)$_3$]$^{2+}$ and the phenyl rings on [Λ-Ni^{IV}PhMeL(2)]$^{2+}$. Additional data were taken from ref 38.

repulsion is unlikely to produce effects that are significant enough to explain the observed stereoselectivities. For example, the proportion of the rate carried by the C_2 axis face is 15.8% for [Λ-Ni^{IV}PhMeL(2)]$^{2+}$ and 13.9% for [Λ-Ni^{IV}MePhL(2)]$^{2+}$ but is 15.4% for [Λ-Ni^{IV}Me$_2$L(2)]$^{2+}$, which shows stereoselectivity closer to that of [Λ-Ni^{IV}MePhL(2)]$^{2+}$ than that of [Λ-Ni^{IV}PhMeL(2)]$^{2+}$. Some modification of the model is required.

The reductant [Co(phen)$_3$]$^{2+}$ presents a hydrophobic aspect and will tend to associate predominantly with hydrophobic faces of the oxidant. For [Λ-Ni^{IV}Me$_2$L(2)]$^{2+}$, this amounts to almost the whole ion apart from the hydrophilic C_2 face where the oxime oxygens are located. Addition of hydrophobic phenyl groups to the complex ion on the amine and oxime–imine framework away form this C_2 face will have little effect on the proportion of the reaction taking place through the hydrophilic face, and hence the stereoselectivities will be rather insensitive to these changes, as is observed with [Λ-Ni^{IV}MePhL(2)]$^{2+}$ and the dibenzyl derivative [Λ-Ni^{IV}Me$_2$L(3)]$^{2+}$. For [Λ-Ni^{IV}PhMeL(2)]$^{2+}$, the phenyl groups straddle the hydrophilic C_2 face, increasing its hydrophobic character. Indeed, the two phenyl rings form a cleft that might support a stacking interaction as shown in Figure 5. An interaction of this sort in addition to electrostatic forces provides an explanation for the modest rate enhancement in the cross-reaction between [Λ-Ni^{IV}PhMeL(2)]$^{2+}$ and [Co(phen)$_3$]$^{2+}$. Thus, the stereoselectivity for [Λ-Ni^{IV}PhMeL(2)]$^{2+}$ can be explained by the placement of the hydrophobic phenyl groups along the normally hydrophilic C_2 axis of the oxidant and the proposal that reaction along this axis exhibits the opposite chirality from that predominating for the rest of the complex ion. A similar conclusion has been reached in the reduction by [Co(edta)]$^{2-}$.

The results strongly suggest that the modest stereoselectivities detected in outer-sphere electron-transfer reactions between metal ion complexes are the result of the multiplicity of orientations of the complexes which give acceptable orbital overlap for electron transfer rather than intrinsically small stereoselectivities for particular orientations. They further suggest that electron transfer in these systems has little intrinsic orientation requirements other than those imposed by the precursor structure.

Acknowledgment. This work is supported by the National Science Foundation (Grant Nos. CHE 84-06113 and CHE 87-02012), which is gratefully acknowledged.

Registry No. [Co(phen)$_3$]$^{2+}$, 16788-34-4; [Ni^{IV}Me$_2$L(1)]$^{2+}$, 55188-33-5; [Ni^{IV}MePhL(1)]$^{2+}$, 55758-54-8; [Ni^{IV}PhMeL(1)]$^{2+}$, 55822-44-1; [Λ-Ni^{IV}Me$_2$L(2)]$^{2+}$, 99342-18-4; [Λ-Ni^{IV}PhMeL(2)]$^{2+}$, 110077-01-5; [Λ-Ni^{IV}Me$_2$L(3)]$^{2+}$, 110077-03-7; [Ni^{IV}Me$_2$L(4)]$^{2+}$, 114157-52-7; [Co(4,7-Me$_2$phen)$_3$]$^{2+}$, 47872-45-7; [Co(5,6-Me$_2$phen)$_3$]$^{2+}$, 47872-55-9; [Co(bpy)$_3$]$^{2+}$, 15878-95-2; [Λ-Ni^{IV}MePhL(2)]$^{2+}$, 110095-00-6.

Supplementary Material Available: Listings of pseudo-first-order rate constants for the oxidation of [Co(phen)$_3$]$^{2+}$ and its derivatives by nickel(IV) (Table SI), nickel(III) (Table SII), and [Co(terpy)$_2$]$^{3+}$ (Table SIII) (14 pages). Ordering information is given on any current masthead page.

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Electron Transfer. 93. Further Reactions of Transition-Metal-Center Oxidants with Vitamin B_{12s} (Cob(I)alamin)[1]

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Received December 29, 1987

Vitamin B_{12s} (cob(I)alamin) reduces europium(III), titanium(IV) ($TiO(C_2O_4)_2^{2-}$), and uranium(VI) in aqueous solution. These oxidants undergo one-electron changes, leading in each case to the cobalt product cob(II)alamin (B_{12r}). The reduction of Eu^{3+}, which is inhibited by "TES" buffer, but not by glycine, is outer sphere. Its limiting specific rate (1×10^2 M^{-1} s^{-1}), incorporated in the Marcus treatment, yields a B_{12s},B_{12r} self-exchange rate of $10^{4.8\pm0.5}$ M^{-1} s^{-1}. Reductions of $TiO(C_2O_4)_2^{2-}$ are accelerated by H^+ and by acetic acid. Kinetic patterns suggest three competing reaction paths involving varying degrees of protonation of the Ti(IV) center or its association with acetic acid. The very rapid reduction of U(VI) ($k = 4 \times 10^6$ M^{-1} s^{-1}) yields U(V) in several buffering media, even when B_{12s} is taken in excess. The much slower conversion of U(V) to U(IV), although thermodynamically favored, appears to be retarded by the extensive reorganization of the coordination sphere of oxo-bound U(V) that must accompany its acceptance of an additional electron. The observed specific rate for the B_{12s}–U(VI) reaction is in reasonable agreement, in the framework of the Marcus formalism, with reported values of the formal potential and the self-exchange rate for U(V,VI).

Vitamin B_{12s} (cob(I)alamin, the cobalt(I) analogue of B_{12a}) reacts rapidly and quantitatively with an imposing array of inorganic and organic oxidants.[2] Much of the early work with this macrocyclic reductant, which dealt with its role in organic syn-

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[1] Joint sponsorship of this work by the National Science Foundation and the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health (Grant No. BRSG S07 RR-07208-8) is gratefully acknowledged.

[2] For reviews, see: (a) Pratt, J. M. *Inorganic Chemistry of Vitamin B_{12}*; Academic: London, 1972; p 96. (b) Halpern, J. In *B_{12}*; Dolphin, D., Ed.; Wiley-Interscience: New York, 1982; Vol. 1, p 501. (c) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105.

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