

Table IV. Comparison of Experimental Rate Constants with Those Calculated by Using Marcus Theory for the Oxidations of Nickel(II) and Nickel(III) by Br₂ and Br₂⁻

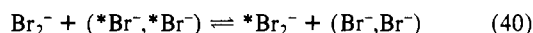
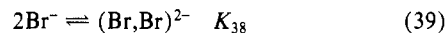
reacn	k_{so}^a M ⁻¹ s ⁻¹	$k_{\text{so}}(\text{calcd})^b$ M ⁻¹ s ⁻¹
[Ni ^{II} L] + Br ₂	2.1 × 10 ⁷	8 × 10 ⁶
[Ni ^{II} LH] ⁺ + Br ₂	7.1 × 10 ⁵	4 × 10 ⁴
[Ni ^{II} LH ₂] ²⁺ + Br ₂	≤ 2 × 10 ³	2 × 10 ⁻¹
[Ni ^{III} L] ⁺ + Br ₂	1.2 × 10 ⁵	4 × 10 ⁵
[Ni ^{II} L] + Br ₂ ⁻	8.5 × 10 ⁸	8 × 10 ⁸
[Ni ^{II} LH] ⁺ + Br ₂ ⁻	2.7 × 10 ⁸	4 × 10 ⁷
[Ni ^{II} LH ₂] ²⁺ + Br ₂ ⁻	≤ 9 × 10 ⁷	2 × 10 ⁴
[Ni ^{III} L] ⁺ + Br ₂ ⁻	10 ⁹ (estimate)	3 × 10 ⁸

^a Experimentally derived value. ^b Calculated by using eq 37 and reduction potentials, association constants, and rate constants documented in the text.

the reaction, k_{aa} is the self-exchange rate for the oxidant, k_{bb} is the corresponding rate for the reductant, and Z is the collision frequency for neutral molecules in solution (10¹¹ M⁻¹ s⁻¹). A value for k_{aa} of 1 × 10⁹ M⁻¹ s⁻¹ was chosen, in line with values for other radical species, and the results of these calculations are presented in Table IV. The calculated rates are all within an order of magnitude of the values observed, certainly consistent with the mechanism shown in Scheme II (or indeed in Scheme I). Similar calculations were performed for the oxidation of [Ni^{III}L]⁺ with Br₂; again, agreement is good. Thus, a number of features of the oxidation of nickel(II) by Br₂ point to an apparent two-electron outer-sphere process: the detection of [Ni^{IV}L]²⁺ as an intermediate in the reaction with nickel(II) in excess and failure to detect [Ni^{III}L]⁺ in the reaction with Br₂ in excess. Nevertheless an explanation involving sequential two-electron transfer within a single ion pair is preferred. The reaction rates are in line with the theoretical treatment for single-electron transfer and would be expected to be much lower for a two-electron process. However, a problem with this explanation is the relatively low rate predicted for electron transfer from Br₂⁻ to [Ni^{III}L]⁺ within the ion pair

compared with ion dissociation. This prediction relies on estimates of both the second-order rate constant for reaction of Br₂⁻ with [Ni^{III}L]⁺ and the ion-pair association constant. Both estimates are subject to considerable uncertainty.

Stanbury³³ has suggested that it is possible to consider electronic self-exchange between species such as Br₂⁻ and the ion pair (Br,Br)²⁻, eq 39 and 40, where the asterisks are used to denote



the different bromine pairs. A value of $K_{39} = 0.05$ M⁻¹ was estimated³¹ for the conditions in this study from which the self-exchange rate, eq 40, can be estimated to be around 1 M⁻¹ s⁻¹. This value is 4 orders of magnitude lower than the corresponding number for the I₂⁻/(I⁻, I⁻) self-exchange rate,³³ in line with the expected trend in bond stretching energies,³⁴ which determine the Franck-Condon barriers to electron transfer. However the accuracy of the calculations and lack of comparable data in the literature preclude more detailed comment.

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Registry No. Ni^{II}L, 59980-38-0; [Ni^{III}LH]⁺, 60306-03-8; Br₂, 7726-95-6; Br₂⁻, 24959-67-9.

Supplementary Material Available: Table V, showing the amount of nickel(IV) produced on mixing aliquots of standard nickel(II) and bromine solutions (1 page). Ordering information is given on any current masthead page.

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Ligand Design for Enhanced Stereoselectivity in the Electron-Transfer Reactions between Nickel(IV) Bis(oxime-imine) Complexes and [Co(edta)]²⁻

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A number of derivatives of the hexadentate bis(oxime-imine) ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, Me₂L(1)H₂, have been prepared in which the methyl groups on the oxime-imine chromophores are replaced by more bulky phenyl groups, MePhL(1)H₂ and PhMeL(1)H₂, or chiral (*S*) methyl (L(2)) and benzyl (L(3)) groups are attached on the amine backbone at the 5- and 12-positions. Nickel(II) complexes of the ligands can be oxidized to the corresponding nickel(III) and nickel(IV) derivatives, and the effect of changing ligand structure on the reduction potentials of the complexes is small. Self-exchange rate constants for the nickel(IV)/nickel(III) change have been estimated from the rates of the cross-reactions between [Ni^{III}MePhL(1)]⁺ and [Ni^{III}PhMeL(1)]⁺ and their chiral (*S,S*,12*S*)-dimethyl nickel(IV) derivatives to be 8 × 10⁵ and 4 × 10⁶ M⁻¹ s⁻¹, respectively, at 25 °C and 0.1 M ionic strength. The kinetics and mechanisms of reduction of [Ni^{IV}MePhL(1)]²⁺ and [Ni^{IV}PhMeL(1)]²⁺ and [Co(edta)]²⁻ have also been investigated. The reactions are biphasic with initial rapid reduction of nickel(IV) to give a nickel(III) transient, which is subsequently reduced. Nickel(IV) reduction is outer sphere in nature, and the rates are in general agreement with the predictions of Marcus theory; however, the nickel(III) step is complicated by disproportionation. Binding of the chiral ligand systems to the nickel ions is deduced from circular dichroism studies to be stereospecific, giving the Λ absolute configuration around the metal in all cases. Stereoselectivity in the oxidation of [Co(edta)]²⁻ by nickel(IV) has been investigated by using these chiral complexes, and in all cases the preferred isomer of the product [Co(edta)]⁻ is Δ with enantiomeric excesses of 7%, 21%, 22%, and 46% for the complexes [Ni^{IV}PhMeL(2)]²⁺, [Ni^{IV}MePhL(2)]²⁺, [Ni^{IV}Me₂L(3)]²⁺, and [Ni^{IV}MePhL(3)]²⁺, respectively. The stereoselectivities are explained by a model that takes into account steric factors in the reactions, in which the C₂ oxime-imine face of the nickel(IV) complex exerts a controlling influence.

Introduction

There is a considerable number of reports of chiral induction in outer-sphere electron-transfer reactions between metal ion complexes in solution.¹⁻⁶ The effects are generally modest, around

30% in the most favorable cases, although in the presence of chiral catalysts such as DNA,⁷ high stereoselectivity can be attained.

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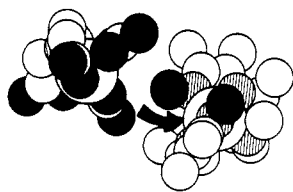
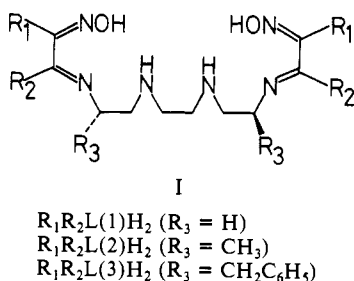


Figure 1. Structure proposed in ref. 4 for the ion-pair precursor responsible for stereoselectivity in the electron transfer between $[\text{Co}(\text{edta})]^{2-}$ and $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$. The arrow shows the interaction between the carboxylate face of the reductant and the C_2 face of the oxidant. Oxygen atoms are denoted by dark solids and nitrogen atoms by stripes.

In previous work^{4,6} it has been shown that stereoselectivity can be used as a sensitive probe of mechanism and of the structure of reaction intermediates. In the reduction of the chiral nickel(IV) complex $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$, where $\text{Me}_2\text{L}(2)\text{H}_2$ is (5*S*,12*S*)-3,5,12,14-tetramethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (I) by $[\text{Co}(\text{edta})]^{2-}$, $[\text{Co}(\text{pdta})]^{2-}$, and $[\text{Co}(\text{cdta})]^{2-}$,



where edtaH_4 is 1,2-diaminoethane-*N,N,N',N'*-tetraacetic acid and pdtaH_4 and cdtaH_4 are the corresponding 1,2-diaminopropane and 1,2-diaminocyclohexane derivatives, the absence of a dependence on substrate structure of reaction rate and stereoselectivity has been used to deduce the structure of the ion-pair precursor to electron transfer.⁴ This structure is depicted in Figure 1.

In previous work, also, it has been shown that steric factors and chelate ring conformations can have a marked effect on electron-transfer stereoselectivity.⁶ It is of considerable interest to know if, given the structure of the stereoselectivity-determining precursor complex, the reactants can be modified in well-defined ways to increase or decrease the observed stereoselectivity in a predictable way. To elucidate this point, four new chiral nickel(IV) complexes have been prepared and characterized and stereoselectivity in the oxidation of $[\text{Co}(\text{edta})]^{2-}$ has been investigated.

Experimental Section

(a) Preparation of Ligands. The compound 1-phenyl-1,2-propanedione 1-oxime was prepared from benzyl methyl ketone as described in the literature.⁸ Both 1-phenyl-1,2-propanedione 2-oxime (Sigma) and 2,3-butanedione oxime (Sigma) were used as received. The tetraamine (2*S*,9*S*)-2,9-diamino-4,7-diazadecane was prepared and purified as described previously.^{3,4} An analogous modification of the method of Job and Bruce⁹ was used to prepare the (2*S*,9*S*)-2,9-diamino-1,10-diphenyl-4,7-diazadecane from L-phenylalanine and 1,2-diaminoethane. The compound was purified by vacuum distillation (0.05 mmHg, 220–235 °C) to yield a viscous colorless liquid.

The ligands 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $\text{Me}_2\text{L}(1)\text{H}_2$, and (5*S*,12*S*)-3,5,12,14-tetramethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $\text{Me}_2\text{L}(2)\text{H}_2$, were prepared by published routes.^{3,10} The dibenzyl analogue

(5*S*,12*S*)-5,12-dibenzyl-3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $\text{Me}_2\text{L}(3)\text{H}_2$, was prepared by refluxing stoichiometric amounts of (2*S*,9*S*)-2,9-diamino-1,10-diphenyl-4,7-diazadecane and 2,3-butanedione oxime in dry ether for 5 h. After the mixture was allowed to stand overnight, the solvent was removed and the crude ligand dried under vacuum for 24 h.

Similar procedures were used for the preparation of 3,14-diphenyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $\text{MePhL}(1)\text{H}_2$, (5*S*,12*S*)-5,12-dimethyl-3,14-diphenyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $\text{MePhL}(2)\text{H}_2$, (5*S*,12*S*)-5,12-dibenzyl-3,14-diphenyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime, $\text{MePhL}(3)\text{H}_2$, by using 1-phenyl-1,2-propanedione 2-oxime and the appropriate tetraamine, and 2,13-dimethyl-1,14-diphenyl-3,6,9,12-tetraazatetradeca-2,12-diene-1,14-dione dioxime, $\text{PhMeL}(1)\text{H}_2$, and (4*S*,11*S*)-1,14-diphenyl-2,4,11,13-tetramethyl-3,6,9,12-tetraazatetradeca-2,12-diene-1,14-dione dioxime, $\text{PhMeL}(2)\text{H}_2$, by using 1-phenyl-1,2-propanedione 1-oxime and the appropriate tetraamine. The crude products were used in subsequent metal complexation reactions. In no case was any attempt made to recrystallize the ligands.

(b) Preparation of Nickel(II) Complexes. The complexes $[\text{Ni}^{\text{II}}\text{Me}_2\text{L}(1)\text{H}_2](\text{ClO}_4)_2$, $[\text{Ni}^{\text{II}}\text{Me}_2\text{L}(1)\text{H}_2](\text{NO}_3)_2$, and $[\Delta\text{-Ni}^{\text{II}}\text{Me}_2\text{L}(2)\text{H}_2](\text{ClO}_4)_2$ were prepared as described previously.^{3,11} The complexes $[\text{Ni}^{\text{II}}\text{MePhL}(1)\text{H}_2](\text{ClO}_4)_2$, $[\text{Ni}^{\text{II}}\text{MePhL}(2)\text{H}_2](\text{ClO}_4)_2$, $[\text{Ni}^{\text{II}}\text{PhMeL}(1)\text{H}_2](\text{ClO}_4)_2$, and $[\text{Ni}^{\text{II}}\text{PhMeL}(2)\text{H}_2](\text{ClO}_4)_2$ were prepared by stoichiometric reaction of the ligands with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Alfa) in warm ethanol.¹¹ The crude products were obtained by cooling the solutions to 0 °C and could be recrystallized from aqueous ethanol. The dibenzyl complexes $[\text{Ni}^{\text{II}}\text{Me}_2\text{L}(3)\text{H}_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}^{\text{II}}\text{MePhL}(3)\text{H}_2](\text{NO}_3)_2$ were similarly prepared from the ligands and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in ethanol. In these cases, the crude products were obtained from ethanol at 0 °C by the dropwise addition of propan-2-ol and dried under vacuum.

Good elemental analyses (C, H, N; M. W. H. Laboratories, Phoenix, AZ) for all the previously unreported nickel(II) complexes were obtained except in the case of $[\text{Ni}^{\text{II}}\text{MePhL}(2)\text{H}_2](\text{ClO}_4)_2$ and $[\text{Ni}^{\text{II}}\text{MePhL}(3)\text{H}_2](\text{NO}_3)_2$ where there appeared to be contamination by a small amount of unreacted ligand, despite several recrystallizations. However satisfactory results were obtained for the nickel(IV) complexes that were used in the kinetic and stereoselectivity studies.

(c) Preparation of Nickel(IV) Complexes. Typically, oxidation of the nickel(II) complexes 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.¹¹ Dark needles of the nickel(IV) complexes are obtained by the dropwise addition of saturated NaClO_4 . In this way the complexes $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(1)](\text{ClO}_4)_2$, $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(2)](\text{ClO}_4)_2$, $[\text{Ni}^{\text{IV}}\text{MePhL}(1)](\text{ClO}_4)_2$, $[\text{Ni}^{\text{IV}}\text{MePhL}(2)](\text{ClO}_4)_2$, $[\text{Ni}^{\text{IV}}\text{PhMeL}(1)](\text{ClO}_4)_2$, and $[\text{Ni}^{\text{IV}}\text{PhMeL}(2)](\text{ClO}_4)_2$ were prepared. For the dibenzyl complexes $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(3)](\text{ClO}_4)_2$ and $[\text{Ni}^{\text{IV}}\text{MePhL}(3)](\text{ClO}_4)_2$ this procedure yielded dark oily solids, which were crystallized by dissolution in acetone to which water was added dropwise until the first appearance of solids. Dark needles of the nickel(IV) complexes formed on standing at 0 °C.

(d) Cyclic Voltammetry Studies. Cyclic voltammetry measurements were made in 2.5×10^{-2} M buffer at an ionic strength of 0.10 M (NaNO_3) and at 25.0 ± 0.1 °C with either the nickel(II) or the nickel(IV) complex at $(1-2) \times 10^{-3}$ M concentration unless otherwise noted. A three-electrode system consisting of a platinum or carbon-paste working electrode, a platinum-wire auxiliary electrode and a saturated calomel (KCl) reference electrode was used. Voltammograms were generated with use of a Princeton Applied Research Corp. Model 173 potentiostat in conjunction with a Model 175 universal programmer and a Model 176 current to voltage converter and were recorded on a Houston Instruments Model 2000 X-Y recorder.

(e) Kinetic Measurements. Solutions of $[\text{Co}(\text{edta})]^{2-}$ were prepared as outlined previously.³ The kinetics of reduction of the nickel(IV) complexes by $[\text{Co}(\text{edta})]^{2-}$ were investigated under pseudo-first-order conditions with an excess of reductant in the presence of 1.0×10^{-2} M buffer at 0.10 M ionic strength (NaNO_3) unless otherwise noted. The reactions are biphasic in nature, and only the initial reaction, reduction of nickel(IV) to nickel(III), is reported in detail. Above pH 6, the second phase of the reaction, nickel(III) reduction, which exhibits complex kinetic behavior, is sufficiently slow not to interfere with the more rapid reaction.³

Reactions were monitored at the absorption maximum of the nickel(IV) complexes around 500 nm with a Durrum D-110 stopped-flow

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spectrophotometer thermostated at 25.0 ± 0.1 °C. Data were collected with a Nicolet 3091 digital oscilloscope. Under pseudo-first-order conditions with an excess of [Co(II)], plots of $\log(A - A_\infty)$ against time were generally linear for at least 3 half-lives and the observed pseudo-first-order rate constants, k_{obs} , were evaluated from the slopes by least-squares analysis with an Apple II+ computer. In instances where the subsequent reaction was thought to interfere with the linearity of the plot, the apparent A_∞ of the reaction was varied to obtain the best straight line, generally a small correction. The pH of solutions was monitored immediately after reaction with a Beckman SelectIon 2000 meter equipped with a Corning combination glass electrode with a saturated calomel (NaCl) reference.

Reductions of $[\Lambda\text{-Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$ by $[\text{Ni}^{\text{III}}\text{MePhL}(1)]^+$ and of $[\Lambda\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$ by $[\text{Ni}^{\text{III}}\text{PhMeL}(1)]^+$ were examined briefly around pH 7, by stopped-flow spectrophotometry at 500 nm in 1.0×10^{-2} M phosphate buffer and 0.1 M ionic strength (NaNO_3). The absorbance changes are small and the reactions are rapid, but good estimates of the rate can be made. With $[[\Lambda\text{-Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}] = 4.4 \times 10^{-6}$ M, pseudo-first-order rate constants of 31 ± 5 and 13 ± 2 s^{-1} are obtained for $[[\text{Ni}^{\text{III}}\text{MePhL}(1)]^+] = 4.0 \times 10^{-5}$ M (pH 7.12) and 1.7×10^{-5} M (pH 7.12), respectively, giving a second-order rate constant for the reaction of $(8 \pm 3) \times 10^5$ $\text{M}^{-1} \text{s}^{-1}$. With $[[\Lambda\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}] = 2.9 \times 10^{-6}$ M, pseudo-first-order rate constants 140 ± 50 s^{-1} and 80 ± 35 s^{-1} are obtained for $[[\text{Ni}^{\text{III}}\text{PhMeL}(1)]^+] = 3.8 \times 10^{-5}$ M (pH 7.27) and 1.8×10^{-5} M (pH 7.14), respectively, giving a second-order rate constant for the reaction of $(4 \pm 2) \times 10^6$ $\text{M}^{-1} \text{s}^{-1}$.

(f) Stereoselectivity Studies. Stereoselectivities in the reductions of the chiral nickel(IV) and nickel(III) complexes by $[\text{Co}(\text{edta})]^{2-}$ were determined by measuring the optical activity of the $[\text{Co}(\text{edta})]^-$ produced in the reaction.^{3,4} After the reactions had gone to completion, the product solutions were passed through a cation-exchange resin (Amberlite IR-120) in the sodium form to remove optically active nickel(II) species. The results are quoted as enantiomeric excess for the cobalt(III) complex.¹² Circular dichroism spectra were measured on an Aviv circular dichroism spectropolarimeter, Model 60DS (Aviv Associates, Lakewood, NJ), calibrated against an aqueous solution of $[\Lambda(+)\text{-Co}(\text{en})_3]\text{Cl}_3$ ($\Delta\epsilon_{493} = 1.90$ $\text{M}^{-1} \text{cm}^{-1}$).¹³ Visible spectra were run on a Varian DMS 100 spectrophotometer.

Results and Discussion

(a) Spectra and Structure of the Nickel Complexes. The UV-visible spectroscopic characteristics of the nickel(IV) oxime-imine complexes are shown in Table I. Those for the corresponding nickel(III) and nickel(II) species are presented in Table SI, available as supplementary material. For a given oxidation state, the forms of the spectra are similar, suggesting that these six-dentate ligands provide a distorted octahedral environment as has been shown for $[\text{Ni}^{\text{III}}\text{Me}_2\text{L}(1)\text{H}_2]^{2+}$, $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(1)]^{2+}$,¹⁴ and $[\Lambda\text{-Ni}^{\text{II}}\text{Me}_2\text{L}(2)\text{H}_2]^{2+}$.⁴ For the nickel(IV) complexes $[\text{Ni}^{\text{IV}}\text{MePhL}(1)]^{2+}$ and $[\text{Ni}^{\text{IV}}\text{PhMeL}(1)]^{2+}$ there is disagreement between the extinction coefficient obtained in the present work and those reported by Chakravorty and co-workers;¹¹ however, the present data are much more in line with those for the other nickel(IV) complexes. In Tables I and SI also are shown the circular dichroism spectroscopic parameters for the complexes prepared from chiral ligands. Again the spectra are all very similar to the corresponding spectra reported⁴ for $[\Lambda\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ and $[\Lambda\text{-Ni}^{\text{III}}\text{Me}_2\text{L}(2)]^+$, both in general form and in the magnitudes of the values for $\Delta\epsilon$. For the nickel(IV) complexes, the low-energy band around 420 nm has $\Delta\epsilon$ of -15.3 for $[\Lambda\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$, -15.8 for $[\text{Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$, -26.1 for $[\text{Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$, -27.4 for $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(3)]^{2+}$, and -22.9 for $[\text{Ni}^{\text{IV}}\text{MePhL}(3)]^{2+}$, all very similar. The values for the band around 320 nm are likewise all around -30 apart from $[\text{Ni}^{\text{IV}}\text{MePhL}(3)]^{2+}$, which has a much larger value of -49 , possibly the result of interactions between the benzene rings in the ion. The nickel(III) complexes are also similar with $\Delta\epsilon$ values for the peak around 330 nm between -16.9 and -24.1 for all of the complexes.

There are two important conclusions that can be drawn from these spectra. The similarities in the form of the spectra strongly

Table I. Spectroscopic Parameters for Nickel(IV) Complexes in Aqueous Solution^b

complex	λ_{max} , nm	ϵ , $\text{M}^{-1} \text{cm}^{-1}$	λ , nm	$\Delta\epsilon$, $\text{M}^{-1} \text{cm}^{-1}$	
$[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(1)]^{2+}$	500	6300 ^a			
	430	5960 ^a			
$[\text{Ni}^{\text{IV}}\text{MePhL}(1)]^{2+}$	515	5520 \pm 20			
	515	3360 ^a			
	436	5040			
	425	3200 ^a			
$[\text{Ni}^{\text{IV}}\text{PhMeL}(1)]^{2+}$	523	8290 \pm 80			
	520	2850 ^a			
	441	7810			
	440	2510 ^a			
$[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$	495	7250 \pm 100	535	+3.33	
	433	5920	454	-5.00	
	300 (sh)	1.45×10^4	418	-15.33	
	253 (sh)	3.80×10^4	359	-0.83	
			326	-21.67	
$[\text{Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$	502	7475 \pm 110	522	+8.16	
	433	6280	460	-5.52	
	306	2.54×10^4	420	-26.1	
	262	3.54×10^4	361	-2.11	
			327	-30.4	
			285	+20.3	
			264	-29.3	
			245	+2.93	
	$[\text{Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$	510	9880 \pm 360	534	+5.22
		434	8335	427	-15.8
273 (sh)		2.58×10^4	378	-6.01	
			363	-6.25	
			310	-26.5	
$[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(3)]^{2+}$	506	8100 \pm 150	544	+4.16	
	445	6850	466	-4.93	
	302 (sh)	2.77×10^4	420	-27.4	
	254 (sh)	6.58×10^4	369	-4.73	
			320	-32.0	
			284	+52.7	
			255	-64.3	
	$[\text{Ni}^{\text{IV}}\text{MePhL}(3)]^{2+}$	503	8400 \pm 200	533	+5.78
		442	7450	427	-22.9
		308	3.53×10^4	363	-4.71
267		4.57×10^4	328	-49.0	
			285	+30.2	
		265	-20.4		
		245	+8.17		

^aReference 11. ^bNickel(IV) spectra were measured at pH 3.

suggest first that all the complexes have the same absolute configuration as $[\Lambda\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ and second that, like this latter complex, they are formed with high stereoselectivity. The ligand wrapping in $[\Lambda\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ was shown³ by chromatography under conditions in which resolution of the racemic complex $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(1)]^{2+}$ is possible¹⁵ to be, within experimental limits, a stereospecific process. Similar experiments have been attempted with the more substituted derivatives with disappointing results since the chromophores are much less robust and decompose during elution. Only in the case of $[\text{Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$ was elution on CM-Sephadex C-25-120 cation exchange resin by 0.05 M potassium (+)-antimonytartrate (pH 4) successful. The complex moved as a single band and all fractions obtained had approximately the same molar ellipticity, allowing for the presence of a small amount of the reduced product $[\text{Ni}^{\text{III}}\text{MePhL}(2)]^+$ in the first few fractions collected.

In view of the similarities in the circular dichroism parameters, it is likely that all the complexes can be considered to be formed stereospecifically with the Λ configuration, and this will be assumed for the remainder of the paper.

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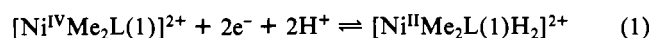
(15) Heaney, P. J.; Lappin, A. G.; Peacock, R. D.; Stewart, B. J. *Chem. Soc. Chem. Commun.* **1980**, 769-770.

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

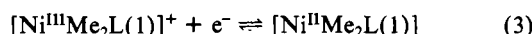
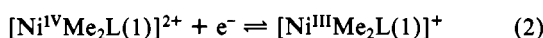
complex	E°, V vs. nhe	
	Ni ^{IV} /III	Ni ^{III} /II
[Ni ^{IV} Me ₂ L(1)] ²⁺	0.65 ^a (0.66) ^b	0.42 ^a (0.39) ^b
[Ni ^{IV} MePhL(1)] ²⁺	0.69 (0.69) ^b	0.42 (0.40) ^b
[Ni ^{IV} PhMeL(1)] ²⁺	(0.71) ^b	(0.38) ^b
[Ni ^{IV} Me ₂ L(2)] ²⁺	0.67 (0.66) ^c	0.40 (0.42) ^c
[Ni ^{IV} MePhL(2)] ²⁺	0.69	0.41
[Ni ^{IV} PhMeL(2)] ²⁺	0.71	0.40
[Ni ^{IV} Me ₂ L(3)] ²⁺	0.65	<i>d</i>
[Ni ^{IV} MePhL(3)] ²⁺	0.73	0.45

^aReference 17. ^bReference 16. ^cReference 3. ^dNot well resolved.

(b) Cyclic Voltammetry of the Nickel Complexes. The effects of changing ligand structure on the reduction potentials of a number of racemic nickel(IV) and nickel(III) complexes have been investigated previously,¹⁶ and cyclic voltammetry studies were undertaken over the pH range 7–10 with the novel chiral reagents to extend these investigations. All of the complexes show cyclic voltammetry behavior similar to that described previously for [Ni^{IV}Me₂L(1)]²⁺^{16,17} and [Δ-Ni^{IV}Me₂L(2)]²⁺.³ At low pH (<5) the voltammograms show a single, quasi-reversible, strongly pH-dependent redox couple corresponding to a two-electron change, eq 1. Above this pH both nickel(IV) and nickel(III) reductions

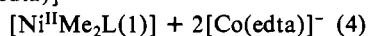


are detected, and between pH 7 and 10, these are pH independent, corresponding to the processes in eq 2 and 3. Cyclic voltammetry

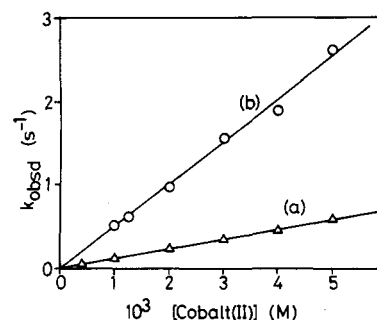


data for these two couples are summarized in Table II for all the complexes. The couples are quasi-reversible with peak-peak separations generally in excess of 60 mV (60–120 mV) at low scan rates, increasing with increasing scan rates. The nickel(III) reduction appears to be less electrochemically reversible than the nickel(IV) reduction, regardless of complex structure. For the two complexes [Δ-Ni^{IV}Me₂L(3)]²⁺ and [Δ-Ni^{IV}MePhL(3)]²⁺ difficulties were experienced with both complex decomposition and lack of electrochemical reversibility, and the data, where obtained, are less reliable. Nevertheless, it can be seen that the effects of structure on the reduction potentials are very small.¹⁶ There is an increase in the reduction potential for the nickel(IV)/nickel(III) couple as methyl groups on the oxime-imine chromophore are replaced by phenyl groups, but for the nickel(III)/nickel(II) couple, the effect is negligible. Likewise substitution of methyl or benzyl groups for protons on the amine backbone appears to have little effect on the reduction potentials as noted previously.³

(c) Kinetics and Mechanisms of Reduction by [Co(edta)]²⁻. Reduction of [Ni^{IV}Me₂L(1)]²⁺ and [Co(edta)]²⁻ has a 1:2 stoichiometry as depicted in eq 4.³ Addition of 1 equiv of [Co(edta)]²⁻



produces stoichiometric amounts of [Co(edta)]⁻ and the nickel(III) intermediate, which is stable above pH 5 as [Ni^{III}Me₂L(1)]⁺. Kinetically, under pseudo-first-order conditions with cobalt(II) in excess, the reaction is biphasic with an initial, rapid, and pH-independent phase corresponding to around 50% of the absorbance change at 500 nm, associated with reduction of nickel(IV) to nickel(III) and followed by the slower, more complex, and pH-dependent reduction of nickel(III) to nickel(II). In a previous paper,⁴ the effect of changing structure on the [Co(edta)]²⁻ reductant was examined. In the present study, the effects of

**Figure 2.** Plots of pseudo-first-order rate constants for the reduction of [Ni^{IV}MePhL(1)]²⁺ (a) and [Ni^{IV}PhMeL(1)]²⁺ (b) by [Co(edta)]²⁻ as a function of reductant concentration at 25 °C and 0.1 M ionic strength.**Table III.** Second-Order Rate Constants for the Oxidation of [Co(edta)]²⁻ and Derivatives by Nickel(IV) Complexes at 25.0 °C and 0.1 M Ionic Strength

	<i>k</i> _{so} , M ⁻¹ s ⁻¹
[Ni ^{IV} Me ₂ L(1)] ²⁺ + [Co(edta)] ²⁻	33 ± 2 ^a
[Ni ^{IV} Me ₂ L(1)] ²⁺ + [Co(pdta)] ²⁻	48 ± 3 ^b
[Ni ^{IV} Me ₂ L(1)] ²⁺ + [Co(cdta)] ²⁻	45 ± 2 ^b
[Ni ^{IV} MePhL(1)] ²⁺ + [Co(edta)] ²⁻	122 ± 4
[Ni ^{IV} PhMeL(1)] ²⁺ + [Co(edta)] ²⁻	500 ± 25
[Δ-Ni ^{IV} PhMeL(2)] ²⁺ + [Co(edta)] ²⁻	590 ± 12

^aReference 3. ^bReference 4.

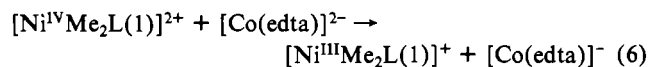
changing structure on the nickel(IV) oxidant are of interest.

The kinetics of reduction of [Ni^{IV}MePhL(1)]²⁺ and [Ni^{IV}PhMeL(1)]²⁺ were examined under pseudo-first-order conditions with an excess of [Co(edta)]²⁻ as a function of [cobalt(II)] and pH. Studies with the chiral reagents [Δ-Ni^{IV}MePhL(2)]²⁺, [Δ-Ni^{IV}PhMeL(2)]²⁺, [Δ-Ni^{IV}Me₂L(3)]²⁺, and [Δ-Ni^{IV}MePhL(3)]²⁺ were not generally carried out because these reactions exhibit stereoselectivity, which complicates the kinetic analysis. However, for [Δ-Ni^{IV}PhMeL(2)]²⁺, where the stereoselectivity is too small to have much effect, a limited study is reported, bearing out the assumption³ that methyl substituents on the amine backbone have little effect on the reaction rates.

As with the previous work^{3,4} the reactions are biphasic. Above pH 6, the first phase, reduction of nickel(IV), is well separated from the subsequent nickel(III) reduction, allowing detailed investigations. The reaction is first order in both nickel(IV) and cobalt(II) concentrations and is pH independent. Pseudo-first-order rate constants, *k*_{obsd}, are presented in Table SII, available as supplementary material. Plots of *k*_{obsd} against cobalt(II) concentration are shown in Figure 2, and the rate law, eq 5, is

$$-d[\text{Ni}(\text{IV})]/dt = k_{\text{so}}[\text{Co}(\text{II})][\text{Ni}(\text{IV})] \quad (5)$$

consistent with the simple bimolecular outer sphere electron transfer reaction, eq 6. The second-order rate constant for these and related reactions are summarized in Table III.

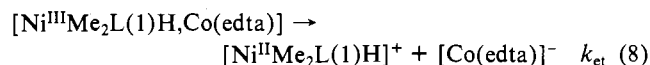
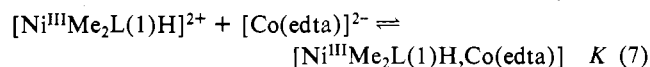


At pH 7, the slower phase, reduction of nickel(III), does not exhibit first-order kinetics because of complications from the slow disproportionation of nickel(III),¹⁸ which is faster than direct reduction by [Co(edta)]²⁻ and is driven by the subsequent, more rapid reduction of the nickel(IV) product. With [Ni^{III}Me₂L(1)]⁺, the reaction becomes pseudo first order at lower pH where the more reactive [Ni^{III}Me₂L(1)H]²⁺ predominates and the rate of direct reduction exceeds the rate of disproportionation. However, for the phenyl derivatives [Ni^{III}MePhL(1)]⁺ and [Ni^{III}PhMeL(1)]⁺, the protonation constants are much lower¹⁹ than for [Ni^{III}Me₂L(1)]⁺ and good pseudo-first-order kinetic behavior is

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not observed above pH 3.5, by which point complications from protonation of $[\text{Co}(\text{edta})]^{2-}$ become important.²⁰ Although the reactions in these cases are similar to the simpler reaction of $[\text{Ni}^{\text{III}}\text{Me}_2\text{L}(1)]^+$, which shows kinetic evidence for a hydrogen-bond stabilized electron-transfer precursor complex,³ eq 7 and 8,



they were not studied in great detail. Estimates of the overall second order rate constants, Kk_{et} , are $\sim 50 \text{ M}^{-1} \text{ s}^{-1}$ and $\sim 60 \text{ M}^{-1} \text{ s}^{-1}$, respectively, for $[\text{Ni}^{\text{III}}\text{MePhL}(1)\text{H}]^{2+}$ and $[\text{Ni}^{\text{III}}\text{PhMeL}(1)\text{H}]^{2+}$, a trend similar to that shown by the corresponding nickel(IV) complexes.

(d) Self-Exchange Rates and the Marcus Analysis of the Rate Data. The second-order rate constants for nickel(IV) reduction span an order of magnitude, and it is worthwhile examining these outer-sphere electron-transfer rates from the point of view of Marcus theory^{21,22} in an attempt to understand the energetics of the processes. Marcus theory relates the rate of a cross-reaction between two complexes, k_{12} , to the driving force for the reaction and the self-exchange rates for the individual reagents, k_{11} and k_{22} . The self-exchange rate for the reductant $[\text{Co}(\text{edta})]^{2-/-}$ is rather imprecisely known at 25 °C and 0.1 M ionic strength²³ but is generally accepted²⁴ to be close to $2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$. Reduction potential data are likewise somewhat controversial with values of 0.40²⁵ and 0.37 V²⁶ reported for the conditions of this study.

The self-exchange rate of the complex $[\text{Ni}^{\text{IV/III}}\text{Me}_2\text{L}(1)]^{2+/-}$ has been relatively well established¹⁸ from cross-reaction rate data as $4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and a close approximation to the self-exchange rate is obtained¹⁸ from the rate of the cross-reaction between the chiral complex $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ and the racemic $[\text{Ni}^{\text{III}}\text{Me}_2\text{L}(1)]^+$, which is measured by stopped-flow spectrophotometry to be $6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. These two species have nearly identical reduction potentials³ and very similar redox reactivity with other reagents,¹⁹ and although the absorption spectra of the complexes are very similar, there are sufficient differences in the extinction coefficients to allow the reaction to be monitored. In the reaction there is the potential for stereoselectivity although in practice this is not observed as the reactions are fast, absorbance changes are small, and consequently data quality is insufficient to resolve biphasic behavior resulting from slightly differing reactivities of $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ with $[\Delta\text{-Ni}^{\text{III}}\text{Me}_2\text{L}(1)]^+$ and $[\Delta\text{-Ni}^{\text{III}}\text{Me}_2\text{L}(1)]^+$. Similar measurements have been made on the cross-reactions between $[\Delta\text{-Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$ and racemic $[\text{Ni}^{\text{III}}\text{MePhL}(1)]^+$ and between $[\Delta\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$ and racemic $[\text{Ni}^{\text{III}}\text{PhMeL}(1)]^+$, giving rate constants of $(8 \pm 3) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and $\sim (4 \pm 2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Data for the latter reaction are close to the limits of stopped-flow detection and are somewhat less reliable. These values are assumed to be close to the self-exchange rates of the complexes involved. It can be seen that replacing a methyl group by a phenyl group on the oxime-imine framework increases the self-exchange rate by almost 2 orders of magnitude. This increase in rate is likely to be the result of a decrease in the electrostatic repulsion²⁷ between the nickel(V) and nickel(III) complexes with the increased bulk of the phenyl derivatives rather than the result of increased delocalization of electron density over the phenyl rings since space-filling models reveal that the presence of the adjacent methyl group requires an orientation of the phenyl ring perpendicular to the oxime-imine chromophore, restricting extensive π -overlap.

Table IV. Summary of Marcus Calculations for the Oxidation of $[\text{Co}(\text{edta})]^{2-}$ ^a

complex	E_1° , V	k_{11} , $\text{M}^{-1} \text{ s}^{-1}$	a_1 , Å	k_{12} , $\text{M}^{-1} \text{ s}^{-1}$	$k_{12}(\text{calcd})$, $\text{M}^{-1} \text{ s}^{-1}$
$[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(1)]^{2+}$	0.66	6×10^4	5.4	33	60
$[\text{Ni}^{\text{IV}}\text{MePhL}(1)]^{2+}$	0.69	8×10^5	6.4	122	309
$[\text{Ni}^{\text{IV}}\text{PhMeL}(1)]^{2+}$	0.71	4×10^6	6.9	500	900
$[\Delta\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$	0.71	4×10^6	6.9	590	900

^aThe following parameters are used for $[\text{Co}(\text{edta})]^{2-}$: $E_2^\circ = 0.40 \text{ V}$, $k_{22} = 2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, $a_2 = 5.2 \text{ Å}$.

Marcus theory is conveniently expressed in free energy terms as eq 9 and 10, where ΔG^{**} represents an electrostatically corrected free energy of activation and ΔG_r is the electrostatically

$$\Delta G_{12}^{**} = \frac{1}{2}(\Delta G_{11}^{**} + \Delta G_{22}^{**} + \Delta G_r^\circ(1 + \alpha^{**})) \quad (9)$$

$$\alpha^{**} = \Delta G_r^\circ / 4(\Delta G_{11}^{**} + \Delta G_{22}^{**}) \quad (10)$$

corrected free energy change. The electrostatic correction involves evaluation of work functions, ω , for the approach of charged reagents in the reaction medium, which may be approximated²⁷ by using eq 11, where z_1 and z_2 are the charges on the reactants,

$$\omega_{12} = z_1 z_2 e^2 / D_s r_{12} (1 + \beta \mu^{1/2} r_{12}) \quad (11)$$

e is the electronic charge, D_s is the static dielectric constant of the solvent, β is the Debye-Huckel constant, and r_{12} is the effective reaction distance. The effective reaction distance, r_{12} , is generally assumed to be equal to the sum of the average radii of the reactants ($a_1 + a_2$), approximately by using eq 12, where the d values are

$$a_1 = \frac{1}{2}(d_x d_y d_z)^{1/3} \quad (12)$$

diameters along orthogonal axes. However, for complexes of relatively low symmetry with a biased reaction orientation preference, this can be a meaningful variable. Haim^{28,29} and other workers³⁰ have used this parameter in a very simple analysis to imply orientation information in electron-transfer reactions between metal ion complexes. However detailed analysis is impractical since steric factors and variations in the microscopic precursor formation constants must also be considered. Consequently, a general treatment using eq 12 to determine the effective radii is employed. Radii, determined from appropriate CPK models for $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(1)]^{2+}$, $[\text{Ni}^{\text{IV}}\text{MePhL}(1)]^{2+}$, $[\text{Ni}^{\text{IV}}\text{PhMeL}(1)]^{2+}$, and $[\Delta\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$ are 5.4, 6.4, 6.9, and 6.9 Å, respectively, and for $[\text{Co}(\text{edta})]^{2-}$ the average radius is 5.2 Å. In Table IV are summarized the results of the Marcus calculations. The calculated rate constants for the cross reactions of the nickel(IV) complexes with $[\text{Co}(\text{edta})]^{2-}$ are in fairly good agreement with those derived from experimental measurements but are consistently lower by a factor of 2–3. This may be the result of some bias in the self-exchange rate data or of the approximations in the treatment, but there appear to be no readily identifiable trends that can be related to changes in the steric bulk of the ligands. Koval and co-workers³¹ have demonstrated that steric factors can be detected by comparisons of experimental rate data with the predictions of Marcus theory and suggest that the effects may be due to nonadiabaticity. In the present work there is no evidence for such an effect, but the steric factors are much smaller and less symmetrically distributed.

(e) Electron-Transfer Stereoselectivity. A major difficulty in the detection of stereoselectivity in electron-transfer reactions between metal ion complexes in solution is the racemization of the reactants or reaction products by an electronic self-exchange process.¹ Although the self-exchange rates for the nickel(IV)/nickel(III) systems are fast, the use of chiral ligands that complex stereospecifically with the metal ion no matter the oxidation state circumvents this problem and is the approach used in this work.

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Table V. Stereoselectivity Studies of the Oxidation of $[\text{Co}(\text{edta})]^{2-}$ by Nickel(IV) Complexes at 25 °C

complex	ionic medium, ^a M	$[\text{Ni}(\text{IV})]$, M	$[\text{Co}(\text{edta})]^{2-}$, (M)	enantiomeric excess, % Δ
$[\Delta\text{-Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$	0.10, pH 5.17	1.14×10^{-4}	1.11×10^{-3}	20.3 ± 0.8
	0.10, pH 5.17	1.14×10^{-4}	1.11×10^{-3}	20.8 ± 0.8
	0.10, pH 5.17	1.14×10^{-4}	1.11×10^{-4}	21.0 ± 0.8^b
$[\Delta\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$	0.10, pH 5.17	1.14×10^{-4}	1.11×10^{-4}	21.2 ± 0.8^b
	0.10, pH 5.08	6.48×10^{-5}	6.47×10^{-4}	6.0 ± 0.8
	0.10, pH 5.08	6.48×10^{-5}	1.22×10^{-4}	7.0 ± 0.8
$[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(3)]^{2+}$	0.10, pH 5.08	6.48×10^{-5}	6.47×10^{-5}	7.4 ± 0.8^b
	0.10, pH 4.49	7.83×10^{-5}	9.45×10^{-4}	22.9 ± 0.8
	0.10, pH 4.49	7.83×10^{-5}	9.45×10^{-4}	22.2 ± 0.8
$[\Delta\text{-Ni}^{\text{IV}}\text{MePhL}(3)]^{2+}$	0.10, pH, 4.49	7.83×10^{-5}	9.45×10^{-5}	22.3 ± 0.8^b
	0.01, pH 5.18	7.76×10^{-5}	1.11×10^{-3}	46.7 ± 0.8
	0.01, pH 5.18	8.04×10^{-5}	8.08×10^{-4}	46.5 ± 0.8
	0.01, pH 5.03	8.04×10^{-5}	8.08×10^{-5}	46.0 ± 0.8^b

^a 1×10^{-2} M acetate buffer. ^b Exclusively the nickel(IV) reduction; others are combinations of nickel(IV) and nickel(III) with the former predominating.

The reactant of choice as a probe molecule for the detection of stereoselectivity is $[\text{Co}(\text{edta})]^{2-}$ since the self-exchange rate of the $[\text{Co}(\text{edta})]^{2-/-}$ system is very slow,^{23,24} and so problems of racemization from this source are unimportant.

In previous work,⁴ stereoselectivity in the reduction of $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ by $[\text{Co}(\text{edta})]^{2-}$ and its derivatives has been examined. As mentioned above, the stoichiometry of the reaction is 1:2, eq 4, and the reaction is biphasic with the initial rapid reduction of nickel(IV) to give nickel(III) as a reaction intermediate followed by reduction of this intermediate to nickel(II). It is possible to investigate stereoselectivity in both steps since nickel(III) can be generated independently.^{17,18} For $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$, reaction with racemic $[\text{Co}(\text{edta})]^{2-}$ leads to an enantiomeric excess of 11% $[\Delta\text{-Co}(\text{edta})]^-$ in the initial (nickel(IV)) step and 10% $[\Delta\text{-Co}(\text{edta})]^-$ in the second (nickel(III)) step.³ These stereoselectivities are very little affected when the derivatives $[\text{Co}(\text{pdta})]^{2-}$ and $[\text{Co}(\text{cdta})]^{2-}$ are used as reductants,⁴ implicating the carboxylate face of the reductant in the reaction. In addition, comparisons with ion-pairing stereoselectivities between $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(1)]^{2+}$ and $[\text{Co}(\text{edta})]^-$ pinpoint the precursor to electron transfer as the most likely source of the reaction stereoselectivity, and a model of the ion pair precursor to the electron transfer for both steps was deduced.⁴ This model is illustrated in Figure 1 and involves approach of the pseudo- C_3 carboxylate face of $[\text{Co}(\text{edta})]^{2-}$ to the C_2 oxime face of the nickel complex. The importance of the C_2 oxime face is suggested by rate enhancement in the nickel(III) step when one of the oxime groups is protonated and is capable of hydrogen bonding with the carboxylate face of the reductant.

The reactions of the chiral nickel(IV) complexes prepared in this work with $[\text{Co}(\text{edta})]^{2-}$ are similar to those described above for $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$. The stoichiometries are 1:2, consistent with eq 4, and well-defined nickel(III) intermediates are formed, indicating the biphasic nature of the process. Stereoselectivities for both steps were determined and are presented in Table V.

In all the reactions, two points remain invariant. The first is that the product isomer in enantiomeric excess is always $[\Delta\text{-Co}(\text{edta})]^-$. The second is that the stereoselectivities for both nickel(IV) and nickel(III) reductions are similar in every case. Previously it was argued that the similarity of the stereoselectivities for reductions of $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ and $[\Delta\text{-Ni}^{\text{III}}\text{Me}_2\text{L}(2)\text{H}]^{2+}$ pointed to a similar orientation of the two oxidants toward $[\text{Co}(\text{edta})]^{2-}$ in their respective reactions. In retrospect this conclusion may be based on a somewhat fortuitous result. The observed nickel(III) reductions reported with the phenyl- and benzyl-substituted derivatives in this paper contain a substantial reaction component of the nickel(IV) stereoselectivity since the major reaction pathway involves nickel(III) disproportionation and generation of the $[\text{Co}(\text{edta})]^-$ product by reduction of nickel(IV). Consequently little can be said about stereoselectivity in the nickel(III) reaction. To emphasize the point that, in general, nickel(IV) and nickel(III) stereoselectivities can differ markedly, it should be noted that in the oxidation of $[\text{Co}(\text{edta})]^{2-}$ by $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(4)]^{2+}$ ($\text{Me}_2\text{L}(4)\text{H}_2 = (8\text{S})\text{-}3,8,14\text{-trimethyl-}4,7,10,13\text{-tetraaza-$

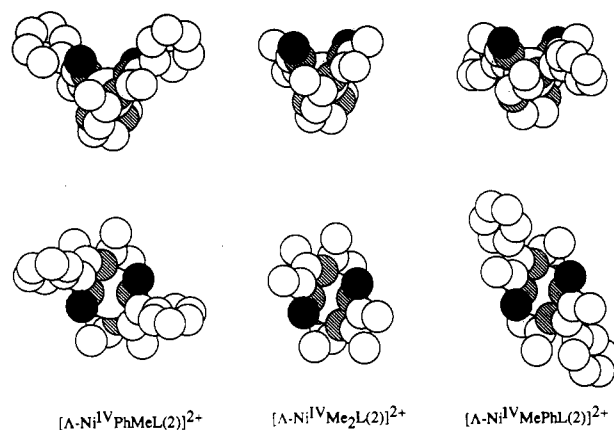
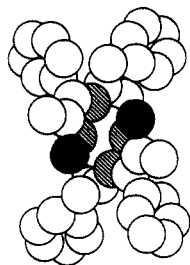


Figure 3. Views along (bottom row) and perpendicular to (top row) the C_2 axes of the complexes $[\text{Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$, $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$, and $[\text{Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$.

hexadeca-3,13-diene-2,15-dione dioxime), which shows direct reactions of both $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(4)]^{2+}$ and $[\text{Ni}^{\text{III}}\text{Me}_2\text{L}(4)\text{H}]^{2+}$ as was observed with $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$, the nickel(IV) stereoselectivity is 3.5% $\Delta\Delta$ and the nickel(III) stereoselectivity is 8.5% $\Delta\Delta$, both at 0.1 M ionic strength. However the nickel complexes in this case are not formed stereospecifically. Consequently, the following discussion refers solely to nickel(IV) reduction.

There is a marked effect of oxidant structure on the stereoselectivity. Values range from 7% to 46% in marked contrast to the nearly identical stereoselectivity found when the structure of the reductant is changed from $[\text{Co}(\text{edta})]^{2-}$ to $[\text{Co}(\text{pdta})]^{2-}$ and $[\text{Co}(\text{cdta})]^{2+}$. The data for the most substituted complex $[\text{Ni}^{\text{IV}}\text{MePhL}(3)]^{2+}$ are reported at 0.01 M ionic strength due to insolubility at higher concentrations of nitrate ion. This is likely to increase the stereoselectivity by around 10% since studies with $[\text{Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$ at a variety of ionic strengths show a slight trend of increasing stereoselectivity with decreasing ionic strength.

The precursor model deduced from earlier studies⁴ is extremely useful as a basis for discussion of the structural effects. If this model is correct, important information about the effects of changing ligand structure can be obtained by considering the approach of $[\text{Co}(\text{edta})]^{2-}$ along the C_2 axis of the nickel oxidant. The three oxidants $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$, $[\Delta\text{-Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$, and $[\Delta\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$ form an interesting series in which phenyl groups replace each pair of methyl groups on the oxime-imine framework. In $[\Delta\text{-Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$ there is enhancement of the stereoselectivity while in $[\Delta\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$ there is reduction of the stereoselectivity, relative to the dimethyl derivative $[\Delta\text{-Ni}^{\text{IV}}\text{Me}_2\text{L}(2)]^{2+}$. Figure 3 shows space-filling representations of the C_2 axis of the three molecules. The phenyl ring in $[\Delta\text{-Ni}^{\text{IV}}\text{PhMeL}(2)]^{2+}$ provides a steric barrier to approach along the C_2 axis while in $[\Delta\text{-Ni}^{\text{IV}}\text{MePhL}(2)]^{2+}$ this barrier is moved to the periphery of the C_2 face and approach to the face is not restricted. The differences in stereoselectivity cannot be understood exclu-

[Δ -Ni^{IV}MePhL(3)]²⁺**Figure 4.** View along the C_2 axis of [Δ -Ni^{IV}MePhL(3)]²⁺.

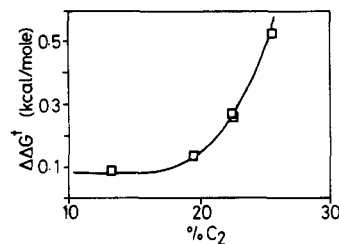
sively in terms of contact between the reductant complex and the C_2 face. Although previous work points to the C_2 axis of the nickel complex as dominant in determining the stereoselectivity of the reaction product, it need not be the exclusive reaction site. When there is a steric barrier along the C_2 axis as in [Δ -Ni^{IV}PhMeL(2)]²⁺, the proportion of the overall reaction occurring along this axis is reduced. However in [Δ -Ni^{IV}MePhL(2)]²⁺, the steric barrier is on the periphery of the oxime face and there is little change in the approach along the C_2 axis compared with [Δ -Ni^{IV}Me₂L(2)]²⁺. The enhanced stereoselectivity can however be rationalized in terms of a greater proportion of the overall reaction taking place along the C_2 axis.

This effect may be compounded since the current understanding⁶ of the stereoselectivity phenomenon would predict that if the C_2 axis interaction leads to a predominance of [Δ -Co(edta)]⁻, interactions along the adjacent pseudo- C_3 axes lead to a predominance of [Λ -Co(edta)]⁻. That the overall enantiomeric excess is of the Δ isomer is a reflection of the stronger interaction along the C_2 axis but is in fact a balance of interactions along both axes. Blocking the C_2 axis will reduce the [Δ -Co(edta)]⁻ component in the product as observed while blocking the C_3 approach, accomplished by placing bulky groups on the periphery of the important C_2 face, leads to a decrease in [Λ -Co(edta)]⁻ and hence an increase in [Δ -Co(edta)]⁻ as is also observed. There is precedence for this type of behavior in the reduction of [Co(edta)]⁻ by [Co(en)₃]²⁺ and its derivatives.⁶

The effect of replacing the chiral methyl groups on the amine backbone of the ligand by more bulky benzyl groups can be seen by comparing the stereoselectivities of [Δ -Ni^{IV}Me₂L(2)]²⁺ (11%) and [Δ -Ni^{IV}Me₂L(3)]²⁺ (23%). The bulky groups, though free to rotate, are, like the phenyl rings in [Δ -Ni^{IV}MePhL(2)]²⁺, also on the periphery of the C_2 face, and again the stereoselectivity is enhanced. An additive effect of the peripheral bulk is seen in [Δ -Ni^{IV}MePhL(3)]²⁺, Figure 4, where the stereoselectivity of 46% is the highest reported to date for an outer-sphere reaction between metal ion complexes in aqueous solution.

These stereoselectivities are relatively modest and account for a small difference in the activation energies of the diastereomeric pairs. For example an enantiomeric excess of 11% represents a difference of around 130 cal mol⁻¹ while the largest enantiomeric excess, 46%, represents a difference of 590 cal mol⁻¹. It is therefore not surprising that the trends in stereoselectivity are not reflected in the trends in the overall reaction rate constants.

However, with some knowledge of the dimensions of the oxidants, Marcus theory can be used to estimate the proportion of the reaction occurring in each case through the C_2 face, assuming

**Figure 5.** Plot of $\Delta\Delta G^\ddagger$, the difference in free energy of activation for reaction of the chiral nickel(IV) complexes with [Δ -Co(edta)]²⁻ and [Λ -Co(edta)]²⁻, as a function of the calculated percentage of the reaction taking place through the C_2 face of the oxidant.

that only steric factors influence the microscopic precursor formation constants. The complexes can be approximated by spheroids and the limiting rates of electron transfer calculated for reaction along orthogonal axes that include the C_2 axis of interest. In Figure 5, the difference in free energy of activation for reaction of [Δ -Co(edta)]²⁻ and [Λ -Co(edta)]²⁻ with the nickel(IV) complexes, $\Delta\Delta G^\ddagger$, is plotted against the calculated percentage of the reaction occurring by the C_2 face. There is a dependence consistent with the proposed model. When the proportion of the reaction taking place through the C_2 face of the complexes is small, the stereoselectivity is also small, but beyond a point that corresponds roughly to a spherical complex (16.66% ($1/6$) of the reaction through the C_2 axis), the stereoselectivity increases dramatically. What appears to be important is that the more specific the interaction (greater the proportion through a single face of the complex) the greater the stereospecificity.

It is of interest to note that [Co(edta)]²⁻ itself appears to have a fairly specific mode of interaction, using the pseudo- C_3 carboxylate face in at least two systems that have been closely examined.^{4,32} In this respect it may be a unique probe for stereoselectivity.

Conclusions

Current understanding of stereoselectivity phenomena in electron-transfer processes between metal ion complexes is not well advanced, but the observation of well-defined structural dependencies for the phenomenon in conjunction with kinetic data offers an opportunity for detailed investigation. The results in this paper confirm the previously proposed model for the precursor interaction between derivatives of [Ni^{IV}Me₂L(1)]²⁺ and [Co(edta)]²⁻ in which stereoselectivity is determined mainly through the interaction involving the pseudo- C_3 carboxylate face of the reductant and the C_2 oxime face of the oxidant. However, electron transfer does not take place exclusively through this interaction. Stereoselectivity can be enhanced by increasing the proportion of the reaction taking place through the C_2 face with steric factors.

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Supplementary Material Available: Listings of spectroscopic parameters for the nickel(III) and nickel(II) complexes (Table SI) and pseudo-first-order rate constants for the reduction of nickel(IV) complexes by [Co(edta)]²⁻ (Table SII) (4 pages). Ordering information is given on any current masthead page.

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