

The association constant obtained for the Fe^{III}(EDTA)-ascorbate complex is probably too large for an outer-sphere complex between two negatively charged species,³⁰ and there is considerable evidence that EDTA, although nominally sexadentate, occupies, on coordination with transition-metal ions, only five positions, leaving the sixth bound to donor water,³¹ which is easily lost. It appears then that EDTA-bound Fe^{III} is less effective than aquo-bound Fe^{III} in polarizing ligating ascorbate prior to attack by Cr^{IV}(O₂)₂. When that ordinarily preferred path becomes disfavored, electron transfer

from ascorbate to Fe^{III} assumes the catalytic burden (albeit less efficiently). Persistence of a less advantageous route may be linked to a formal potential of Fe(II,III) in the proper range. When Cu^{II}, a much weaker oxidant than Fe^{III}, is sequestered, it is no longer able to oxidize ascorbate effectively. With the V(IV,V) couple, on the other hand, complexation of the more poorly reducing VO²⁺ appears to halt its reduction of Cr^{IV}, a reaction for which an inner-sphere route has been shown to operate.⁴

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Registry No. EDTA, 60-00-4; Fe, 7439-89-6; Cr^{IV}(dien)(O₂)₂, 59419-71-5; ascorbic acid, 50-81-7.

(30) We thank a reviewer for calling our attention to this point.

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Contribution from the Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana 46556

Stereoselectivity in the Reduction of [Co(ox)₃]³⁻ by [Co(en)₃]²⁺ and Its Derivatives

Rosemary A. Marusak, Peter Osvath, Margaret Kemper, and A. Graham Lappin*

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The oxidation of cobalt(II) by [Co(ox)₃]³⁻ in 1,2-diaminoethane solutions proceeds by both inner-sphere and outer-sphere pathways leading to formation of [Co(en)₂(ox)]⁺ and [Co(en)₃]³⁺ with rate constants 3300 and 390 M⁻¹ s⁻¹, respectively, at 25.0 °C and 0.10 M ionic strength. When optically active [Co(ox)₃]³⁻ is used, both pathways show stereoselectivity. In the inner-sphere pathway, stereoselectivity is small, 1.5% ΔΔ, a consequence of the separation of the reacting centers by the oxalate bridge. In the outer-sphere pathway, stereoselectivity is 9% ΔΔ. The effect on the stereoselectivity of varying the structure of the reductant for the series [Co(sep)]²⁺, [Co(sen)]²⁺, [Co(en)₃]²⁺, [Co(±-bn)₃]²⁺, and [Co(±-chxn)₃]²⁺ has been investigated for this pathway. Outer-sphere stereoselectivity has also been examined in the reactions of [Co(mal)₃]³⁻ with [Co(en)₃]²⁺ and [Co(±-chxn)₃]²⁺. The stereoselectivity data are consistent with a mechanism in which the carboxylate faces of [Co(ox)₃]³⁻ or [Co(mal)₃]³⁻ are presented to various orientations of the reductants in strong precursor ion pairs and are dependent on the relative importance of hydrogen-bonding and electrostatic interactions between the complexes.

Introduction

Stereoselectivity in the oxidation of [Co(en)₃]²⁺ (en = 1,2-diaminoethane) and its derivatives by [Co(edta)]⁻, [Co(pdta)]⁻, and [Co(cdda)]⁻ (edta⁴⁻ = 1,2-diaminoethane-*N,N,N',N'*-tetraacetate(4-)) has been investigated in considerable detail.¹⁻³ A picture of the complex that is the precursor to electron transfer has been deduced in which the pseudo-C₃ carboxylate face of [Co(edta)]⁻ is strongly hydrogen bonded to amine hydrogens on the reductants. It is of considerable interest to know if other oxidants possessing a C₃ carboxylate face behave similarly, and so studies with [Co(ox)₃]³⁻ (ox²⁻ = oxalate(2-)) were initiated with the hope that the higher symmetry of the complex might simplify the interpretation of the stereoselectivity data. Previously, it was noted that chiral discrimination in interactions with tris-bidentate chelates is thought to arise from the different helicities described by the C₂ and C₃ axes.^{4,5} For example, in [Δ-Co(ox)₃]³⁻, the complex has C₃ axes and C₂ axes of differing helicities, each capable of sustaining hydrogen bonding interactions between carboxylate groups and the amine hydrogen atoms on the reductants. In this example, these can be described as *P*(C₃)*M*(C₂) where *P* indicates a plus or clockwise helical arrangement and *M* a minus arrangement.

A feature of previous work with [Co(edta)]⁻ as oxidant was the investigation of the effects of chelate ring conformation in the reductants on the electron-transfer stereoselectivity.² Chelate ring

conformation in [Co(en)₃]³⁺ and its derivatives may be described as *lel* if the C-C bond in the five-membered ring lies parallel to the C₃ axis and *ob* if the C-C bond lies oblique to this axis. Four conformational isomers are possible, *lel*₃, *lel*₂*ob*, *lel* *ob*₂, and *ob*₃, where each of the three chelate rings is designated.⁶ Conformational isomers in [Co(en)₃]³⁺ are interconvertible by low-energy rotations, but in the complexes [Co(±-bn)₃]³⁺ and [Co(±-chxn)₃]³⁺ ((±-bn = *rac*-2,3-diaminobutane, (±-chxn = *rac*-1,2-diaminocyclohexane), they are diastereomers and can be separated readily.^{2,7} With [Co(edta)]⁻ there is a strong trend² in stereoselectivity with a preference for ΔΔ interactions for *lel*₃ isomers and ΔΔ interactions for *ob*₃ isomers, although the trend is markedly solvent dependent.⁸

The oxidant [Co(ox)₃]³⁻ is readily resolved.^{9,10} It has a reduction potential of 0.57 V¹¹ (vs NHE) and an electronic self-exchange rate estimated variously as 3 × 10⁻⁷ s⁻¹ or 1.4 × 10⁻¹² M⁻¹ s⁻¹,¹³ ideal for stereoselectivity studies since self-exchange racemization is slow. However, the complex is heat and light sensitive and is prone to rapid racemization, even in the solid state.^{10,14} The reactions of [Co(ox)₃]³⁻ with [Co(en)₃]²⁺ and its

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- These designations refer to the following isomers. *lel*₃: Δ(λλλ), Δ(δ,δ,δ). *lel*₂*ob*: Δ(δλλ), Δ(λ,δ,δ). *lel* *ob*₂: Δ(δ,δ,λ), Δ(λ,λ,δ). *ob*₃: Δ(δ,δ,δ), Δ(λ,λ,λ).
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derivatives involve more complex pathways than the corresponding reactions of $[\text{Co}(\text{edta})]^-$, and although they are indeed stereoselective, the results have not proved significantly easier to explain. Consequently, a number of experiments were carried out with the structurally related oxidant $[\text{Co}(\text{mal})_3]^{3-}$ ($\text{mal}^{2-} = \text{malonate}(2-)$).

Experimental Section

(a) Preparation of Complexes. The preparation of $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 3.5\text{H}_2\text{O}$ ($\epsilon_{605} = 165 \text{ M}^{-1} \text{ cm}^{-1}$)¹⁵ was carried out by the method of Bailar and Jones.⁹ Resolution of the complex was achieved¹⁰ with use of $[\text{Ni}(\text{phen})_3]^{2+}$. Both Δ and Λ isomers were used in this study, and the absolute configuration is taken as $[\Lambda(-)_{589}\text{-Co}(\text{ox})_3]^{3-}$ ($\Delta\epsilon_{622} = 3.80 \text{ M}^{-1} \text{ cm}^{-1}$).^{16,17} Sodium salts were prepared by recrystallization from solutions of sodium perchlorate. The optically active complex was generated immediately prior to use, and due to light sensitivity, all manipulations involving the complex were carried out in darkened rooms. The optical activity of solutions of the complex was checked before and after use in experiments, and the results were corrected for racemization. In general this amounted to 10–12% over a 2-h period. The preparation of $\text{K}_3[\text{Co}(\text{mal})_3] \cdot 4\text{H}_2\text{O}$ ($\epsilon_{608} = 148 \text{ M}^{-1} \text{ cm}^{-1}$) was carried out by the method of Kmenten and Spees.¹⁸ The complex is extremely light and temperature sensitive, and it was resolved with use of $[\Delta\text{-Co}((-)\text{-pn})_3]^{3+}$.¹⁹ Solutions of $[\text{Co}(\text{mal})_3]^{3-}$ (2 mmol in 50 mL) were treated with $[\Delta\text{-Co}((-)\text{-pn})_3]^{3+}$ (1 mmol in 50 mL), and the resulting solution was cooled in ice for 3 min and filtered and the filtrate passed through a cation-exchange column in the K^+ form (Dowex 50x4; 5 cm \times 2 cm) to remove any extraneous cations. The resulting solution contains the $[\Delta(+)\text{-Co}(\text{mal})_3]^{3-}$ ion ($\Delta\epsilon_{593} = +0.85 \text{ M}^{-1} \text{ cm}^{-1}$),¹⁹ which is reported to have a half-life for racemization of ~ 4 h. Freshly prepared solutions were found to be slightly more optically active than reported by Butler and Snow¹⁹ with $\Delta\epsilon_{593} = +0.92 \text{ M}^{-1} \text{ cm}^{-1}$, and it was assumed that this represents optical purity. The complex was used within 15 min of resolution, and all manipulations were carried out in the dark. Preparation and resolution of $[\text{Co}(\text{en})_2(\text{ox})]\text{Cl} \cdot \text{H}_2\text{O}$ ($\epsilon_{500} = 103 \text{ M}^{-1} \text{ cm}^{-1}$) were achieved by literature methods.²⁰ The absolute configuration of the complex is $[\Lambda(+)\text{-Co}(\text{en})_2(\text{ox})]$ ($\Delta\epsilon_{520} = 2.65 \text{ M}^{-1} \text{ cm}^{-1}$).²¹ Experimental details concerning the remaining complexes used in this study have been described previously.²

(b) Stoichiometry in the Oxidation of $[\text{Co}(\text{en})_3]^{2+}$. The stoichiometry and products of the reaction between $[\text{Co}(\text{ox})_3]^{3-}$ and $[\text{Co}(\text{en})_3]^{2+}$ were investigated by using HPLC and conventional ion-exchange chromatography. Typically, $[\text{Co}(\text{ox})_3]^{3-}$ (10^{-3} M) was added to a solution containing cobalt(II) (10^{-2} M) in excess 1,2-diaminoethane ($0.3\text{--}1.0 \times 10^{-1} \text{ M}$) and appropriate supporting electrolyte, with rapid stirring and under an atmosphere of argon to prevent aerial oxidation of the cobalt(II) complex. In some experiments, oxalate ion and $^{13}\text{C}_2$ oxalate ion (ICN Biomedicals Inc., 99%) ($3 \times 10^{-3} \text{ M}$) were added to the cobalt(II) solution. After completion of the reaction, the mixture was cooled and ice-cold 6 M HCl was added such that the pH of the resulting solution was less than 1. Aliquots of this solution were analyzed with use of a Waters HPLC system incorporating a model 501 pump, Model U6K universal injector, and Model 481 spectrophotometer for detection. The separations were accomplished by using a Waters Protein Pak SP-5PW Sephadex ion-exchange column and the components identified spectrophotometrically at 346 nm, where interference from cobalt(II) ion is minimized. The sample front is indicated by a schlieren gradient due to the high 1,2-diaminoethane concentration, and there are two well-defined cation peaks corresponding to $[\text{Co}(\text{en})_2(\text{ox})]^+$ and $[\text{Co}(\text{en})_3]^{3+}$ from which the ratio of these two products can be determined.

After dilution of the acidic reaction product mixture, $[\text{Co}(\text{en})_3]^{3+}$ was isolated on Sephadex SP-C-25 (1 \times 10 cm column), washed with water and 0.1 M HCl, and eluted with 1.0 M HCl. The $[\text{Co}(\text{en})_2(\text{ox})]^+$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions were isolated on Dowex 50x2-400 (1 \times 20 cm column) and washed with water, and the former complex was eluted with 0.01 M HCl. The resulting HCl solutions were evaporated to dryness at 30 $^\circ\text{C}$ under reduced pressure. Concentrations were determined spectrophotometrically by using literature extinction coefficients.

In oxidation of $[\text{Co}(\text{en})_3]^{2+}$ ($[\text{Co}(\text{II})] = 1.1 \times 10^{-2} \text{ M}$, $[\text{en}] = 1.2 \times 10^{-1} \text{ M}$) by $[\text{Co}(\text{mal})_3]^{3-}$ ($1.2 \times 10^{-3} \text{ M}$), $0.71 \pm 0.06 \text{ mol}$ of $[\text{Co}(\text{en})_3]^{3+}$ is produced for each mole of oxidant. Errors are significantly larger because of difficulties in handling the $[\text{Co}(\text{mal})_3]^{3-}$. However, analysis of the solution indicates that there does not appear to be a significant amount of a secondary product, such as $[\text{Co}(\text{en})_2(\text{mal})]^+$, formed. It seems likely that some decomposition of $[\text{Co}(\text{mal})_3]^{3-}$ takes place during the reaction, but this was not further investigated.

(c) Stereoselectivity Experiments. For $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}((\pm)\text{-bn})_3]^{2+}$, and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$, conditions for stereoselectivity experiments with both $[\text{Co}(\text{ox})_3]^{3-}$ and $[\text{Co}(\text{mal})_3]^{3-}$ were similar to those for the stoichiometry determinations described above. Full details are given in Table SI, available as supplementary material. The major product under these conditions, the tris-bidentate chelate, was isolated on Sephadex SP-C-25 (1 \times 10 cm column), washed with water and 0.1 M HCl, eluted with 1.0–5.0 M HCl, and the resulting solution was evaporated to dryness. Stereoselectivities were determined by measuring the optical purity of the cobalt amine complexes. This involves a single measurement for $[\text{Co}(\text{en})_3]^{3+}$, but for $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ the solutions contain a mixture of isomers, which were separated as outlined previously.² Stereoselectivities for each isomer were determined individually. For $[\text{Co}(\text{sen})]^{2+}$ conditions were similar except that a much smaller ($5 \times 10^{-3} \text{ M}$) excess of ligand was used.

In the case of the $[\text{Co}(\text{sep})]^{2+}$ reaction, there are two problems with a comparable experiment. The cobalt(II) complex is not destroyed on addition of acid, entailing anaerobic separation of $[\text{Co}(\text{sep})]^{2+}$ from $[\text{Co}(\text{sep})]^{3+}$. The second problem is the high self-exchange rate of $[\text{Co}(\text{sep})]^{3+/2+}$, which would result in self-exchange racemization of the product and subsequent difficulty in determining stereoselectivity. To avoid these problems, the oxidation was carried out with an excess ($\times 5\text{--}10$) of $[\text{rac-Co}(\text{ox})_3]^{3-}$, which was reduced by $[\Lambda\text{-Co}(\text{sep})]^{2+}$, and the optical activity of the unreduced $[\text{Co}(\text{ox})_3]^{3-}$ was determined after the solutions had been passed through a strong cation-exchange resin in the Na^+ form (Amberlite CG 120, Type 1, 100–200 mesh). The reduction of $[\text{Co}(\text{ox})_3]^{3-}$ by $[\Lambda\text{-Co}(\text{sep})]^{2+}$ is more rapid than racemization of $[\text{Co}(\text{ox})_3]^{3-}$, resulting in a dependence of the apparent stereoselectivity on the excess concentration, but previous studies with $[\text{Co}(\text{edta})]^-$ indicate² that the errors introduced are small, of the order of 10%, and comparable with corrections required to account for the racemization of $[\text{Co}(\text{ox})_3]^{3-}$.

In the three cases of reactions of $[\text{Co}(\text{ox})_3]^{3-}$ with $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}((\pm)\text{-bn})_3]^{2+}$, and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$, there is evidence for a minor oxalate-containing product, but due to problems with the multiplicity of diastereomers, only for the reaction with $[\text{Co}(\text{en})_3]^{2+}$ was an attempt made to determine stereoselectivity for this product. At high 1,2-diaminoethane concentrations the circular dichroism spectrum of the reaction products is dominated by that of the major product, $[\text{Co}(\text{en})_3]^{3+}$, indicating that stereoselectivity in the inner-sphere pathway is comparatively weak. Under conditions where $[\text{Co}(\text{II})]:[\text{en}]$ is 1:2, however, the dominant product is $[\text{Co}(\text{en})_2(\text{ox})]^+$, with only trace amounts of $[\text{Co}(\text{en})_3]^{3+}$, allowing determination of the stereoselectivity in $[\text{Co}(\text{en})_2(\text{ox})]^+$.

Circular dichroism spectra were measured on an Aviv circular dichroism spectrophotometer, Model 60DS (Aviv Associates, Lakewood, NJ), calibrated against an aqueous solution of $[\Lambda(+)\text{-Co}(\text{en})_3]\text{Cl}_3$ ($\Delta\epsilon_{493} = 1.90 \text{ M}^{-1} \text{ cm}^{-1}$).²² Samples were prepared in long path length cells (10 cm) at $\sim 10^{-4} \text{ M}$ concentration of chloride ion salts unless otherwise reported. Visible spectra were run on a Varian DMS 100 spectrophotometer.

(d) Kinetic Measurements. The kinetics of reduction of $[\text{Co}(\text{ox})_3]^{3-}$ by $[\text{Co}(\text{en})_3]^{2+}$ were investigated under pseudo-first-order conditions with an excess of reductant at 0.10 M ionic strength (perchlorate media). In a typical case, the oxidant concentration was $1 \times 10^{-4} \text{ M}$, with cobalt(II) concentrations in the range $(1\text{--}10) \times 10^{-3} \text{ M}$ and 1,2-diaminoethane concentrations an order of magnitude higher.²³ Solutions were basic and in general were buffered by the addition of small amounts of perchloric acid, taking advantage of the first protonation of the excess ligand. The apparent strong pH dependence of the reaction can be explained by changes in the concentrations of free 1,2-diaminoethane. The pH was measured immediately after reaction with a Beckman SelectIon 2000 meter equipped with a Corning combination glass electrode with a saturated calomel (NaCl) reference. A Durrum D-110 stopped-flow spectrophotometer, modified to enable solutions to be handled under an atmosphere of N_2 and thermostatted at $25.0 \pm 0.1 \text{ }^\circ\text{C}$, was used for

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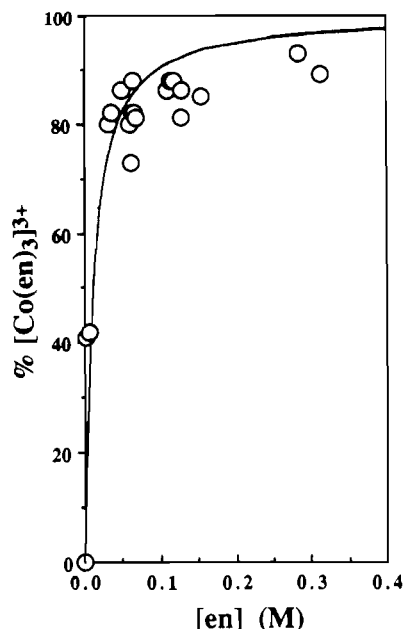


Figure 1. Plot of % $[\text{Co}(\text{en})_3]^{3+}$ product as a function of $[\text{en}]$ for the oxidation of $[\text{Co}(\text{en})_3]^{2+}$ by $[\text{Co}(\text{ox})_3]^{3-}$ at 25.0 °C and 0.10 M ionic strength.

kinetics experiments. Data were collected by using a Nicolet 3091 digital oscilloscope. Reactions were monitored at 605 nm, following the decrease in absorbance due to $[\text{Co}(\text{ox})_3]^{3-}$. NMR spectra were run on a General Electric GN-300 system.

Results and Discussion

(a) Reaction Products. The stoichiometry of the oxidation of cobalt(II) in 1,2-diaminoethane solutions by $[\text{Co}(\text{ox})_3]^{3-}$ is consistent with the expected one-electron-transfer process; however, two oxidation products, $[\text{Co}(\text{en})_2(\text{ox})]^+$ and $[\text{Co}(\text{en})_3]^{3+}$, are detected, and the ratio of these two products varies with the experimental conditions (Figure 1), indicative of a mechanism involving a minimum of two pathways. The $[\text{Co}(\text{en})_3]^{3+}$ product, which dominates at high 1,2-diaminoethane concentrations, almost certainly arises from the outer-sphere reaction between $[\text{Co}(\text{ox})_3]^{3-}$ and $[\text{Co}(\text{en})_3]^{2+}$. However, the $[\text{Co}(\text{en})_2(\text{ox})]^+$ may arise from the outer-sphere oxidation of $[\text{Co}(\text{en})_2(\text{ox})]$ or from an inner-sphere pathway in which coordinated oxalate in $[\text{Co}(\text{ox})_3]^{3-}$ acts as a bridge to $[\text{Co}(\text{en})_2]^{2+}$. To distinguish between these two possibilities, the reaction was carried out in the presence of ^{13}C -labeled oxalate ion. If $[\text{Co}(\text{en})_2(\text{ox})]^+$ arises from oxidation of $[\text{Co}(\text{en})_2(\text{ox})]$, oxalate can exchange freely with the labeled oxalate and the label will be incorporated into the cobalt(III) product. However, if an inner-sphere mechanism is operating, there is no incorporation of the label because the oxalate in the $[\text{Co}(\text{en})_2(\text{ox})]^+$ product is transferred directly from $[\text{Co}(\text{ox})_3]^{3-}$, which is unlabeled during the electron-transfer process. Oxalate exchange in $[\text{Co}(\text{ox})_3]^{3-}$ is slow on the time scale of these experiments.

There are three peaks in the ^{13}C NMR spectrum of $[\text{Co}(\text{en})_2(\text{ox})]^+$, two corresponding to the 1,2-diaminoethane carbons at 45.91 and 48.01 ppm (referenced to the downfield peak of 3-trimethylsilyl-1-propanesulfonic acid, 0 ppm) and one, with a significantly longer relaxation time, corresponding to the oxalate carbons at 171.38 ppm. When $[\text{Co}(\text{en})_2(\text{ox})]^+$ is isolated from a reaction run with unenriched $[\text{Co}(\text{ox})_3]^{3-}$ in the presence of isotopically enriched free $^{13}\text{C}_2$ oxalate ion (10%), the spectrum obtained is unchanged within experimental uncertainty from that obtained in the absence of added, enriched oxalate, indicating less than 2% incorporation of the label. It can be concluded that the oxalate in $[\text{Co}(\text{en})_2(\text{ox})]^+$ originates in $[\text{Co}(\text{ox})_3]^{3-}$ and that this product is formed predominantly by an inner-sphere mechanism.

There is evidence from reaction stoichiometry studies for inner-sphere pathways in the $[\text{Co}(\text{ox})_3]^{3-}$ oxidations of $[\text{Co}(\pm\text{-bn})_3]^{2+}$ and $[\text{Co}(\pm\text{-chxn})_3]^{2+}$, and possibly for $[\text{Co}(\text{mal})_3]^{3-}$ oxidations of $[\text{Co}(\text{en})_3]^{2+}$ and $[\text{Co}(\pm\text{-chxn})_3]^{2+}$, but these were not investigated in detail. There is no evidence for an inner-sphere

Table I. Pseudo-First-Order Rate Constants for the Oxidation of Cobalt(II) in 1,2-Diaminoethane Solutions at pH \sim 11.2, 0.10 M Ionic Strength, and 25.0 °C

$10^3[\text{Co}(\text{II})]$, M	$10^2[\text{en}]^a$, M	k_{obsd} , s^{-1}
1.24	5.30	0.56 ± 0.01
2.48	5.60	1.07 ± 0.01
5.00	5.60	2.04 ± 0.06
9.85	5.40	4.11 ± 0.06
2.50	1.14	3.25 ± 0.05
2.50	2.38	1.40 ± 0.02
2.50	4.66	1.09 ± 0.01
2.50	11.05	1.00 ± 0.01

^a Total $[\text{en}]$. Solutions were buffered by the addition of 5.0×10^{-3} M HClO_4 ; free-en concentrations were calculated by assuming complete formation of $[\text{Co}(\text{en})_2]^{2+}$ and considering the equilibria involving $[\text{Co}(\text{en})_3]^{2+}$ ($K_3 = 2000 \text{ M}^{-1}$), Hen^+ ($\text{p}K_{a2} = 9.89$), and H_2en^{2+} ($\text{p}K_{a1} = 7.08$).

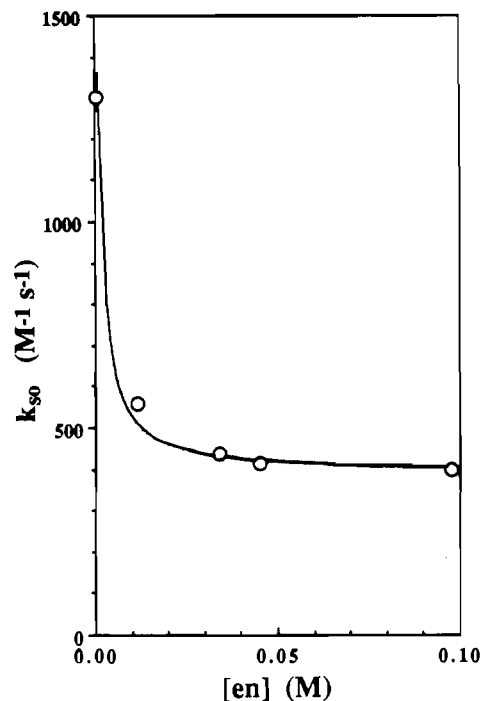


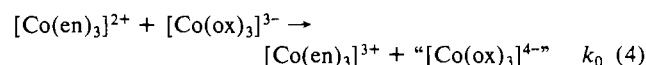
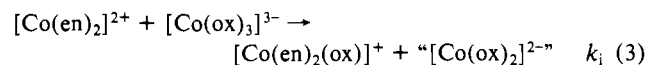
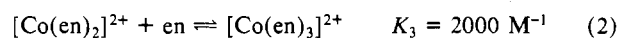
Figure 2. Plot of the second-order rate constant, k_{50} , as a function of $[\text{en}]$ for the oxidation of $[\text{Co}(\text{en})_3]^{2+}$ by $[\text{Co}(\text{ox})_3]^{3-}$ at 25.0 °C and 0.10 M ionic strength.

pathway in the oxidations of $[\text{Co}(\text{sen})]^{2+}$ and $[\text{Co}(\text{sep})]^{2+}$ by $[\text{Co}(\text{ox})_3]^{3-}$.

(b) Kinetics and Mechanism. The rate of reduction of $[\text{Co}(\text{ox})_3]^{3-}$ by cobalt(II) in 1,2-diaminoethane solutions was examined spectrophotometrically at 605 nm under pseudo-first-order conditions with an excess of reductant. The reaction is pseudo-first-order for over 3 half-lives (eq 1), and the pseudo-first-order

$$-d[[\text{Co}(\text{ox})_3]^{3-}]/dt = k_{\text{obsd}}[[\text{Co}(\text{ox})_3]^{3-}] \quad (1)$$

rate constants, k_{obsd} , are dependent on both the reductant and 1,2-diaminoethane concentrations (Table I). At constant $[\text{en}]$, the reaction is first-order in $[\text{cobalt}(\text{II})]$, and the second-order rate constant shows inhibition by $[\text{en}]$ (Figure 2). This inhibition can be understood in terms of a mechanism involving $[\text{Co}(\text{en})_2]^{2+}$ and $[\text{Co}(\text{en})_3]^{2+}$ as inner-sphere and outer-sphere reductants in competing pathways, as suggested by the stoichiometry results (eq 2-4). At very low 1,2-diaminoethane concentrations, the



observed rate constant decreases, presumably as a result of formation of significant amounts of the less reactive $[\text{Co}(\text{en})_3]^{2+}$ complex, but detailed studies were not carried out in this range.

Least-squares analysis of the rate law, eq 5, gives best fit parameters $k_0 = 390 \pm 20 \text{ M}^{-1} \text{ s}^{-1}$ and $k_1 = 3300 \pm 300 \text{ M}^{-1} \text{ s}^{-1}$

$$k_{\text{obsd}} = \{(k_1 + K_3 k_0 [\text{en}]) / (1 + K_3 [\text{en}])\} [\text{Co}(\text{II})]_{\text{T}} \quad (5)$$

with a value for K_3 of 2000 M^{-1} .²⁰ The ratio of the rate constants k_1/k_0 can also be estimated from stoichiometry studies, and the solid curve in Figure 1 represents the calculated dependence on $[\text{en}]$ with a ratio of 22, in reasonable agreement with the kinetic data when differences in the reaction conditions are taken into account.

It is of interest to note that at high 1,2-diaminoethane concentrations, where the outer-sphere pathway predominates, there is no evidence for rate-limiting behavior, indicative of stable precursor-complex formation. The charge product of the reactants is the same as that of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and SO_4^{2-} , for which ion-pairing constants of 70 M^{-1} have been measured under comparable conditions.^{24,25} An upper limit of 20 M^{-1} can be estimated for the association constant of $[\text{Co}(\text{en})_3]^{2+}$ and $[\text{Co}(\text{ox})_3]^{3-}$ from the present study, a not unreasonable value, from which the electron-transfer rate within the precursor complex is estimated to be around 20 s^{-1} .

(c) **The Outer-Sphere Pathway.** If the pathways leading to $[\text{Co}(\text{en})_3]^{2+}$ is indeed an outer-sphere electron-transfer reaction, the rates should be in reasonable agreement with the predictions of 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 6 and 7, where

$$\Delta G_{12}^* = \frac{1}{2}(\Delta G_{11}^* + \Delta G_{22}^* + \Delta G^\circ(1 + \alpha^*)) \quad (6)$$

$$\alpha^* = \Delta G^\circ / 4(\Delta G_{11}^* + \Delta G_{22}^*) \quad (7)$$

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 shown in eq 8, where w_{12} is the work

$$w_{12} = z_{11} z_{22} e^2 / D_s r_{12} (1 + \beta_\mu^{1/2} r_{12}) \quad (8)$$

term, D_s is the static dielectric constant for the medium, $\beta = (8\pi N e^2 / 1000 D_s k T)^{1/2}$, 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 9, where d_x , d_y , and d_z are orthogonal diameters of the metal

$$a_{11} = 1/2(d_x d_y d_z)^{1/3} \quad (9)$$

complex.²⁸ The self-exchange rate for $[\text{Co}(\text{ox})_3]^{3-/4-}$ is not well-known but has been estimated as $2.8 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ at 0.1 M ionic strength¹² and $1.4 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}$ at 0.2 M ionic strength¹³ from Marcus' theory. Rates calculated on the basis of these estimates are 3×10^4 and $100 \text{ M}^{-1} \text{ s}^{-1}$, respectively. When compared with the observed rate, $390 \text{ M}^{-1} \text{ s}^{-1}$, the lower of the self-exchange estimates gives much better agreement and adds some credence to the assignment of an outer-sphere mechanism. It is significant that the lower estimate of the self-exchange rate was determined from cross-reaction rates of $[\text{Ru}(\text{NH}_3)_6]^{2+}$ and $[\text{Ru}(\text{en})_3]^{2+}$, which are structurally related to $[\text{Co}(\text{en})_3]^{2+}$.

The tris chelate products formed as a result of the outer-sphere oxidations of $[\text{Co}(\pm\text{-bn})_3]^{2+}$ and $[\text{Co}(\pm\text{-chxn})_3]^{2+}$ by $[\text{Co}(\text{ox})_3]^{3-}$ and in the oxidation of $[\text{Co}(\pm\text{-chxn})_3]^{2+}$ by $[\text{Co}(\text{mal})_3]^{3-}$ consist of diastereomers that are readily separated by ion-exchange

Table II. Isomer Distributions in the Oxidations of $[\text{Co}(\pm\text{-bn})_3]^{2+}$ and $[\text{Co}(\pm\text{-chxn})_3]^{2+}$ by $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{ox})_3]^{3-}$, and $[\text{Co}(\text{mal})_3]^{3-}$ in Aqueous Solution

isomer	% product				
	$[\text{Co}(\pm\text{-bn})_3]^{3+}$		$[\text{Co}(\pm\text{-chxn})_3]^{3+}$		
	a	b	a	b	c
<i>lel</i> ₃	32	38	37	36	33
<i>lel</i> _{2ob}	41	39	36	44	39
<i>lel ob</i> ₂	22	19	19	18	22
<i>ob</i> ₃	6	4	8	2	6

^a $[\text{Co}(\text{edta})]^-$, NO_3^- media, >98% total recovery. ^b $[\text{Co}(\text{ox})_3]^{3-}$, NO_3^- media, ~80% total recovery. ^c $[\text{Co}(\text{mal})_3]^{3-}$, Cl^- media, ~70% total recovery.

chromatography, and for which stereoselectivities can be determined. The relative amounts of each diastereomer are summarized in Table II, together with those for the corresponding values for reactions with $[\text{Co}(\text{edta})]^-$. Results with all three oxidants show the same general trends but differ in detail. Specifically, there is a 5% increase in the presence of *lel* conformers with $[\text{Co}(\text{ox})_3]^{3-}$ as oxidant compared with $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{mal})_3]^{3-}$. The distribution of product diastereomers is dependent on both the distribution of isomers in the reduced form and their relative reactivities. Various studies^{29,30} suggest that the *lel ob*₂ isomer predominates in the cobalt(II) complexes, with amounts decreasing in the order *lel*₃, *lel ob*₂, and *ob*₃. Thus, the product analyses primarily reflect the thermodynamic distribution of the cobalt(II) complexes. Differences in reactivity of the diastereomers have been examined³¹ but appear to be a minor perturbation. One plausible explanation is that the less thermodynamically stable²³ *ob*₃ and *lel ob*₂ isomers are more prone to exist as bis complexes and hence are more susceptible to reduction by the competing inner-sphere pathway that is present in the reaction with $[\text{Co}(\text{ox})_3]^{3-}$.

(d) **Outer-Sphere Stereoselectivity.** In the reactions with $[\text{Co}(\text{edta})]^-$ it was demonstrated² that there is a strong correlation between electron-transfer stereoselectivity and ion-pairing stereoselectivity determined by using the oxidized form of the reductant as a substitution-inert probe. From this observation, it was deduced that stereoselectivity in the precursor complex formation dominated the overall electron-transfer stereoselectivity rather than some electronic effect even though some theoretical predictions^{2,32} stress the importance of the electronic component. Similar ion-pairing experiments are not possible with $[\text{Co}(\text{ox})_3]^{3-}$, since the complex is prone to racemization. However, resolution of $[\text{Co}(\text{en})_3]^{3+}$ can be effected by using $[\text{Co}(\text{ox})_3]^{3-}$. The least soluble diastereomeric pair is $\Delta\Delta$,³³ but this does not necessarily indicate the stereochemical preference in the ion pair. Studies with $[\text{Cr}(\text{mal})_3]^{3-}$ and $[\text{Co}(\text{en})_3]^{3+}$ show a $\Delta\Delta$ ion-pairing preference,⁵ but with $[\text{Co}(\pm\text{-chxn})_3\text{-lel}]^{3+}$, the preference is $\Delta\Delta$, paralleling the results for ion-pairing with $[\text{Co}(\text{edta})]^-$. Comparisons with the relevant electron-transfer stereoselectivities reveal that in each instance electron-transfer stereoselectivity reflects the ion-pairing stereoselectivity with the implication that it is the precursor ion-pair structure that is critical in determining the stereochemical preference in these reactions.

The stereoselectivity data are presented in Table III in two forms, as the enantiomeric excess and as $\Delta\Delta G^*$, the difference in activation free energies of the $\Delta\Delta$ reaction pair and those for the $\Delta\Delta$ pair ($\Delta G^*_{\Delta\Delta} - \Delta G^*_{\Delta\Delta}$). There are several trends that require discussion, one as a result of changes in the structure of the reductant, another as a result of changes in chelate ring

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Table III. Electron-Transfer Stereoselectivity in the Oxidation of Cobalt(II) Amine Complexes by $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{ox})_3]^{3-}$, and $[\text{Co}(\text{mal})_3]^{3-}$

	$[\text{Co}(\text{edta})]^-$		$[\text{Co}(\text{ox})_3]^{3-}$		$[\text{Co}(\text{mal})_3]^{3-}$				
	%	$\Delta\Delta G^*$ ^a	%	$\Delta\Delta G^*$	%	$\Delta\Delta G^*$			
$[\text{Co}(\text{en})_3]^{2+}$	11.5	$\Delta\Delta^b$	-137	7.6	$\Delta\Delta^d$	-90	0.6	$\Delta\Delta^d$	-7
$[\text{Co}(\text{sen})]^{2+}$	9.8	$\Delta\Delta^c$	-116	6.6	$\Delta\Delta^d$	-78			
$[\text{Co}(\text{sep})]^{2+}$	17.6	$\Delta\Delta^d$	-203	>21	$\Delta\Delta^d$	-302			
$[\text{Co}((\pm)\text{-bn})_3\text{-}l\text{el}_3]^{2+}$	14.2	$\Delta\Delta^e$	173	28	$\Delta\Delta^f$	341			
$[\text{Co}((\pm)\text{-bn})_3\text{-}l\text{el}_2\text{ob}]^{2+}$	0.15	$\Delta\Delta^e$	2	14	$\Delta\Delta^f$	167			
$[\text{Co}((\pm)\text{-bn})_3\text{-}l\text{el}\text{ob}_2]^{2+}$	12.5	$\Delta\Delta^e$	-149	9	$\Delta\Delta^f$	107			
$[\text{Co}((\pm)\text{-bn})_3\text{-}ob_3]^{2+}$	25	$\Delta\Delta^e$	-302	14	$\Delta\Delta^f$	167			
$[\text{Co}((\pm)\text{-chxn})_3\text{-}l\text{el}_3]^{2+}$	24	$\Delta\Delta^e$	290	38	$\Delta\Delta^g$	-474	23	$\Delta\Delta^h$	277
$[\text{Co}((\pm)\text{-chxn})_3\text{-}l\text{el}_2\text{ob}]^{2+}$	5	$\Delta\Delta^e$	59	56	$\Delta\Delta^g$	-749	26	$\Delta\Delta^h$	315
$[\text{Co}((\pm)\text{-chxn})_3\text{-}l\text{el}\text{ob}_2]^{2+}$	7	$\Delta\Delta^e$	-83	68	$\Delta\Delta^g$	-982	24	$\Delta\Delta^h$	277
$[\text{Co}((\pm)\text{-chxn})_3\text{-}ob_3]^{2+}$	16	$\Delta\Delta^e$	-191	51	$\Delta\Delta^g$	-666	15	$\Delta\Delta^h$	173

^a $\Delta\Delta G^*$ (cal) = $\Delta G^*_{\Delta\Delta} - \Delta G^*_{\Delta\Lambda}$. ^bIonic strength 0.2 M. ^cIonic strength 0.056 M. ^dIonic strength 0.10 M. ^eIonic strength 0.052 M. ^fIonic strength 0.39 M. ^gIonic strength 0.060 M. ^hIonic strength 0.049 M.

conformation, and a third as a result of changes in oxidant structure. In previous work with $[\text{Co}(\text{edta})]^-$, these trends were explained in terms of steric and hydrogen-bonding interactions in the formation of the precursor complex for electron transfer. Some elaboration of these effects is now required.

Since the stereoselectivity is dependent on the conformation of the chelate rings, it is important to discuss steric effects in complexes with similar conformations. There are four complexes for which stereoselectivities are available for the $l\text{el}_3$ conformers, $[\text{Co}(\text{sep})]^{2+}$, $[\text{Co}(\text{sen})]^{2+}$, $[\text{Co}((\pm)\text{-bn})_3\text{-}l\text{el}_3]^{2+}$, and $[\text{Co}((\pm)\text{-chxn})_3\text{-}l\text{el}_3]^{2+}$, exhibiting a trend where steric bulk in the complex changes from the C_3 axis to the C_2 plane. The data² for oxidation by $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{sep})]^{2+}$ (17% $\Delta\Delta$), $[\text{Co}(\text{sen})]^{2+}$ (10% $\Delta\Delta$), $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ (15% $\Delta\Delta$), and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ (25% $\Delta\Delta$), reflect a shift in the balance between interactions along the C_3 axis and in the C_2 plane as a result of these steric barriers and the differing helicities exhibited by the C_3 and C_2 axes. The limited data for $[\text{Co}(\text{mal})_3]^{3-}$ also appears to be consistent with this explanation. However, in the $[\text{Co}(\text{ox})_3]^{3-}$ reactions, while there is a general trend in stereoselectivity with ligand structure for three of the series, $[\text{Co}(\text{sep})]^{2+}$ (>21% $\Delta\Delta$), $[\text{Co}(\text{sen})]^{2+}$ (7% $\Delta\Delta$), and $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ (28% $\Delta\Delta$), the $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ complex, which has the most extensive steric bulk in the C_2 plane, shows a strong, 38% $\Delta\Delta$ stereoselectivity, quite out of order.

Changes in stereoselectivity as a result of changes in chelate ring conformation in the reactions with $[\text{Co}((\pm)\text{-bn})_3]^{3+}$ and $[\text{Co}((\pm)\text{-chxn})_3]^{3+}$ also differ with the different oxidants. In the oxidation by $[\text{Co}(\text{ox})_3]^{3-}$, both show a very similar trend, increasing $\Delta\Delta$ character from $l\text{el}_3$ to $l\text{el}\text{ob}_2$, decreasing thereafter. This contrasts with the results² from the reactions with $[\text{Co}(\text{edta})]^-$, where the linear trend in the stereoselectivities with $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ from $\Delta\Delta$ to $\Delta\Lambda$ as the chelate ring conformation is changed from $l\text{el}_3$ to ob_3 was correlated with changes in the hydrogen-bonding structure between the reactants, and with $[\text{Co}(\text{mal})_3]^{3-}$, where the $\Delta\Delta$ stereoselectivity is almost invariant with ring conformation in the reaction with $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$.

It is in the reactions of $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ that the differences in stereoselectivities with the different oxidants are most marked. However, the fact that the changes with chelate ring structure for $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ parallel each other strongly suggests that the discrepancies in the $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ system are not unique but that they prevail in the other systems also, masked by a more diverse population of precursor complex structures. From the point of view of interpretation, what is important in the $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ reaction is that it is sterically crowded and the reactions are forced to take place to a large degree along the C_3 axis of the reductant. This should simplify the analysis, and the implication is that the interactions along this axis are very sensitive to oxidant structure and charge.

The data for $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ oxidations are presented in Figure 3. Any explanation that rationalizes these data must take account of the trends with changing chelate ring conformation as well as the changes in oxidant structure. There need be no unifying feature since the three oxidants, while capable of em-

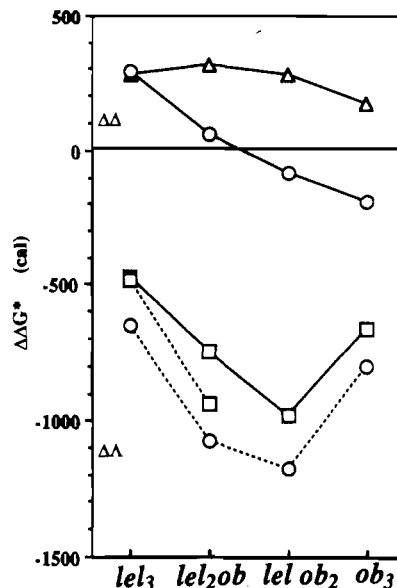


Figure 3. Stereoselectivity shown as $\Delta\Delta G^*$ ($\Delta G^*_{\Delta\Delta} - \Delta G^*_{\Delta\Lambda}$) in the reactions of $[\text{Co}(\text{edta})]^-$ (circles), $[\text{Co}(\text{ox})_3]^{3-}$ (squares), and $[\text{Co}(\text{mal})_3]^{3-}$ (triangles) in water and DMSO (dashed line) as a function of chelate ring conformation.

ploying similar C_3 carboxylate faces in interactions with $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$, do have differing structures. However, a further piece of information strongly suggests that direct comparisons can be made between the different systems and that they do employ comparable C_3 or pseudo- C_3 faces in interactions with $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$. In DMSO solution, the oxidant $[\text{Co}(\text{edta})]^-$ behaves in a way that is remarkably similar⁸ to that shown by $[\text{Co}(\text{ox})_3]^{3-}$ in water (Figure 3), while this latter oxidant appears little affected by the change in solvent.³⁴ Thus it seems likely that these two oxidants interact with $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ through the common structural feature, the (pseudo)- C_3 carboxylate face.

The observations on stereoselectivity require an explanation in which the C_3 axis of the $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ complex is presented to the pseudo- C_3 or C_3 carboxylate faces of the oxidants. This dictates the orientation for approach of the reactants in the electron-transfer reaction and implies that the differences in stereoselectivity are the result of differences in the assembly of the reactants approaching along a mutual C_3 axis. To explain the results, two limiting structures with opposing stereoselectivities are suggested for these interactions: one, with $\Delta\Delta$ stereoselectivity, in which hydrogen bonding between the reactants is dominant, and the other, with $\Delta\Lambda$ stereoselectivity, where electrostatic interactions between the complexes dominate, resulting in a more intimate arrangement with interpenetrating coordination spheres. Simplified representations of these two limiting forms are shown in Figure 4 for the $[\text{Co}(\text{ox})_3]^{3-}$ - $[\text{Co}(\text{en})_3\text{-}l\text{el}_3]^{2+}$ system.

It is generally recognized that electron-transfer reactions take place over a range of distances. If the range over which the

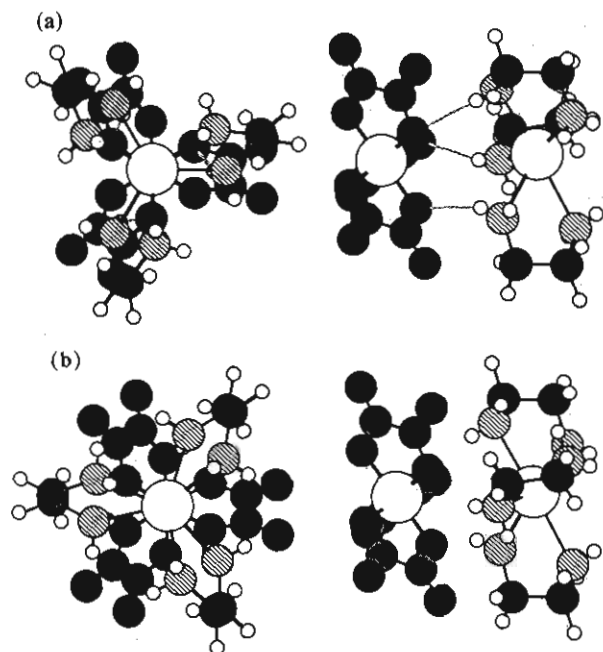


Figure 4. Minimum energy orientations for the C_3-C_3 interactions of $[\text{Co}(\text{en})_3\text{-}l\text{el}_3]^{2+}$ with $[\text{Co}(\text{ox})_3]^{3-}$ at (a) hydrogen-bonded distances, $\Delta\Delta$ pair, and (b) closest contact distances, $\Delta\Lambda$ pair. Oxygen atoms are black, carbon atoms are shaded, and nitrogen atoms are striped.

electron is transferred varies depending on the relative importance of hydrogen-bonding and electrostatic interactions, then the electron-transfer stereoselectivity will also vary. As a starting point, consider the reaction between $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\pm)\text{-chxn})_3\text{-}l\text{el}_3]^{2+}$ in aqueous media, where the charge product is low and the amine nitrogen configuration on the reductant favors strong linear hydrogen bonds.² This reaction shows the $\Delta\Delta$ stereoselectivity expected of a strongly hydrogen-bonded system. The contribution from hydrogen bonding can be reduced either by changing the chelate ring conformations from *l*el to *o*b, where the amine nitrogen configuration on the reductant is less favorable for strong linear hydrogen bonds,² or by lowering the solvent dielectric (from water to DMSO) and enhancing the electrostatic contribution. In both instances there should be a change from $\Delta\Delta$ to $\Delta\Lambda$, as observed. The $[\text{Co}(\text{ox})_3]^{3-}$ system in aqueous solution has a much higher charge product, and will be representative of the intimate interaction with $\Delta\Lambda$ stereoselectivity. There is a trend with changing reductant chelate ring conformation, but it is much less well-defined than that with $[\text{Co}(\text{edta})]^-$, consistent with the reduced importance of hydrogen bonding, and the stereoselectivities are comparable in DMSO.³⁴

Data for the $[\text{Co}(\text{mal})_3]^{3-}$ system appear to be anomalous, since the charge product is identical with that for $[\text{Co}(\text{ox})_3]^{3-}$ and the stereoselectivity is $\Delta\Delta$, virtually independent of chelate ring conformation. However, with the $[\text{Co}(\text{mal})_3]^{3-}$ reagent, the three carboxylate groups on the C_3 face are arranged such that the terminal carboxyl oxygen atoms project above the plane of the bound oxygen atoms, providing a steric barrier along the C_3 axis and preventing approach of the oxidant closer than hydrogen-bonding distances. The result is a $\Delta\Delta$ stereoselectivity that does not show a strong dependence on reductant chelate ring conformation, since the distance of approach is governed by the steric barrier. Particularly noteworthy is a report¹⁹ of the X-ray structure of $[\Delta\text{-Co}((-)\text{-pn})_3][\Lambda\text{-Cr}(\text{mal})_3]\cdot 3\text{H}_2\text{O}$, which shows a C_3-C_3 hydrogen-bonding arrangement between the complexes with im-

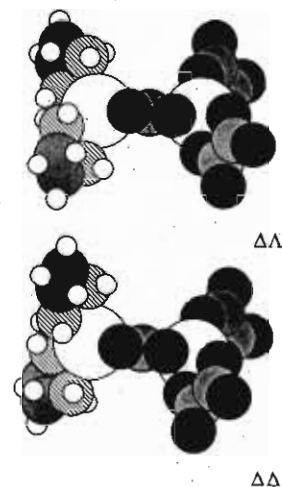


Figure 5. Space-filling representations of the diastereomeric, oxalate-bridged, inner-sphere intermediates proposed for the reaction of $[\text{Co}(\text{ox})_3]^{3-}$ with $[\text{Co}(\text{en})_2]^{2+}$, showing the separation between the chiral centers.

portant intermolecular contacts involving the terminal carboxyl oxygens.

As noted previously, trends with chelate ring conformation for the $[\text{Co}(\pm)\text{-bn})_3]^{2+}$ and $[\text{Co}(\pm)\text{-chxn})_3]^{2+}$ systems are similar for each oxidant and appear to be diagnostic of the type of interaction that dominates in the precursor complex. This implies that hydrogen-bonding interactions predominate in the reactions of all of the reductants with $[\text{Co}(\text{edta})]^-$ and that in the corresponding reactions with $[\text{Co}(\text{ox})_3]^{3-}$ the precursor complexes are more intimate. That the stereoselectivities for the $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{ox})_3]^{3-}$ complexes are for the most part comparable must be considered fortuitous, a result of the balance of a variety of interactions between the reactants.

These observations have implications for recent theoretical discussions^{35,36} of electron-transfer rates that have raised the issue of whether, in the precursor to electron transfer, there is significant interpenetration of the coordination spheres, leading to restricted rotation and large steric factors, or a more limited interaction at the initial contact distance. Clearly, the stereoselectivity studies indicate that interpenetration can and does occur, but in studies of the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}$ self-exchange rate^{35,36} where the reactants have similar charges, interpenetration seems unlikely. Some idea of the magnitude of this steric effect in the reaction of $[\text{Co}(\text{ox})_3]^{3-}$ with divalent ions can be deduced from the discrepancies in the self-exchange rate evaluated from cross-reactions with $[\text{Ru}(\text{en})_3]^{2+}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+}$, which should behave similarly to $[\text{Co}(\text{en})_3]^{2+}$, compared to the rate evaluated from the reaction with $[\text{Co}(\text{terpy})_2]^{2+}$ where, presumably, interpenetration is less likely.

(e) The Inner-Sphere Pathway. The inner-sphere pathway in the reaction of $[\text{Co}(\text{ox})_3]^{3-}$ with $[\text{Co}(\text{en})_3]^{2+}$ most likely proceeds by a mechanism in which an oxalate of the oxidant is doubly bridged to the reductant, as shown in Figure 5. A singly bridged precursor would involve subsequent ring closure to form the $[\text{Co}(\text{en})_2(\text{ox})]^+$ product, and such ring closure reactions are relatively slow in cobalt(III) complexes.³⁷ No evidence for a monocoordinated oxalate product was obtained. Evidence for inner-sphere electron transfer through doubly bridged oxalate has been presented previously in the chromium(II) reductions of cobalt(III)³⁸ and chromium(III)³⁹ oxalate derivatives.

There is no evidence for inner-sphere pathways with $[\text{Co}(\text{sen})]^{2+}$ and $[\text{Co}(\text{sep})]^{2+}$, as might be expected. Although the inner-sphere pathway is detected in the oxidations of $[\text{Co}(\pm)\text{-bn})_3]^{2+}$ and

(34) In DMSO solution, reaction of $[\text{Co}(\text{ox})_3]^{3-}$ with $[\text{Co}(\text{en})_3]^{2+}$ (0.10 M ionic strength (NaClO_4), 23 °C) gives 98% $[\text{Co}(\text{en})_3]^{3+}$ with a stereoselectivity of 17% $\Delta\Delta$, while, with $[\text{Co}(\pm)\text{-chxn})_3]^{2+}$ (0.063 M ionic strength (Cl^-), 23 °C), the products are 84% *l*el₃ with a stereoselectivity of 39% $\Delta\Delta$ and 14% *l*el₂*o*b with a stereoselectivity of 66% $\Delta\Delta$. Other isomers are below detection limits. In neither case is there evidence for an inner-sphere pathway.

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$[\text{Co}(\pm\text{-chxn})_3]^{2+}$, a complex mixture of isomers is anticipated, and structural effects in the inner-sphere pathway were not investigated in any detail. However, it is noted that in both of these reactions, the presence of the inner-sphere pathway is accompanied by an increase in the proportion of *lel* conformers in the outer-sphere product. As mentioned above, this may be the result of the greater propensity for dissociation of the *ob* conformer in the outer-sphere electron-transfer precursor complex. For example, it is known^{40,41} that association of anions such as PO_4^{3-} , which has a trigonal arrangement of oxygen atoms similar to that found in $[\text{Co}(\text{ox})_3]^{3-}$, with $[\text{Co}(\text{en})_3]^{3+}$ promotes formation of the *lel*₃ conformer. Such ion pairs are relatively long-lived, with an intramolecular (outer-sphere) electron-transfer rate estimated to be in the region of 20 s^{-1} , much slower than typical cobalt(II) ligand-substitution processes. It is not unreasonable to expect that these ion pairs are intermediates common to both inner- and outer-sphere electron-transfer pathways. Inner-sphere pathways are also possible in the reactions of $[\text{Co}(\text{mal})_3]^{3-}$ but were not investigated.

The discovery of an inner-sphere pathway that has the potential for showing stereoselectivity is of considerable interest. There is only one report of this type of behavior in the literature.⁴² When optically active $[\text{Co}(\text{ox})_3]^{3-}$ is used, two diastereomeric inner-sphere electron-transfer precursor configurations are possible (Figure 5). Chiral discrimination in the electron-transfer reaction will result if these configurations have significantly different stabilities or if orbital overlap through the oxalate bridge differs. Chiral discrimination may also result if the reactions leading to the bridged precursor show stereoselectivity.

The circular dichroism spectrum of the products of reaction of optically active $[\Delta\text{-Co}(\text{ox})_3]^{3-}$ with cobalt(II) in relatively high-concentration 1,2-diaminoethane solution is dominated by the signal from the major product $[\Delta\text{-Co}(\text{en})_3]^{3+}$. When this product is removed by ion-exchange chromatography, the solutions show a very weak circular dichroism signal indicating the presence of $[\Delta\text{-Co}(\text{en})_2(\text{ox})]^+$. There are two possible explanations. Either the inner-sphere pathway has very small stereoselectivity, or the $[\text{Co}(\text{en})_2(\text{ox})]^+$ product racemizes rapidly under the conditions of the experiment. This latter possibility was examined by the addition of optically active $[\text{Co}(\text{en})_2(\text{ox})]^+$ (0.00125 M) to argon-purged solutions containing cobalt(II) (0.0125 M) in excess 1,2-diaminoethane (0.125 M). Racemization does occur with a rate constant of $8 \times 10^{-3} \text{ s}^{-1}$ at 25 °C, but on addition of HCl in conditions comparable to the reaction workup, the rate of racemization is slowed by about 2 orders of magnitude. This racemization is much too slow to explain the very low optical activity in the $[\text{Co}(\text{en})_2(\text{ox})]^+$ product, and it is concluded that

the inner-sphere pathway shows little stereoselectivity. At low 1,2-diaminoethane concentrations, $[\text{Co}(\text{II})]:[\text{en}] = 1:2$, where $[\text{Co}(\text{en})_2(\text{ox})]^+$ is the dominant product, the Δ isomer is formed in 1.5% optical purity when the oxidant is $[\Delta\text{-Co}(\text{ox})_3]^{3-}$, consistent with experiments at higher 1,2-diaminoethane concentrations.

At first sight, this small stereoselectivity seems rather surprising. Although not extensively investigated, diastereomeric discrimination has been detected in binuclear cobalt(III) complexes.^{43,44} In these instances, the bridging groups are single atoms or pairs of atoms and the metal centers are correspondingly closer together. The nonbridging ligands, which are responsible for chiral discrimination, are not in intimate contact in the proposed $[(\text{ox})_2\text{Co}(\mu\text{-ox})\text{Co}(\text{en})_2]^-$ precursor, and consequently, diastereoselectivity is weak. There are two implications of this observation. The Co-Co distance in the proposed inner-sphere precursor is around 5 Å, close to typical values for outer-sphere complexation. Where there is detection of significant stereoselectivity in outer-sphere complexation and in outer-sphere electron transfer, this must involve intimate contact between the reagents, consistent with the outer-sphere reactions discussed above. The second implication is that stereoselectivity in the intramolecular electron-transfer step within the inner-sphere complex is weak.

(f) Conclusions. The oxidation of $[\text{Co}(\text{en})_3]^{2+}$ by $[\text{Co}(\text{ox})_3]^{3-}$ proceeds by parallel inner-sphere and outer-sphere pathways leading to $[\text{Co}(\text{en})_2(\text{ox})]^+$ and $[\text{Co}(\text{en})_3]^{3+}$, respectively. The inner-sphere pathway takes place through an oxalate chelate bridge, which holds the metal centers apart and thereby restricts stereoselectivity to modest levels. Stereoselectivity in the outer-sphere reaction is larger, and for the series of related reductants, $[\text{Co}(\text{sep})]^{2+}$, $[\text{Co}(\text{sen})]^{2+}$, $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}(\pm\text{-bn})_3]^{2+}$, and $[\text{Co}(\pm\text{-chxn})_3]^{2+}$, shows a strong dependence on structure. Comparisons of the stereoselectivity data for the oxidants $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{ox})_3]^{3-}$, and $[\text{Co}(\text{mal})_3]^{3-}$ lead to the conclusions that electron transfer with $[\text{Co}(\text{ox})_3]^{3-}$ as oxidant occurs primarily at distances where the coordination spheres of the reactants interpenetrate whereas the corresponding reactions with $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{mal})_3]^{3-}$ occur at hydrogen-bonding distances. This behavior is dictated by the balance between electrostatic, steric, and hydrogen-bonding forces in the electron-transfer precursor complexes and is dependent on the reaction medium.

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Supplementary Material Available: A listing of experimental conditions for stereoselectivity experiments (Table SI) (2 pages). Ordering information is given on any current masthead page.

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