

Stereoselectivity as a Probe of Reaction Mechanism in the Oxidation of $[\text{Co}(\text{en})_3]^{2+}$ and Its Derivatives by $[\text{Co}(\text{edta})]^-$

Peter Osvath and A. Graham Lappin*

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Stereoselectivities in the oxidations of $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}(\text{sen})]^{2+}$, $[\text{Co}(\text{sep})]^{2+}$, $[\text{Co}((\pm)\text{-bn})_3]^{2+}$, and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ by $[\text{Co}(\text{edta})]^-$ have been examined under a variety of conditions. For the conformationally restricted complexes $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ the stereoselectivity shows a trend from 15% $\Delta\Delta$ for $[\text{Co}((\pm)\text{-bn})_3\text{-}l\text{el}_3]^{2+}$ (25% $\Delta\Delta$ for $[\text{Co}((\pm)\text{-chxn})_3\text{-}l\text{el}_3]^{2+}$) to 25% $\Delta\Delta$ for $[\text{Co}((\pm)\text{-bn})_3\text{-}ob_3]^{2+}$ (16% $\Delta\Delta$ for $[\text{Co}((\pm)\text{-chxn})_3\text{-}ob_3]^{2+}$). For $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}(\text{sen})]^{2+}$, and $[\text{Co}(\text{sep})]^{2+}$, stereoselectivities are 11% $\Delta\Delta$, 10% $\Delta\Delta$, and 18% $\Delta\Delta$, respectively. Kinetic studies are consistent with outer-sphere reactions. The stereoselectivities are correlated with ion-pairing stereoselectivities for the interactions of $[\text{Co}(\text{edta})]^-$ with the appropriate cobalt(III) amine complexes, supporting an important role for precursor complex structure in determining the chiral induction. The trends in the data are explained in terms of a balance of interactions along the C_2 and C_3 axes of the reductant complexes.

Introduction

Structural details of outer-sphere electron-transfer reactions between complex ions in solution are difficult to probe because the interactions involved are generally weak. Attempts have been made¹⁻³ to infer such information from work term calculations in the Marcus analysis of rate data,⁴ but this method lacks sensitivity. The chiral induction that has been observed⁵⁻¹⁰ in a number of outer-sphere electron-transfer reactions has the potential for providing information about the interactions between the complexes. However, interpretation of stereoselectivity data presents some difficulties.

It is generally accepted that an outer-sphere electron-transfer reaction involves initial formation of a precursor complex between reactants, followed by transfer of the electron within this precursor (eq 1 and 2). Stereoselectivity can arise from either of these two steps.^{6,8,9}



Information on precursor complex stereoselectivity can be deduced from ion-pairing studies with isostructural, optically stable analogues, and in a previous study⁹ it was shown that, in some cases, the precursor complex stereoselectivity can be correlated with the overall stereoselectivity in the electron-transfer reaction. As an example, the oxidation of $[\text{Co}(\text{en})_3]^{2+}$ (en = 1,2-diaminoethane) by $[\Delta\text{-Co}(\text{edta})]^-$ (edta⁴⁻ = 1,2-diaminoethane-*N,N,N',N'*-tetraacetate(4-)) is a stereoselective electron-transfer reaction⁵ in which the $[\text{Co}(\text{en})_3]^{3+}$ formed shows a 10% excess of the Δ isomer, indicating a preferred $\Delta\Delta$ interaction. Precursor ion-pair stereoselectivity, determined from the ion pair between $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{en})_3]^{3+}$ is also $\Delta\Delta$;¹¹ hence, it is reasonable that the structural arrangement of the precursor ion pair determines the overall electron-transfer stereoselectivity.

Current interpretation of ion-pairing stereoselectivity in an octahedral complex depends on the chiral discrimination that arises from the different helicities described by the chelate rings when viewed along the C_2 and C_3 axes.¹² In $[\Delta\text{-Co}(\text{en})_3]^{3+}$ the helicity along the C_3 axis is minus (*M*) and along the C_2 axis is plus (*P*),

giving the designation $M(C_3)P(C_2)$ whereas $[\Delta\text{-Co}(\text{edta})]^-$ is designated $P(C_3)M(C_2)$. Homochiral pairwise interactions (*PP* or *MM*) are believed¹¹ to be favored, and thus a model for the structure of the precursor ion pair is proposed in which the pseudo- C_3 axis of $[\text{Co}(\text{edta})]^-$ with three localized carboxylate charges is presented to the C_2 axis of $[\text{Co}(\text{en})_3]^{2+}$.

One factor that has been suggested¹³ to affect stereoselectivity is chelate ring conformation which may be defined in $[\text{Co}(\text{en})_3]^{3+}$ and its derivatives as *l_{el}* if the C-C bond of the five-membered ring lies parallel to the C_3 axis and *ob* if the C-C bond lies oblique to this axis. Four distinct conformational isomers are possible, designated by the trival terms (*l_{el}*), (*l_{el}ob*), (*l_{el}ob₂*), and (*ob₃*), where the conformation of each of the three chelate rings is indicated.¹⁴ While conformational isomers of the complex $[\text{Co}(\text{en})_3]^{3+}$ are interconvertible by simple rotations, the corresponding isomers of the related complexes $[\text{Co}((\pm)\text{-chxn})_3]^{3+}$ ($(\pm)\text{-chxn}$ = *trans*-1,2-diaminocyclohexane) and $[\text{Co}((\pm)\text{-bn})_3]^{3+}$ ($(\pm)\text{-bn}$ = *rac*-2,3-diaminobutane) are diastereomers because the ligands each have two chiral centers. This allows the oxidation of $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ and $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ by $[\Delta\text{-Co}(\text{edta})]^-$ to be used as a probe of the effects of ring conformation on electron-transfer stereoselectivity.

In this paper the influence of ion-pairing stereoselectivity and of chelate ring conformation on electron-transfer stereoselectivity are investigated. A preliminary account of part of the work has been published.¹⁵

Experimental Details

(a) Preparation of Ligands. 1,1,1-Tris(((2-aminoethyl)amino)methyl)ethane (sen) was prepared by reaction of 1,1,1-tris(hydroxymethyl)ethane (Aldrich) with PBr_3 (Aldrich) to form the tribromide,¹⁶ which was refluxed (30 h) with excess 1,2-diaminoethane.¹⁷ After removal of unreacted 1,2-diaminoethane and treatment with aqueous sodium hydroxide, the residue was extracted with pyridine. The pyridine solution was dried (Na_2SO_4) and the pyridine removed to give crude "sen", which was vacuum distilled (0.02 mmHg, 130-145 °C). 2,3-Diaminobutane dihydrochloride was prepared by reduction of a basic solution of dimethylglyoxime with Ni/Al alloy (Alfa)^{18,19} followed by steam distillation and acidification with HCl. The desired *rac*-2,3-diaminobutane dihydrochloride was obtained by fractional crystallization ($\times 3$) from methanol. Contamination by the meso isomer was readily monitored by ¹³C NMR spectroscopy²⁰ and was less than 2%. Attempts to

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- These designations refer to the following isomers: *l_{el}*, $\Delta(\lambda, \lambda, \lambda)$, $\Delta(\delta, \delta, \delta)$; *l_{el}ob*, $\Delta(\delta, \lambda, \lambda)$, $\Delta(\delta, \delta, \lambda)$; *l_{el}ob₂*, $\Delta(\delta, \delta, \lambda)$, $\Delta(\delta, \lambda, \lambda)$; *ob₃*, $\Delta(\delta, \delta, \delta)$, $\Delta(\lambda, \lambda, \lambda)$.
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remove the meso contaminant by the method of Billo and Vitiello²¹ proved less successful. Other ligands, 1,2-diaminoethane (Aldrich), *rac*-1,2-diaminocyclohexane (Aldrich), and 1,2-diaminoethane-*N,N,N',N'*-tetraacetic acid disodium salt (Baker Analyzed), were used as obtained.

(b) Preparation of Complexes. The complexes $[\Lambda-(+)_D\text{-Co}(\text{en})_3]\text{Cl} \cdot (d\text{-tartrate}) \cdot 5\text{H}_2\text{O}$ and $[\Delta-(-)_D\text{-Co}(\text{en})_3]\text{Cl} \cdot (l\text{-tartrate}) \cdot 5\text{H}_2\text{O}$ were prepared by the published procedure.²² The corresponding bromide salt $[\Lambda-(+)_D\text{-Co}(\text{en})_3]\text{Br} \cdot (d\text{-tartrate}) \cdot \text{H}_2\text{O}$ was prepared by substituting HBr for HCl in this procedure. Other salts, $[\Lambda-(+)_D\text{-Co}(\text{en})_3](\text{ClO}_4)_3$, $[\Delta-(-)_D\text{-Co}(\text{en})_3](\text{ClO}_4)_3$, and $[\Lambda-(+)_D\text{-Co}(\text{en})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$, were obtained by recrystallization from solutions containing excess NaClO_4 or NaBr as appropriate.²²

The complex $[\text{Co}(\text{sen})]\text{Cl}_3$ was prepared by the addition of $\text{Na}_2\text{Co}(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ ²³ to an acidified solution of *sen*.^{17,24} The resulting mixture was filtered, and the filtrate was diluted and loaded onto a column of SP Sephadex C-25 120 (2.4 × 45 cm). Elution with Na_2HPO_4 (0.1 M) produced a band of $\text{Co}(\text{H}_2\text{O})_6^{2+}$, a minor unidentified red band, and a major yellow band, which was absorbed onto a column of Dowex 50X2-400 ion-exchange resin (0.6 × 4 cm). This column was washed successively with water, 0.2 M HCl, and 1 M HCl, and the product was removed with 5 M HCl; the solution was evaporated to dryness under reduced pressure, producing the desired product.

$[\Lambda\text{-Co}(\text{sep})]\text{Cl}_3 \cdot \text{H}_2\text{O}$ was prepared by a modification of the method of Sargeson and co-workers.²⁵ To a stirred solution of $[\Lambda\text{-Co}(\text{en})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ (9.3 g) and Li_2CO_3 (18.8 g) in water (100 mL) were added separately ammonia (4.8 M, 375 mL) and aqueous formaldehyde (37%, 444 mL) in portions over 2 h. The mixture was stirred for a further 1 h, excess Li_2CO_3 was removed by filtration, and concentrated acetic acid was added to pH 4. After dilution to 2 L with water, this mixture was adsorbed onto a column of Dowex 50X4-200 (3.5 × 10 cm) and washed with Na_2HPO_4 (0.2 M, 1.8 L), eluting a purple band. The column was washed successively with 0.2, 0.5, and 1 M HCl, and the product was eluted with 2 M HCl. Evaporation to near dryness followed by addition of acetone gave the product (yield 6.9 g), which could be recrystallized from aqueous acetone. Samples of the racemic complex $[\text{Co}(\text{sep})]\text{Cl}_3 \cdot \text{H}_2\text{O}$ were obtained in an analogous way. Triflate (triflate = trifluoromethanesulfonate) salts were prepared from the chloride salts by precipitation (×2) from concentrated triflic acid followed by recrystallization from aqueous sodium triflate–dilute triflic acid solution.

Solutions of $[\text{Co}(\text{sep})]^{2+}$ and $[\Lambda\text{-Co}(\text{sep})]^{2+}$ were prepared by reduction of solutions of the corresponding cobalt(III) complexes using Zn/Hg amalgam (30 mesh) at pH 5, under argon.

$[\text{Co}(\pm)\text{-bn}]_3\text{Cl}_3$ was prepared by heating a mixture of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (0.17 g), *rac*-*bn*-2HCl (0.49 g), sodium hydroxide (0.2 g), and activated charcoal (0.3 g, Fisher) in 125 mL of water at 70 °C for 24 h. After filtration, the solution was adsorbed on a column of Dowex 50X2-400 (1.2 × 5 cm), which was washed successively with 0.2 and 1.0 M HCl, and the mixture of isomers was eluted with 5 M HCl. The solid product was obtained on evaporation to dryness.

Other complexes, $\text{Na}[\Delta-(+)_S_{46}\text{-Co}(\text{edta})] \cdot 4\text{H}_2\text{O}$ ²⁷ and $\text{Na}[\text{Co}(\text{edta})]_3$ ²⁸ were prepared by literature methods.

(c) Separation of Diastereomers. The separation of diastereomers of $[\text{Co}(\pm)\text{-bn}]_3^{3+}$ and $[\text{Co}(\pm)\text{-chxn}]_3^{3+}$ was carried out by SP Sephadex C-25 120 (1.2 × 45 cm) ion-exchange chromatography.²⁹ Initial experiments using 0.1 or 0.2 M Na_2SO_4 , pH 4.0, as eluent gave separation into three bands in both cases: (*lel*₁), (*lel*₂), and an unresolved mixture of (*lel*₃) and (*ob*₃). Elution with 0.1 M Na_2HPO_4 or 0.2 M Na_3PO_4 yielded the four expected bands for both systems in the order (*lel*₁), (*lel*₂), (*lel*₃), and (*ob*₃). After separation, each eluted band was adsorbed onto a short (0.6 × 4 cm) column of Dowex 50X2-400 ion-exchange resin, washed successively with water, 0.5 M HCl, and 1.0 M HCl and removed by elution with 5.0 M or concentrated HCl. Samples were stripped of solvent under aspirator vacuum at less than 40 °C. The proportions of the various isomers were determined spectrophotometrically.^{30,31} (Extinction coefficients for isomers of $[\text{Co}(\pm)\text{-bn}]_3^{3+}$ were

determined from atomic absorption measurements of the cobalt concentrations of solutions.)

(d) Chromatographic Resolution of Complexes. Resolution of the diastereomers of $[\text{Co}(\pm)\text{bn}]_3^{3+}$ was carried out on SP Sephadex C-25 120 columns (1.2 × 45 cm) with 0.1 or 0.2 M sodium tartrate (pH 7.0) as eluent. In all cases, two well-separated bands were obtained. After collection, the optical isomers were absorbed on short Dowex columns, eluted with HCl, and stripped of solvent as described above.

In order to check the optical purity of samples of $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{sen})]^{3+}$, and $[\text{Co}(\text{sep})]^{3+}$, chromatographic resolution of racemic samples of these complexes was carried out. This was achieved on an SP Sephadex C-25 120 column (1.2 × 30 cm) with 0.2 M potassium antimonyl tartrate as eluent.³² Again, the optical isomers were absorbed on short Dowex columns, washed with copious amounts of water, eluted with HCl, and stripped of solvent as described above.

(e) Stereoselectivity Experiments. All stereoselectivity studies were run at 23 ± 1 °C unless otherwise noted, under an argon atmosphere to prevent aerial oxidation of the cobalt(II) complexes. Except in the case of $[\text{Co}(\text{sep})]^{2+}$, a 10-fold excess of the cobalt(II) reductant (ca. 10^{-2} M, perchlorate or nitrate salts) over $[\Delta\text{-Co}(\text{edta})]^-$ (ca. 10^{-3} M) was used. With $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}(\pm)\text{-bn}]_3^{2+}$, and $[\text{Co}(\pm)\text{-chxn}]_3^{2+}$, high pH and high amine concentration (ca. 10^{-1} M) ensured quantitative formation of the tris complexes. Stepwise stability constants for $[\text{Co}(\text{en})_3]^{2+}$ are $10^{5.6}$, $10^{4.9}$, and $10^{3.3}$ M⁻¹ at 25 °C and 0.1 M ionic strength.³³ For $[\text{Co}(\text{sen})]^{2+}$, a smaller (5×10^{-3} M) excess ligand was used.

Under these conditions, the reactions are rapid with half-lives generally less than 1 s. After completion of the reactions, the mixtures were quenched by the addition of 1 M HCl to pH 1, and after dilution (×10), the cobalt(III) amine complexes were isolated on Dowex 50X2-400 (H⁺) ion-exchange resin. The resin was washed with 1 M HCl to remove cobalt(II), water, and then 2 M HCl, and finally the complexes were eluted with 5 M or concentrated HCl. After solvent was removed under reduced pressure, the amount of cobalt(III) complex was recorded. The stoichiometry of the reactions was measured by comparing the amount of cobalt(III) amine complex obtained with the amount of $[\Delta\text{-Co}(\text{edta})]^-$ used in the reaction.

Stereoselectivities were determined by measuring the optical purity of the cobalt amine complexes by comparison with optically pure samples. This involves a single measurement for $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{sen})]^{3+}$, but for $[\text{Co}(\pm)\text{-bn}]_3^{3+}$ and $[\text{Co}(\pm)\text{-chxn}]_3^{3+}$ the solutions contain a mixture of isomers. In these two cases, the mixtures were separated as outlined above and the stereoselectivity for each isomer was determined individually.

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 involves the high self-exchange rate³⁴ of $[\text{Co}(\text{sep})]^{3+/2+}$, which would result in self-exchange racemization of the product³⁵ and subsequent difficulty in determining the stereoselectivity. To avoid these problems the oxidation was carried out with an excess (×3–10) of *rac*- $[\text{Co}(\text{edta})]^-$, which was reduced by $[\Lambda\text{-Co}(\text{sep})]^{2+}$, and the optical activity of the unreduced $[\text{Co}(\text{edta})]^-$ 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 $[\text{Co}(\text{edta})]^-$ by $[\Lambda\text{-Co}(\text{sep})]^{2+}$ is more rapid than racemization of $[\text{Co}(\text{edta})]^-$, resulting in a strong dependence of the apparent stereoselectivity on the excess concentration. A limiting value for the stereoselectivity with an infinitely large excess was obtained by extrapolation.

(f) Ion-Pairing Stereoselectivities. Samples of racemic $[\text{Co}(\text{en})_3]^{3+}$ were absorbed as a 2-mm band on a 10 cm × 1.2 cm column of Dowex 50X2-400 cation-exchange resin. The sample was eluted (8 days) with a solution of $\text{Na}[\Delta-(+)_S_{46}\text{-Co}(\text{edta})]^-$ (0.10 M) containing sodium perchlorate (0.10 M) recycled with use of a peristaltic pump. After the band had spread to over 20 mm, the column was washed with 10^{-4} M HCl and the resin containing the cobalt(III) complex was divided into eight sections removed sequentially. $[\text{Co}(\text{en})_3]^{3+}$ was removed from each section with concentrated HCl, and after the solvent was stripped under reduced pressure, the circular dichroism spectrum of each sample was recorded in aqueous solution.

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Table I. Percent Isomer Distributions for Formation of $[\text{Co}(\pm\text{-bn})_3]^{3+}$

isomer	$[\text{Co}(\pm\text{-bn})_3]^{3+ a}$			av	$[\text{Co}(\pm\text{-bn})_3]^{3+ b}$		$[\text{Co}(\pm\text{-chxn})_3]^{3+ c}$
	0.2 M SO_4^{2-}	0.1 M HPO_4^{2-}	0.1 M HPO_4^{2-}		obsd	calcd	
<i>lel</i> ₃	46.6	46.8	45.4	46.1 ± 0.7	60	17	46.7
<i>lel</i> _{2ob}	34.3	34.4	35.4	34.9 ± 0.5	28	49	34.7
<i>lel ob</i> ₂ }	19.1	15.0	15.3	15.2 ± 0.2	12	31	14.3
<i>ob</i> ₃ }		3.8	4.0				

^aThis work; 70 °C + charcoal. ^bReference 38; calculated results are the result of strain energy computations. ^cReference 30; 100 °C + charcoal.

In a parallel experiment, racemic $[\text{Co}(\text{edta})]^-$ was absorbed as a narrow band on CG 400 (100–200 mesh) anion-exchange resin in the perchlorate form (20 × 1.2 cm) and eluted with $[\Lambda\text{-}(+)\text{-Co}(\text{en})_3]^{3+}$ (4×10^{-3} M). The partially resolved $[\text{Co}(\text{edta})]^-$ was collected in several fractions, and after removal of $[\text{Co}(\text{en})_3]^{3+}$ by cation-exchange chromatography, the CD spectrum of each fraction was determined.

(g) Circular Dichroism Experiments. Circular dichroism spectra were measured on a Aviv circular dichroism spectrophotometer, Model 60DS (Aviv Associates, Lakewood, NJ), calibrated against an aqueous solution of $[\Lambda\text{-}(+)\text{-Co}(\text{en})_3]\text{Cl}_3$ ($\Delta\epsilon_{493} = 1.90 \text{ M}^{-1} \text{ cm}^{-1}$).³⁵ The spectra of $[\text{Co}(\text{en})_3]^{3+}$ and its derivatives are very sensitive to anion effects, the result of ion-pairing phenomena.^{36,37} Consequently, the spectra are concentration-dependent, and unless otherwise stated, samples were prepared in long path length cells (10 cm) at $\sim 10^{-4}$ M concentration of chloride ion salts. Precautions were taken to compare spectra at approximately the same concentrations.

Visible spectra were run on a Varian DMS 100 spectrophotometer.

(h) Kinetic Measurements. The kinetics of reduction of $[\text{Co}(\text{edta})]^-$ by $[\text{Co}(\text{sep})]^{2+}$ were investigated under pseudo-first-order conditions with an excess of oxidant at 0.10 M ionic strength (triflate media) and pH 5.0 (10^{-2} M acetate). A Durrum D-110 stopped-flow spectrophotometer thermostated at 25.0 ± 0.1 °C was used. Data were collected by using a Nicolet 3091 digital oscilloscope. Reactions were monitored at a variety of wavelengths in the visible region. The reactions are very fast, close to the limits of the stopped-flow technique. With $[[\text{Co}(\text{sep})]^{2+}] = 1.0 \times 10^{-4}$ M, half-lives of 10 ± 1 and 6 ± 2 ms were obtained for $[[\text{Co}(\text{edta})]^-] = 1.0 \times 10^{-3}$ and 3.0×10^{-3} M respectively. The reaction rate is dependent on $[\text{Co}(\text{edta})]^-$ concentration but the faster data are unreliable, close to the dead time of the stopped-flow instrument. Assuming a second-order reaction, a rate constant of $6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ can be estimated.

Results and Discussion

(a) Separation and Resolution of Diastereomers of $[\text{Co}(\pm\text{-bn})_3]^{3+}$. Elution of $[\text{Co}(\pm\text{-bn})_3]^{3+}$ on SP Sephadex C-25 120 cation-exchange resin with 0.10 M sodium phosphate (pH 7.0) results in the appearance of four well-defined bands in the relative proportions shown in Table I. Elution with 0.20 M sodium sulfate (pH 4.0) gives similar results, but separation of the two slowest moving bands, 3 and 4, is incomplete. Tapscott and co-workers³⁸ have determined the sequence of elution of the isomers in a comparable experiment with sulfate as eluent as (*lel*₃), (*lel*_{2ob}), (*lel ob*₂), and (*ob*₃) on the basis of NMR data.

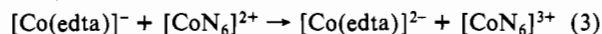
The relative proportions of each band observed in this study differ markedly from those of Tapscott and co-workers,³⁸ as might be expected in view of the different conditions under which the samples were prepared. Interestingly, the proportions are very similar to those found³⁰ for $[\text{Co}(\pm\text{-chxn})_3]^{3+}$ equilibrated over charcoal at 100 °C, suggesting that they are close to the thermodynamic values.

Two detailed conformational analysis studies of the $[\text{Co}(\pm\text{-bn})_3]^{3+}$ system have been published,^{38,39} and although they are in good agreement, the calculated isomer ratios do not resemble those found in the present study. This is not particularly surprising since the calculations are based on isolated, gas-phase molecules while, under the experimental conditions, there are additional

interactions arising from the solvent and the counterion, (chloride in this case).

Racemic mixtures of the diastereomers of $[\text{Co}(\pm\text{-bn})_3]^{3+}$ are completely resolved by chromatography on SP Sephadex C-25 120 with 0.10 M *d*-tartrate (pH 7.0) as eluent. The Λ isomers are eluted first in all cases. Circular dichroism data for all the complexes are presented in Table II. Previously, circular dichroism parameters for the (*lel*₃) and (*ob*₃) isomers of $[\text{Co}(\pm\text{-bn})_3]^{3+}$ were reported by Kojima and Fujita.³¹ There is good agreement in the case of the (*lel*₃) isomer, confirming that this corresponds to the first eluted diastereomer, but agreement is not good with the (*ob*₃) isomer. Circular dichroism spectra for these complexes are somewhat anion- and, hence, concentration-dependent but this does not provide a satisfactory explanation for the discrepancy between the two studies. However, the present data are more in line with the corresponding data for the (*ob*₃) isomers of $[\text{Co}(\pm\text{-chxn})_3]^{3+}$.³⁰

(b) Reaction Products and Stoichiometries. In all the reactions studied, the stoichiometries can be represented by the simple expression



where N_6 represents the amine ligand system used. This indicates that aerial oxidation of the cobalt(II) complexes was prevented.

For the oxidations of $[\text{Co}(\pm\text{-chxn})_3]^{2+}$ and $[\text{Co}(\pm\text{-bn})_3]^{2+}$, the cobalt(III) complexes were separated into conformational diastereomers; the relative amounts of these diastereomers are presented in Table III. The isomer distributions bear little relation to the corresponding distributions in the syntheses of the complexes at higher temperatures in the presence of charcoal. In particular, there is an increased preference for the *lel*_{2ob} conformer at the expense of the *lel*₃ form.

These differences are not surprising since the product distribution reflects the isomer distribution of the cobalt(II) complexes and their relative reactivities. Calculations have shown⁴⁰ that these isomer distributions may vary between the two oxidation states of $[\text{Co}(\text{sep})]^{3+/2+}$. Clearly, detailed calculations in this area would be of some interest.

(c) The Mechanism of Electron Transfer. Reductions of $[\text{Co}(\text{edta})]^-$ by the cobalt(II) complexes examined in this study are rapid processes. Geselowitz and Taube report briefly⁵ on the rate of reduction of $[\text{Co}(\text{edta})]^-$ by $[\text{Co}(\text{en})_3]^{2+}$, where the second-order rate constant is $17 \text{ M}^{-1} \text{ s}^{-1}$ at 0.14 M ionic strength and 30 °C, with no evidence for a potential inner-sphere intermediate. Observations in this laboratory are in general agreement with this report. Under conditions of excess $[\text{Co}(\text{edta})]^-$ the reaction is complicated by the subsequent redox-catalyzed substitution⁴¹ of edta^{4-} by en to give $[\text{Co}(\text{en})_3]^{3+}$.

The kinetics of oxidation of $[\text{Co}(\pm\text{-bn})_3]^{2+}$ and $[\text{Co}(\pm\text{-chxn})_3]^{2+}$ present considerable experimental difficulties because of the number of isomeric forms involved, so they were not examined. An attempt was made to examine the rate of reduction of $[\text{Co}(\text{edta})]^-$ by $[\text{Co}(\text{sep})]^{2+}$, a reaction that must be outer-sphere in nature. The reaction is very fast, limiting data collection, but a second-order rate constant of $(6 \pm 2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and 0.10 M ionic strength is estimated.

It is considered likely that all the electron-transfer reactions between $[\text{Co}(\text{edta})]^-$ and the cobalt(II) amine complexes are

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Table II. Circular Dichroism and UV-Visible Spectroscopic Data^a

complex	isomer	λ , nm	ϵ , M ⁻¹ cm ⁻¹	λ , nm	$\Delta\epsilon$, M ⁻¹ cm ⁻¹
[Δ -Co(en) ₃](ClO ₄) ₃ (6 × 10 ⁻³ M)		467	88 (84)	485	+1.90 (+1.89)
		338	81	427	-0.13 (-0.17)
				345	+0.22 (+0.25)
[Δ -Co(sen)]Cl ₃ (5 × 10 ⁻³ M)		467	113	496 (502)	+0.43 (+0.42)
		340	103	447 (450)	-1.04 (-1.05)
				340 (340)	+0.13 (+0.13)
				460 (465) ^b	+2.72 (+2.78) ^b
[Δ -Co(sep)]Cl ₃ (5 × 10 ⁻³ M) (2 × 10 ⁻³ M)		474	109	353	+1.17
		343	116	460 (461) ^c	+2.33 (+2.37) ^c
				353 (352) ^c	+1.07 (+0.98) ^c
[Δ -Co((±)-bn) ₃]Cl ₃ (5 × 10 ⁻⁴ M)	<i>le</i> ₃	463 (465)	100 (100)	483 (490)	+2.70 (+2.73)
		337.5 (337.5)	94.5 (93)	433 (433)	-0.54 (-0.56)
		210 (210)	2.64 (2.82) × 10 ⁴	342 (345)	+0.31 (+0.32)
				215 (214)	-43 (-41)
				481	+2.57
				410	-0.027
	<i>le</i> ₂ <i>ob</i>	464	98	350	+0.25
		337	92	215	-38.1
		212	2.73 × 10 ⁴	474	+2.68
				384	+0.037
				359	+0.13
				322	+0.087
	<i>le</i> <i>ob</i> ₂	464	98	214	-29.3
		338	96	468 (470)	+2.42 (+3.47)
		212	2.83 × 10 ⁴	(370)	(+0.068)
				340 (342)	-0.081 (-0.94)
				(312)	(+0.29)
				(244)	(+0.94)
	<i>ob</i> ₃	464 (465)	98 (98)	213 (212)	-23.5 (-25.5)
		337 (338)	93 (91)	(499)	(+2.45)
		212 (213)	2.88 (3.09) × 10 ⁴	(444)	(-0.77)
				(348)	(+0.20)
				(227)	(-48)
				(495)	(+2.76)
[Δ -Co((±)-chxn) ₃]Cl ₃	<i>le</i> ₃	(472)	(101)	(444)	(-0.77)
		(342)	(94)	(348)	(+0.20)
		(223)	(2.79 × 10 ⁴)	(227)	(-48)
				(495)	(+2.76)
	<i>le</i> ₂ <i>ob</i>	(473)	(102)	(418)	(0.0)
		(342)	(98)	(355)	(+0.22)
		(224)	(2.89 × 10 ⁴)	(229)	(-38)
				(488)	(+3.51)
	<i>le</i> <i>ob</i> ₂	(473)	(102)	(391)	(+0.05)
		(342)	(98)	(361)	(+0.14)
		(225)	(2.89 × 10 ⁴)	(229)	(-28)
				(479)	(+4.45)
<i>ob</i> ₃	(473)	(101)	(344)	(-0.03)	
	(343)	(93)	(317)	(+0.03)	
	(225)	(2.95 × 10 ⁴)	(295)	(+0.01)	
			(266)	(+0.1)	
Na[Δ -Co(edta)]·4H ₂ O	535	331	(228)	(-17)	
	381	222	575 (585)	-1.79 (-1.85)	
			500	+0.83	
			412	-0.30	
			359	-0.37	

^aNumbers in parentheses are taken from the following literature sources. [Δ -Co(en)₃]³⁺: McCaffery, A. J.; Mason, S. F.; Ballard, R. E. *J. Chem. Soc.* **1965**, 2883-2892. [Δ -Co(sen)]³⁺: ref 24. [Δ -Co(sep)]³⁺: footnote b or c. [Δ -Co((±)-bn)₃]³⁺: ref 31. [Co((±)-chxn)₃]³⁺: ref 30. [Δ -Co(edta)]⁻: Gillard, R. D.; Mitchell, P. F.; Weick, C. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1635-1636. ^bSakaguchi, U.; Tsuge, A.; Yoneda, H. *Inorg. Chem.* **1983**, *22*, 3745-3749. ^cReference 34.

Table III. Isomer Distributions in the Oxidation of [Co((±)-bn)₃]²⁺ and [Co((±)-chxn)₃]²⁺ by [Co(edta)]⁻

isomer	% product			
	[Co-((±)bn) ₃] ³⁺		[Co-((±)chxn) ₃] ³⁺	
	a	b	c	d
<i>le</i> ₃	32	31	37	36
<i>le</i> ₂ <i>ob</i>	41	41	36	37
<i>le</i> <i>ob</i> ₂	22	} 28	19	} 27
<i>ob</i> ₃	6		8	

^aClO₄⁻ media; total recovery >98%. ^bNO₃⁻ media; total recovery 98%. ^cNO₃⁻ media; total recovery 98%. ^dCl⁻/NO₃⁻ media; total recovery 97%.

outer-sphere in nature. However, it should be noted that the measured rate constants for both [Co(en)₃]²⁺ and [Co(sep)]²⁺ reactions are somewhat higher (ca. ×30) than predicted by calculation using Marcus theory and reported reduction poten-

tial^{34,42,43} and self-exchange rate data^{34,44,45} for the complexes. Little credence can be put on the calculated rate constants since the self-exchange rate for [Co(edta)]⁻²⁻ is not reliably known, and it may be that the value should be revised. An alternative explanation for the discrepancy is that there is additional precursor complex stabilization in the cross-reactions over what is expected purely on electrostatic grounds. In the light of the significant stereoselectivities detected in these reactions, an explanation involving hydrogen bonding in the electron-transfer-precursor complex is plausible.

(d) Ion-Pairing Stereoselectivity. In an effort to obtain information on the stereoselectivity of the precursor complex formed between [Co(edta)]⁻ and [Co(en)₃]²⁺, ion-pairing stereoselectivity

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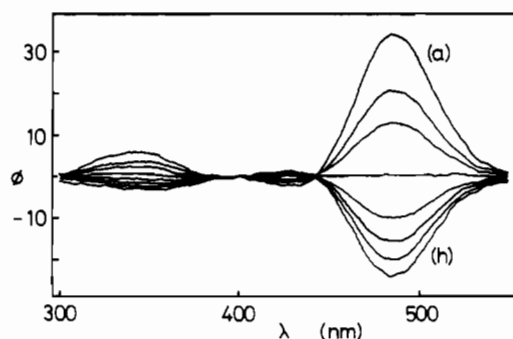


Figure 1. Circular dichroism spectra of solutions of $[\text{Co}(\text{en})_3]^{3+}$ removed from a cation-exchange column after elution by $[\Delta-(+)\text{-Co}(\text{edta})]^-$. The ellipticity, ϕ , is in millidegrees, and the spectra have been normalized such that the absorbance of each solution at 467 nm is unity. The fastest eluted fraction is denoted (a) while the slowest fraction is denoted (h).

between $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{en})_3]^{3+}$ was investigated. The sequence of circular dichroism spectra presented in Figure 1 illustrates the partial resolution of $[\text{Co}(\text{en})_3]^{3+}$ by the eluent $[\Delta\text{-Co}(\text{edta})]^-$ in a cation-exchange chromatography experiment. The mobility of the cation is determined in part by the strength of ion pairing within the mobile phase. Hence, the isomer that is eluted faster forms a stronger ion pair with $[\Delta\text{-Co}(\text{edta})]^-$ than does its enantiomer. The first eluted isomer is $[\Delta\text{-Co}(\text{en})_3]^{3+}$, indicating that the preferred ion pair is $[\Delta\text{-Co}(\text{en})_3]^{3+}$, $[\Delta\text{-Co}(\text{edta})]^-$.

In a related experiment, partial resolution of $[\text{Co}(\text{edta})]^-$ was obtained on anion-exchange resin with $[\Delta\text{-Co}(\text{en})_3]^{3+}$ as eluent, and the first eluted isomer was $[\Delta\text{-Co}(\text{edta})]^-$. Again, this is consistent with a preferred $\Delta\Delta$ ion pair.

These results are in agreement with those of Yoneda and co-workers,¹¹ who examined the partial resolution of $[\text{Co}(\text{edta})]^-$ on a cation-exchange column saturated with $[\Delta\text{-Co}(\text{en})_3]^{3+}$ and measured retention volumes of $[\Delta\text{-Co}(\text{edta})]^-$ and $[\Delta\text{-Co}(\text{edta})]^-$ on an anionic column with $[\Delta\text{-Co}(\text{en})_3]^{3+}$ as eluent. One problem of chromatographic ion-pairing investigations is the relative stereoselectivities of the bound and mobile phases.⁴⁶ However, the fact that all four experiments give the same result, that the preferred ion pair between $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{en})_3]^{3+}$ is $\Delta\Delta$, suggests that this indeed reflects the mobile phase.

There is a report⁴⁷ of the resolution by fractional crystallization of $[\text{Co}(\text{edta})]^-$ using $[\Delta\text{-Co}(\text{en})_3]^{3+}$ in which the less soluble diastereomeric pair also involves a $\Delta\Delta$ interaction. While this gives little indication of the preferred ion pair in solution, clearly structural analysis of the salt $[\Delta\text{-Co}(\text{en})_3][\Delta\text{-Co}(\text{edta})]_2\text{Cl}\cdot 4\text{H}_2\text{O}$ and its diastereomer would give valuable information on the mode of interaction between the complex ions. Unfortunately, crystals suitable for X-ray diffraction studies have not yet been obtained.

Of considerable relevance to the theme of this paper are ion-pair stereoselectivity data obtained by Yoneda and co-workers¹¹ on the interaction of $[\text{Co}(\text{edta})]^-$ with $[\text{Co}(\text{sep})]^{3+}$ and $[\text{Co}(\text{-chxn})_3\text{-lel}_3]^{3+}$. In the former case a $\Delta\Delta$ preference is found, as with $[\text{Co}(\text{en})_3]^{3+}$, while for the latter the preferred ion pair is $\Delta\Delta$. It seems clear that the differences between these two systems provide an important test of the role of the precursor ion pair in determining electron-transfer stereoselectivity.

(e) Electron-Transfer Stereoselectivity. The stereoselectivity results for reactions run under a variety of conditions are summarized in Table IV. They vary from 25% $\Delta\Delta$ for the reaction of $[\Delta\text{-Co}(\text{edta})]^-$ with $[\text{Co}(\text{-chxn})_3\text{-lel}_3]^{2+}$ to 25% $\Delta\Delta$ for the corresponding reaction with $[\text{Co}(\text{-bn})_3\text{-ob}_3]^{2+}$. There are a number of well-defined trends in the data.

It is worthwhile examining some implications of the stereoselectivity data in terms of a simplified outer-sphere electron-transfer model. In Table V, selected stereoselectivities are expressed in terms of rate ratios for reactions of the diastereomeric pairs and

corresponding differences in the free energies of activation. The effects observed in this study are modest, less than 300 cal mol^{-1} .

The rate constant for an outer-sphere electron-transfer reaction, k , can be expressed^{48,49} in terms of a precursor formation constant, K_0 (eq 1), and an electron-transfer rate constant, k_{et} (eq 2), as shown in eq 4, where (r) denotes that both parameters are de-

$$k = K_0(r) k_{\text{et}}(r) \quad (4)$$

pendent on the distance between the reacting metal centers. Stereoselectivity will result if the preferred reaction pair interacts at some distance, r , but the diastereomeric pair experiences some steric constraint, limiting effective interaction to a longer distance $r + \Delta r$. The precursor formation constant may be estimated with use of eq 5, where δr is the spread of distances over which the

$$K_0(r) = \left(\frac{4\pi N r^2 \delta r}{1000} \right) \exp\left(\frac{-\omega(r)}{RT} \right) \quad (5)$$

reaction takes place and $\omega(r)$ is a measure of the work involved in bringing the reactants together. For a purely electrostatic interaction, $\omega(r)$ is estimated by eq 6, where D_s is the static

$$\omega(r) = \frac{z_A z_B e^2}{D_s r (1 + \beta r)} \quad (6)$$

dielectric constant for the medium, $\beta = (8\pi N e^2 / 1000 D_s k T)^{1/2}$, z_A and z_B are the charges on the two reactants, and r is the sum of their radii.

The electron-transfer step is represented by eq 7, where $\nu_n(r)$ is the effective nuclear frequency, $\kappa_n(r)$ the nuclear factor, and $\kappa_e(r)$ the electronic factor. The nuclear terms can be considered

$$k_{\text{et}}(r) = \nu_n(r) \kappa_n(r) \kappa_e(r) \quad (7)$$

as the sum of internal components describing the inner-sphere reorganization of the complexes, unlikely to be affected by changing the relative configuration of the reaction partners, and external components describing solvent reorganization. In strongly hydrogen-bonding systems where solvent relaxation is affected, this component may be a significant source of stereoselectivity; it can be represented by eq 8, where Δe is the charge transferred

$$\Delta G_{\text{out}}^* = \frac{(\Delta e)^2}{4} \left(\frac{1}{2a_A} + \frac{1}{2a_B} - \frac{1}{r} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \quad (8)$$

between the reactants, a_A and a_B are the radii of the reactants, and D_{op} is the optical dielectric constant (equal to the square of the refractive index). Another source of stereoselectivity in the electron-transfer rate is the electronic factor in the nonadiabatic regime, which shows a strong distance dependence given in eq 9, where β' is $\sim 1.2 \text{ \AA}^{-1}$.

$$\kappa_e = \kappa_e^0 \exp[-\beta'(\Delta r)] \quad (9)$$

Some idea of the magnitude of stereoselectivity predicted by theory for the reaction of $[\text{Co}(\text{edta})]^-$ with $[\text{Co}(\text{en})_3]^{2+}$ at 0.1 M ionic strength is obtained by using a value of $r = 5 \text{ \AA}$ (the sum of a_A and a_B , which are both taken to be 2.5 \AA) for the preferred interaction. Sample calculations are presented in Table VI. It can be seen that a relatively small difference in the effective reaction distance, less than 0.03 \AA , can explain a stereoselectivity of 10% and a stereoselectivity of 25% requires a difference in effective reaction distance in excess of 0.2 \AA . A further point of interest is that the contribution from the electron-transfer step to the difference in activation free energy is larger, by at least 1 order of magnitude, than the contribution from the precursor formation step although, in this instance, the contributions are in the same sense. At small differences in separation the stereoselectivity in the electron-transfer term is dominated by solvent reorganization as the electron moves from one metal center to the other.

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Table IV. Electron-Transfer Stereoselectivity in the Oxidation of Cobalt(II) Amine Complexes by $[\text{Co}(\text{edta})]^-$

$10^4[[\Delta\text{-Co}(\text{edta})]^-]$, M	$10^3[\text{Co}(\text{II})]$, M	$10^2[\text{ligand}]$, M	<i>I</i> , M (medium)	isomer	selectivity, %
Ligand = en					
2.5	5.0	5.0	0.015 (ClO_4^-)		$8 \pm 1 \Delta$
2.5	5.0	5.0	0.013		$10 \pm 2 \Delta^a$
2.7	5.0	5.0	1.0 (ClO_4^-)		$9 \pm 1 \Delta$
18.4	18.0	18.0	1.0 (ClO_4^-)		$9.3 \pm 0.5 \Delta$
18.4	18.0	18.0	1.0 (ClO_4^-)		$9.2 \pm 0.5 \Delta$
18.4	18.0	18.0	0.5 (ClO_4^-)		$11.1 \pm 0.5 \Delta$
18.4	18.0	18.0	0.2 (ClO_4^-)		$11.5 \pm 0.5 \Delta$
18.4	18.0	18.0	0.057 (ClO_4^-)		$11.5 \pm 0.5 \Delta$
18.4	18.0	18.0	0.057 (ClO_4^-)		$12.8 \pm 0.5 \Delta^b$
18.4	18.0	18.0	1.0 (Cl^-)		$10.8 \pm 0.5 \Delta$
18.4	18.0	18.0	1.0 (Cl^-)		$11.1 \pm 0.5 \Delta$
18.4	18.0	18.0	1.0 (Br^-)		$10.6 \pm 0.5 \Delta$
18.4	18.0	18.0	1.0 (Br^-)		$10.6 \pm 0.5 \Delta$
18.4	18.0	18.0	1.0 (I^-)		$11.3 \pm 0.5 \Delta$
18.4	18.0	18.0	1.0 (OAc^-)		$10.0 \pm 0.5 \Delta$
18.4	18.0	18.0	1.0 (PO_4^{3-})		$0.6 \pm 0.1 \Delta$
Ligand = (\pm)-bn					
17.0	16.7	16.3	0.052 (ClO_4^-)	<i>lel</i> ₃	$14.2 \pm 0.2 \Delta$
				<i>lel</i> ₂ <i>ob</i>	$0.15 \pm 0.1 \Delta$
				<i>lel ob</i> ₂	$12.5 \pm 0.5 \Delta$
				<i>ob</i> ₃	$25 \pm 1 \Delta$
17.0	16.7	16.3	0.052 (NO_3^-)	<i>lel</i> ₃	$15.3 \pm 0.5 \Delta$
				<i>lel</i> ₂ <i>ob</i>	$0.3 \pm 0.1 \Delta$
				<i>lel ob</i> ₂	$12.5 \pm 0.5 \Delta$
				<i>ob</i> ₃	$25 \pm 1 \Delta$
Ligand = (\pm)-chxn					
16.7	16.7	16.7	0.052 (NO_3^-)	<i>lel</i> ₃	$24 \pm 2 \Delta$
				<i>lel</i> ₂ <i>ob</i>	$5 \pm 1 \Delta$
				<i>lel ob</i> ₂	$7 \pm 1 \Delta$
				<i>ob</i> ₃	$16 \pm 1 \Delta$
19.0	19.0	19.0	0.059 ($\text{Cl}^-/\text{NO}_3^-$)	<i>lel</i> ₃	$25 \pm 2 \Delta$
				<i>lel</i> ₂ <i>ob</i>	$5 \pm 1 \Delta$
				<i>lel ob</i> ₂	} $\sim 11 \pm 1 \Delta$
				<i>ob</i> ₃	
Ligand = sen					
20.0	18.0	2.30	0.056 (ClO_4^-)		$9.5 \pm 0.5 \Delta$
20.9	18.3	2.34	0.057 (ClO_4^-)		$10.0 \pm 0.5 \Delta$
$10^3[[\text{Co}(\text{edta})]^-]$, M	$10^4[[\Lambda\text{-Co}(\text{sep})]^{2+}]$, M	<i>I</i> , M (medium); pH		selectivity, %	
1.00	2.51	0.10 (triflate); 5.0		$14.7 \pm 0.5 \Delta$	
1.00	2.51	0.11 (triflate); 5.0		$14.5 \pm 0.5 \Delta^c$	
1.20	2.04	0.10 (triflate); 4.95		$15.4 \pm 0.5 \Delta$	
1.43	1.46	0.10 (triflate); 4.90		$16.4 \pm 0.5 \Delta$	
extrapolated to large excess oxidant				17.6Δ	
1.00	2.50	0.10 (ClO_4^-); 5.8		$13.6 \pm 0.5 \Delta$	
1.20	2.00	0.10 (ClO_4^-); 5.4		$14.7 \pm 0.5 \Delta$	
1.42	1.42	0.10 (ClO_4^-); 5.0		$15.3 \pm 0.5 \Delta$	
extrapolated to large excess oxidant				16.5Δ	

^aReference 5. ^b0 °C. ^c 10^{-2} M acetate.

Table V. Selected Stereoselectivities Expressed as Relative Rates and Differences in Free Energies of Activation

stereoselectivity, %	rel rate ratio	$\Delta\Delta G^\ddagger$, cal mol ⁻¹
5	1.11	62
10	1.22	118
15	1.35	178
20	1.50	240
25	1.67	304

This model is crude, but it does identify those interactions that may be important in determining stereoselectivity. However, in the present instance, precursor ion-pair formation appears to have a much greater role than theory suggests since the electron-transfer stereoselectivities parallel the available data for ion-pairing stereoselectivity. Thus, the preferred interaction of $[\Delta\text{-Co}(\text{edta})]^-$ with $[\text{Co}((\pm)\text{-chxn})_3\text{-lel}_3]^{2+}$ is $\Delta\Delta$ and with $[\text{Co}(\text{sep})]^{2+}$ it is $\Delta\Delta$. This clearly suggests that precursor ion-pair structure is important, though, as discussed above, not necessarily exclusively responsible for determining electron-transfer stereoselectivity.

Pispisa and co-workers have examined⁵⁰ the roles of precursor formation and electron-transfer steps in the outer-sphere oxidation of organic substrates by chiral iron(III) systems. They find that electron-transfer stereoselectivity dominates, but in all cases examined, both precursor formation and ion-pairing steps have complementary stereoselectivities, a reflection of the fact that tighter precursor binding promotes closer approach of the reaction centers.

The importance of ion-pair structure in determining the stereoselectivity of the interactions of $[\text{Co}(\text{edta})]^-$ may be due to hydrogen bonding between the complexes, likely to be of considerable importance since hydrogen bonds are strongly directional. Hydrogen bonds preferentially stabilize certain precursor complex structures, thereby enhancing stereoselectivity without recourse to substantial differences in reaction distance. However, the interactions involved are very complex. One example for which crystallographic details are available⁵¹ is the interaction of $[\Delta\text{-}$

Table VI. Energetic Contributions to Stereoselectivity as a Function of Effective Distance Differences for Diastereomeric Pairs

$\Delta r,^a$ Å	$\Delta\Delta G_{0,}^b$ cal mol ⁻¹	$\Delta\Delta G_{out,}^{c,e}$ cal mol ⁻¹	$\Delta\Delta G_e^{d,f}$ cal mol ⁻¹	$\Delta\Delta G^{g,h}$ cal mol ⁻¹
0.01	0.6	7	18	26
0.02	1.3	14	36	51
0.03	1.9	21	54	77
0.04	2.5	25	71	98
0.05	3	36	89	128
0.10	6	71	176	253
0.20	11	142	346	499
0.30	15	213	509	737

^aEffective distance of approach of the preferred pair is 5 Å and of the nonpreferred pair is 5 + Δr Å. ^bDifference in the free energy for formation of the preferred precursor complex at 5 Å and the diastereomer at 5 + Δr Å, calculated by using eq 5. ^cDifference in the activation free energy for solvent reorganization during electron transfer at distances 5 Å and 5 + Δr Å, calculated by using eq 8. ^dDifference in the activation free energy for electron transfer at distances 5 Å and 5 + Δr Å, calculated by using eq 9. ^eOverall difference in activation free energy (sum of b + c + d).

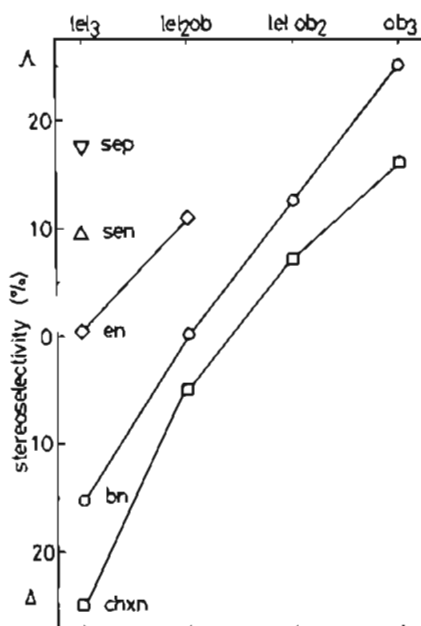


Figure 2. Stereoselectivity as a function of chelate ring conformation for the oxidations of $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}(\pm)\text{-bn}]_3^{2+}$, $[\text{Co}(\pm)\text{-chxn}]_3^{2+}$, $[\text{Co}(\text{sen})]^{2+}$, and $[\text{Co}(\text{sep})]^{2+}$ by $[\Delta\text{-Co}(\text{edta})]^-$. For the last two reactions, a lel_3 conformation is assumed.

$\text{Co}((-)\text{-}1,2\text{-diaminopropane})_3]^{3+}$ with $[\Delta\text{-Cr}(\text{malonate})_3]^{3-}$, in which the origin of the stereoselectivity is in an extended network of hydrogen bonds linking chains of the alternating anions and cations. Direct interactions between the complexes by hydrogen bonds on the C_3 faces are not thought to have a high stereoselectivity. Interestingly, the ion pair $[\Delta\text{-Co}(\text{en})_3]^{3+}$, $[\Delta\text{-Cr}(\text{malonate})_3]^{3-}$ is preferred in solution.¹¹

(f) Trends in Electron-Transfer Stereoselectivity. The interpretation of stereoselectivity data is a complex process, still in its infancy. It seems clear that both direct interactions between complexes and indirect interactions involving the solvent play a role.⁵ As outlined in the Introduction, a useful framework for discussion is that the chiral discrimination arises from the different helicities described by the chelate rings when viewed along the C_2 and C_3 axes. It seems reasonable¹¹ that the axis employed by $[\Delta\text{-Co}(\text{edta})]^-$ in its approach to the amine complex is the pseudo- C_3 axis encircled by three carboxylate groups, and this important assumption will be maintained throughout the remaining discussion.

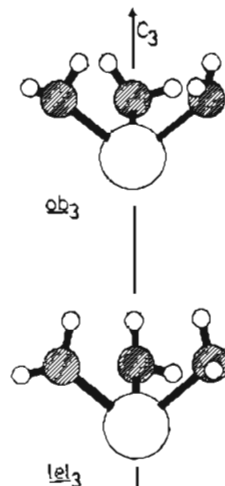


Figure 3. the Co-N-H framework for C_3 faces of (a) $[\Delta\text{-Co}((-)\text{-chxn})_3\text{-ob}_3]^{3+}$ and (b) $[\Delta\text{-Co}((+)\text{-chxn})_3\text{-lel}_3]^{3+}$ showing the orientation of the N-H bonds to the C_3 axes of the complex ions.

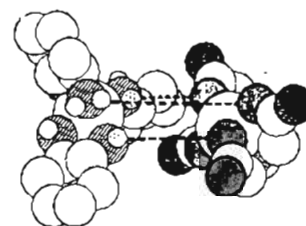


Figure 4. Space-filling representation of the dominant hydrogen-bonding interaction between the pseudo- C_3 carboxylate face of $[\Delta\text{-Co}(\text{edta})]^-$ and the C_3 amine face of $[\Delta\text{-Co}((-)\text{-chxn})_3\text{-lel}_3]^{2+}$.

Perhaps the most important trend is shown in the reactions of the conformationally rigid complexes $[\text{Co}(\pm)\text{-chxn}]_3^{2+}$ and $[\text{Co}(\pm)\text{-bn}]_3^{2+}$. In both these cases the stereoselectivity shows a trend from $\Delta\Delta$ to $\Delta\Delta$ as the number of *ob* conformers increases (Figure 2). A simple explanation for this trend, in keeping with previous work on ion-pairing stereoselectivity,¹¹ is that there is a change in the mode of approach of the $[\Delta\text{-Co}(\text{edta})]^-$ from the C_3 axis of the reductant (C_3C_3),⁵² leading to a $\Delta\Delta$ interaction in the case of the lel_3 isomer, to the C_2 axis of the reductant (C_3C_2),⁵² leading to a $\Delta\Delta$ interaction in the case of the ob_3 isomer. However, it is also noteworthy that the stereoselectivity with $[\text{Co}(\pm)\text{-chxn}]_3^{2+}$ shows a pronounced Δ bias when compared with that for $[\text{Co}(\pm)\text{-bn}]_3^{2+}$ and, further, that this bias is almost independent of chelate ring conformation. If the stereoselectivity were determined by a change in the axis of approach of $[\Delta\text{-Co}(\text{edta})]^-$ to the cobalt amine complex, there should be a marked difference in the stereoselectivities shown by $[\text{Co}(\pm)\text{-chxn}]_3^{2+}$ and $[\text{Co}(\pm)\text{-bn}]_3^{2+}$ for approach along the C_2 axes, where steric effects of the cyclohexane rings are manifest, while for approach along the C_3 axes very similar stereoselectivities should result. This is not observed.

A modified explanation is more consistent with the results. The overall stereoselectivity is determined by a balance of C_3C_3 ($\Delta\Delta$) and C_3C_2 ($\Delta\Delta$) interactions. The C_3C_2 interaction is little affected by changes in ring conformation, but the C_3C_3 interaction is markedly reduced on going from lel_3 to ob_3 .

These effects may be understood by consideration of the forces involved in formation of the precursor complexes. Besides electrostatic attraction, there is strong stabilization of the precursor by hydrogen bonding, evident from the rate enhancement of the cross-reaction of $[\text{Co}(\text{edta})]^-$ with $[\text{Co}(\text{en})_3]^{2+}$ and $[\text{Co}(\text{sep})]^{2+}$. Hydrogen-bonding forces are strongly directional, and examination of the geometric arrangement around the C_2 and C_3 axes of the

(51) Butler, K. R.; Snow, M. R. *J. Chem. Soc., Dalton Trans.* 1976, 251-258.

(52) The designations C_3C_3 and C_3C_2 indicate interactions with the C_3 face of $[\text{Co}(\text{edta})]^-$ and the C_3 and C_2 faces, respectively, of the cobalt amine complexes.

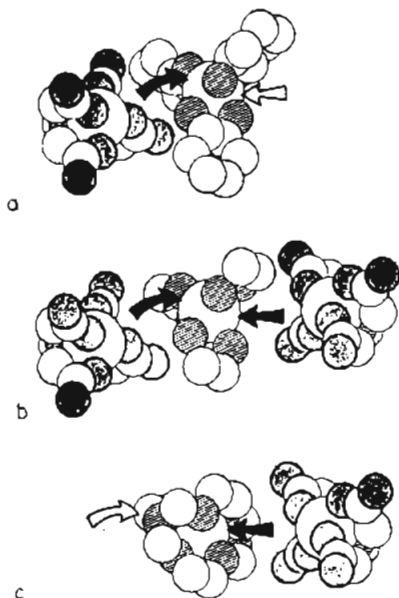


Figure 5. Space-filling representations of the effect on the interaction with $[\text{Co}(\text{edta})]^-$ of changing steric hindrance from the C_2 axis to the C_3 axis of the cobalt amine complex: (a) $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$; (b) $[\text{Co}(\text{en})_3]^{2+}$; (c) $[\text{Co}(\text{sep})\text{-lel}_3]^{2+}$. The dark arrows represent prominent interactions; the light arrows, interactions that have been diminished by the steric hindrance.⁶¹

lel_3 ⁵³ and ob_3 ⁵⁴ isomers of $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ (Figure 3) reveals changes in the positions of the amine hydrogens. These changes are most marked along the C_3 axis, where in the lel_3 isomer amine protons on each coordinated nitrogen lie with the N-H bond almost parallel to the C_3 axis, readily available for a hydrogen-bonding interaction with the pseudo- C_3 carboxylate face of $[\Delta\text{-Co}(\text{edta})]^-$ (Figure 4). In the ob_3 isomer, the N-H bonds are oblique to the C_3 axis, less accessible for hydrogen bonding. Changes along the C_2 axis are much less dramatic. The steric effect of the cyclohexane rings of $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ compared with that of the methyl groups of $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ for approach along the C_2 axis corresponds to a free energy of activation between 60 and 120 cal mol⁻¹. Structural details of $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ are not available, but some increase in the angle subtended along this axis is anticipated with the freely rotating methyl groups when compared with the more rigid cyclohexane ring structure.

The highest stereoselectivities are achieved for the most rigid systems: $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$, $[\text{Co}((\pm)\text{-bn})_3]^{2+}$, and $[\text{Co}(\text{sep})]^{2+}$. The stereoselectivity value for the reaction of $[\text{Co}(\text{sep})]^{2+}$ supports the contention that $\Delta\Delta$ stereoselectivity takes place along the C_2 axis. In this case, even though calculations⁴⁰ suggest that a lel_3 or lel_2ob conformation is favored in $[\text{Co}(\text{sep})]^{2+}$, a strong hydrogen-bonded interaction along the C_3 axis is blocked; hence, the $\Delta\Delta$ contribution is diminished.

Conformationally labile complexes, $[\text{Co}(\text{en})_3]^{2+}$ and $[\text{Co}(\text{sen})]^{2+}$, show reduced stereoselectivities. The single C_3 cap of $[\text{Co}(\text{sen})]^{2+}$ does not restrict the C_3 interaction as in $[\text{Co}(\text{sep})]^{2+}$. However, the $[\text{Co}(\text{sen})]^{2+}$ complex also exists primarily as a lel_3 conformer²⁴ and a similar conformation might be expected for $[\text{Co}(\text{sen})]^{2+}$ so that the available C_3 axis is well set up for a strong C_3C_3 interaction with $[\text{Co}(\text{edta})]^-$. Tris(1,2-diaminoethane) complexes, especially with larger metal ions such as cobalt(II), are expected to exist mainly in the lel_2ob conformation⁵⁵ and it is interesting to compare the stereoselectivities of $[\text{Co}(\text{en})_3]^{2+}$ (11%

Δ) with the values for the lel_2ob conformations⁵⁶ of $[\text{Co}((\pm)\text{-bn})_3]^{2+}$ (0.15% Δ) and $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$ (5% Δ). These show a strong trend consistent with increased steric hindrance for approach of $[\Delta\text{-Co}(\text{edta})]^-$ along the C_2 axis, resulting in an increased C_3 ($\Delta\Delta$) component on going from the 1,2-diaminoethane to the 1,2-diaminocyclohexane complex.

Certain oxyanions, notably PO_4^{3-} , are known to modify tris-(1,2-diaminoethane) chelate ring conformation in solution, specifically inducing the lel_3 conformer.^{24,37,57} A brief investigation of the effects of different anions on stereoselectivity in the oxidation of $[\text{Co}(\text{en})_3]^{2+}$ by $[\Delta\text{-Co}(\text{edta})]^-$ was undertaken (Table III). In all but one instance the effects are minor, but for PO_4^{3-} there is a marked decrease in stereoselectivity from 11% Δ to 0.5% Δ , a pronounced Δ bias consistent with the change in conformation from lel_2ob to lel_3 . This allows comparisons to be made of the lel_3 isomers of all five complexes examined (Figure 2). The trend is from Δ to Δ as steric hindrance shifts from the C_2 axis to the C_3 axis of the cobalt(II) amine complex (Figure 5).

The effects of other anions are much smaller and more difficult to interpret. They can be significant as shown by the change in stereoselectivity for the reaction of $[\text{Co}((\pm)\text{-bn})_3\text{-lel}_2ob]^{2+}$ in ClO_4^- media ($\Delta\Delta$) and NO_3^- media ($\Delta\Delta$). In perchlorate media with $[\text{Co}(\text{en})_3]^{2+}$, an increase in ionic strength reduces stereoselectivity. This may be the result of weaker precursor complex formation or, more likely, the effect of the perchlorate ion in inducing a conformational change in a manner similar to that shown by phosphate ion. Added ions are known to affect the mechanism of electron transfer to cobalt(III) complexes,^{58,59} particularly where charge-transfer interactions are important.⁵⁹ However, such effects are unlikely in this instance.

To summarize then, the pattern of stereoselectivity for the cobalt amine complexes is determined by hydrogen bonding with $[\text{Co}(\text{edta})]^-$, which controls the relative proportion of the reaction taking place along the C_2 and C_3 axes of the reductant. Limiting values of the stereoselectivity along these axes are $>25\% \Delta\Delta$ and $>25\% \Delta\Delta$, respectively. These limiting stereoselectivities can be explained by a steric effect where interaction of the preferred ion pair is more than 0.2 Å closer than the less preferred diastereomer. However, such a situation seems rather unlikely, particularly for the C_3C_3 interaction. The preferred explanation at this stage is that subtle stereoselective differences in the hydrogen bonding direct both the nature and the magnitude of the stereoselectivity, but such effects are difficult to quantify.

(g) Conclusions. Significant stereoselectivities are detected in the oxidations of $[\text{Co}(\text{en})_3]^{2+}$, $[\text{Co}((\pm)\text{-bn})_3]^{2+}$, $[\text{Co}((\pm)\text{-chxn})_3]^{2+}$, $[\text{Co}(\text{sen})]^{2+}$, and $[\text{Co}(\text{sep})]^{2+}$ by $[\text{Co}(\text{edta})]^-$. These can be correlated with ion-pairing stereoselectivities for the corresponding cobalt(III) complexes, suggesting an important role for precursor complex structure but not necessarily implying that the electron-transfer step is devoid of stereoselectivity. Trends in the stereoselectivity with changes in cobalt(II) amine complex structure can be explained in terms of a balance between C_3 ($\Delta\Delta$) and C_2 ($\Delta\Delta$) interactions, which are affected by hydrogen-bonding and steric effects.

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