

protonate the leaving ligand and to prevent the reverse chelation reaction. Addition of base, i.e. deprotonation of the amine ligand, results in chelation and the formation of the sulfite complex. Aquation of the sulfite ligand in Pd(Et₄dien)SO₃ only occurs in strongly acidic medium and competes with the dechelation reaction. A detailed kinetic study of the various reaction steps has been completed and will be reported in a subsequent paper.²⁰

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Stereoselective Electron-Transfer Reactions of (Ethylenediaminetetraacetato)cobaltate(III), (Propylenediaminetetraacetato)cobaltate(III), and (1,2-Cyclohexanediaminetetraacetato)cobaltate(III) with Tris(ethylenediamine)cobalt(II)

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The stereoselectivities of the electron-transfer reactions of [Co(edta)]⁻, [Co(pdta)]⁻ (pdta = propylenediaminetetraacetate), and [Co(cdta)]⁻ (cdta = 1,2-cyclohexanediaminetetraacetate) with [Co(en)₃]²⁺ in aqueous solution and Me₂SO ([en] = 0.3 M, [Co(III)] = [Co(II)] = 0.01 M) have been determined by studying the optical purity of the [Co(en)₃]³⁺ product. In aqueous solution, the ratio of the rate constants of the Δ-Δ and Δ-Λ reactions, $k_{\Delta\Delta}/k_{\Delta\Lambda}$, is 1.2 for all three reactions, and in Me₂SO, the ratios are 2.0, 2.1, and 2.1, respectively. The rate constants of the reactions in aqueous solution ([en] = 1.6 M, [enHCl] = 0.10 M, μ = 1.00 M, 25 °C) were found to be 5.2, 5.2, and 5.0 M⁻¹ s⁻¹, respectively. For the [Co(edta)]⁻/[Co(en)₃]²⁺ reaction, the degree of stereoselectivity is strongly solvent dependent, with $k_{\Delta\Delta}/k_{\Delta\Lambda}$ increasing for the solvent series water < ethylene glycol < methanol \approx ethanol \approx formamide < ethylenediamine < DMF < Me₂SO < sulfolane. In addition, the effect of the ethylenediamine concentration on the rate constant of the [Co(edta)]⁻/[Co(en)₃]²⁺ reaction was studied. As the ethylenediamine concentration is raised from 0.085 to 0.985 M, the second-order rate constant rises from 4.66 to 5.79 M⁻¹ s⁻¹. To account for the similarity in reactivity of the three oxidants with [Co(en)₃]²⁺, a model is proposed for the orientation of the reactants in the activated complex in which the carboxylate groups of the oxidant face the reductant.

Introduction

Stereoselectivity effects offer opportunities for probing subtleties of the activated complexes of reactions. In the study of electron-transfer reactions of metal complexes, little is known about the relative orientation of the reactants in the transition state. Not even the intermetal distance in the transition state in simple electron-transfer reactions is known with certainty. The discovery of stereoselectivity in these reactions had provided a tool that may provide considerable information about their mechanistic details.

What appear to be well-established instances of stereoselective electron-transfer reactions are described in recent reports by Geselowitz and Taube^{1,2} on the reactions of [Co^{II}(en)₃]²⁺ with [Co^{III}(edta)]⁻ and of [Co^{II}(edta)]²⁻ with [Ru^{III}(bpy)₃]³⁺ and several other oxidants. Lappin et al.³ observed stereoselectivity in the reaction of a Ni^{IV} oxime complex with [Co(edta)]²⁻, and Creaser et al.⁴ noted the effect in the reaction of [Co^{II}(sephalchrate)]²⁺ with [Co^{III}(diamsarH₂)]⁵⁺. Stereoselectivity has also been reported for photochemical reactions in the quenching of excited-state [Ru(bpy)₃]²⁺ by [Co^{III}(acac)₃] found by Porter and Sparks⁵ and quenching by [Co(edta)]⁻ reported by Kaizu et al.⁶ Moreover, the opportunities for practical applications of this class of reactions is evident in the recent work of Barton and co-workers,⁷ which has revealed stereoselective binding and redox reactions of metal complexes with DNA.

The goal of the work reported here was to improve our understanding of the stereoselectivity of the [Co(en)₃]²⁺/[Co(edta)]⁻ reaction. We report the results of a study of the solvent dependence of the stereoselectivity of this reaction and the effects observed when [Co(pdta)]⁻ (pdta = propylenediaminetetraacetate) and [Co(cdta)]⁻ (cdta = 1,2-cyclohexanediaminetetraacetate) are

substituted for [Co(edta)]⁻. Additionally, kinetic data are presented for the reactions.

Experimental Section

Preparation of Materials. Reagents. Commercial analytical grade reagents were used unless otherwise specified. Ethylenediamine was distilled over sodium.

Co(O₃SCF₃)₂. Cobalt trifluoromethanesulfonate hexahydrate was prepared by neutralizing CoCO₃ with aqueous CF₃SO₃H and evaporating to dryness. The residue was converted to the anhydrous form by drying it in vacuo at 110 °C.

(+)₅₈₉ and (-)₅₈₉-*cis*-[Co(en)₂(NO₂)₂]Br. *cis*-[Co(en)₂(NO₂)₂]NO₂ was prepared from [Co(en)₂(CO₃)]Cl and resolved with Na₂[Sb₂(+)-tart]₂·2H₂O, and the enantiomers were crystallized as the bromide salts by using the method of Dwyer and Garvan.⁸ Specific rotation data for the less soluble diastereoisomer, (-)₅₈₉-*cis*-[Co(en)₂(NO₂)₂][Sb₂(+)-tart]₂, and the (+)₅₈₉ and (-)₅₈₉ bromide salts of the complex (all 0.3% in water) are given in Table I.

(-)₅₄₆ and (+)₅₄₆-K[Co(edta)]·2H₂O. These complexes were prepared and resolved according to literature methods.^{9,10} Specific rotation data

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Table I. Specific Rotation Data for Prepared Complexes

complex	[α]				
	365 nm	436 nm	546 nm	578 nm	589 nm
(-) ₅₈₉ - <i>cis</i> -[Co(en) ₂ (NO ₂) ₂][Sb ₂ (+)-tart] ₂ ·2H ₂ O			27	52.2	55.5 ^a
(+) ₅₈₉ -[Co(en) ₂ (NO ₂) ₂]Br			111	53.3	42.2
(-) ₅₈₉ -[Co(en) ₂ (NO ₂) ₂]Br			-112	-53.5	-42.2 ^b
(-) ₅₄₆ -K[Co(edta)]·2H ₂ O			-330	-990 ^c	
(+) ₅₄₆ -K[Co(edta)]·2H ₂ O			330	980	
K[(-) ₅₄₆ -[Co(+)-pdta]]·2H ₂ O	625	601	-1050 ^d	-440	
K[(+) ₅₄₆ -[Co(-)-pdta]]·2H ₂ O	-632	-598	1025	450	
Ba[(-) ₅₄₆ -[Co(+)-cdta]] ₂ ·9H ₂ O	700	807	-1030	-970 ^e	-450
Ba[(+) ₅₄₆ -[Co(-)-cdta]] ₂ ·9H ₂ O	-723	-829		999	450

^aLiterature⁸ 47.4. ^bLiterature⁸ -44. ^cLiterature¹⁰ -1000. ^dLiterature¹¹ -1000. ^eLiterature¹² -900.

for the obtained compounds (0.02% in water) appear in Table I. The compounds (-)₅₄₆- and (+)₅₄₆-[NEt₄][Co(edta)] were prepared by eluting the corresponding potassium salts through a column of cation-exchange resin (Bio-Rad AG 50W-X2) in the tetraethylammonium form and carefully evaporating the eluate to dryness.

K[(-)₅₄₆-[Co(+)-pdta]]·2H₂O and K[(+)₅₄₆-[Co(-)-pdta]]·2H₂O. These complexes were prepared according to literature methods.¹¹ Specific rotation data for the obtained compounds (0.02% in water) appear in Table I.

K[(-)₅₄₆-[Co(+)-cdta]]·2H₂O and K[(+)₅₄₆-[Co(-)-cdta]]·2H₂O. These complexes were prepared according to literature methods.¹² Specific rotation data for the obtained compounds (0.02% in water) appear in Table I.

Stereoselectivity Studies. Solutions of [Co(en)₃]³⁺ were allowed to react with each of several chiral oxidants, and the optical purity of the [Co(en)₃]³⁺ product was determined. Studies were conducted with chiral [Co(edta)]⁻ as oxidant in water and selected organic solvents and with [Co(pdta)]⁻ and [Co(cdta)]⁻ as oxidants in water and Me₂SO. It should be noted that the net reaction of [Co(edta)]⁻ with [Co(en)₃]²⁺ occurs more rapidly than the electron self-exchange processes of either couple, preventing self-exchange racemization.¹ It should also be noted that the true oxidant is the six-coordinate [Co(edta)]⁻ species: the hydroxide-catalyzed ring opening of this species is too slow ($k \approx 0.2 \text{ M}^{-1} \text{ s}^{-1}$)¹³ to interfere here.

In a typical experiment, 10 mL of a solution of the oxidant and a Co(II) salt (Co(ClO₄)₂·6H₂O for reactions in water or Me₂SO and Co(O₃SCF₃)₂ for reactions in other solvents) and 10 mL of ethylenediamine solution (in the same solvent) were purged with deoxygenated argon in a Zwickel flask. After 15 min the solutions were mixed. When the distinct purple-to-yellow color change was complete (usually about 5 min), the reaction mixture was acidified by adding 20 mL of argon-purged 1 M HClO₄, and the solution was diluted with water to 0.2 L. This solution was sorbed onto a column (2.3 × 11 cm) of Bio-Rad AG50W-X1 cation-exchange resin in the H⁺ form. The column was washed with 100 mL of 1 M HCl and then 50 mL of 2 M HCl to remove mono- and dications. Finally the yellow [Co(en)₃]³⁺ complex was eluted with 3 M HCl and the eluate evaporated to dryness. The resulting residue was dissolved in 10 mL of water. The visible spectrum of the solution in a 1-cm cuvette was recorded on a Cary 15 spectrophotometer, and the optical rotation of the solution was measured at 365, 436, 546, 578, and 589 nm in a 1-dm cell at 20 °C by using a Perkin-Elmer 141 polarimeter.

Kinetic Studies. The effect of the ethylenediamine concentration on the rate constant of the [Co(edta)]⁻/[Co(en)₃]²⁺ reaction was studied at 25 °C and $\mu = 1.00 \text{ M}$. The conditions studied are shown in Table IV. A solution containing K[Co(edta)], CoCl₂·6H₂O, and Ca(NO₃)₂ and a solution containing an aqueous ethylenediamine/(2-aminoethyl)ammonium chloride buffer were purged with deoxygenated argon for 15 min and then mixed into a 1-cm quartz cuvette by using a hand-operated stopped-flow mixing device (described elsewhere¹⁴). The decrease in absorbance at 535 nm (a maximum for the oxidant complex) was monitored by using a Cary 118 spectrophotometer.

The oxidations of [Co(en)₃]²⁺ by [Co(edta)]⁻, [Co(pdta)]⁻, and [Co(edta)]⁻ were studied at 25 °C and $\mu = 1.00 \text{ M}$ (KCl). A solution containing the potassium salt of the oxidant and CoCl₂·6H₂O and a solution of an aqueous ethylenediamine/(2-aminoethyl)ammonium chloride buffer were purged with deoxygenated argon and then mixed as

Table II. Enantiomeric Excess in [Co(en)₃]³⁺ Product for Reaction of Chiral [Co(edta)]⁻ with [Co(en)₃]²⁺ in Various Solvents^a

solvent	enantiomeric excess		$k_{\Delta-\Lambda}/k_{\Lambda-\Delta}$
	% ^b	% ^c	
H ₂ O	9.0	8.9	1.2
(CH ₂ OH) ₂ ^d	13.0	12.7	1.3
HCONH ₂ ^d	17.3	18.3	1.4
EtOH	17.4	16.5	1.4
MeOH	16.9	17.3	1.4
HCON(CH ₃) ₂ ^d	27.9	31.4	1.9
Me ₂ SO	34.5	31.2	2.0
sulfolane	44.9	35.8	~2.3

^aInitial conditions: [K[Co(edta)]⁻] = [Co(O₃SCF₃)₂] = 0.01 M; [en] = 0.3 M. ^bOxidant: Δ -(+)₅₄₆-[Co(edta)]⁻. Product has excess of Λ -(+)-[Co(en)₃]³⁺. ^cOxidant: Λ -(-)₅₄₆-[Co(edta)]⁻. Product has excess of Δ -(-)-[Co(en)₃]³⁺. ^d[NEt₄][Co(edta)] used instead of K[Co(edta)]⁻.

described above. The conditions studied are shown in Table V. The decrease in absorbance at 535 nm was monitored by using a Cary 15 spectrophotometer.

Results

Absolute Configuration Assignments. To interpret the sense of stereoselectivity of these reactions, assignments of the absolute configuration of the reactants and products are needed. The compounds used here are designated as having either a Δ or Λ absolute configuration, according to the IUPAC definition.¹⁵ This is easily applied to [Co(en)₃]³⁺. For [Co(edta)]⁻ and related complexes, the common practice of denoting the $\Delta\Delta\Delta$ skew-chelate-pair designation as Δ (and the $\Lambda\Lambda\Lambda$ as Λ) will be used. We infer from the following literature reports that the complexes (-)₅₈₉-[Co(en)₃]³⁺, (+)₅₄₆-[Co(edta)]⁻, (+)₅₄₆-[Co((-)-pdta)]⁻, and (+)₅₄₆-[Co((-)-cdta)]⁻ are all of the Δ form.

(+)₅₈₉-[Co(en)₃]³⁺ has been assigned the Λ configuration from numerous X-ray crystal structure determinations^{16,17} and from the comparison of the ORD spectra¹⁸ of (-)₅₈₉-[Co(en)₃]³⁺ and (-)₅₈₉-[Co((-)-pn)]³⁺. The latter has been assigned the Δ configuration on the basis of a crystal structure¹⁹ and the known absolute configuration²⁰ of *R*-(-)-pn. It should be noted that, in our original report,¹ an incorrect absolute configuration assignment was used for [Co(en)₃]³⁺.

The absolute configurations of the complexes Δ -(+)₅₄₆-[Co(edta)]⁻ and Δ -(+)₅₄₆-[Co((-)-pdta)]⁻ have been determined by the anomalous dispersion method^{21,22} and inferred from the ste-

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Table III. Enantiomeric Excess of $[\text{Co}(\text{en})_3]^{3+}$ Product in Reactions of Chiral $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{pdta})]^-$, and $[\text{Co}(\text{cdta})]^-$ with $[\text{Co}(\text{en})_3]^{2+}$ in Water and Me_2SO ^a

oxidant	water			Me_2SO		
	% ^b	% ^c	$k_{\Delta\Delta}/k_{\Delta\Delta}$	% ^b	% ^c	$k_{\Delta\Delta}/k_{\Delta\Delta}$
$[\text{Co}(\text{edta})]^-$	9.0	8.9	1.2	34	31	2.0
$[\text{Co}(\text{pdta})]^-$	7.9	8.0	1.2	34	36	2.1
$[\text{Co}(\text{cdta})]^-$	7.9	7.3	1.2	36	34	2.1

^a Conditions: $[\text{Co}(\text{III})] = [\text{Co}(\text{II})] = 0.010 \text{ M}$; $[\text{en}] = 0.30 \text{ M}$; $\text{Co}(\text{II})$ supplied as $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. ^b Oxidant: $\Delta\text{-}(+)\text{546}$ isomer. Product has excess of $\Lambda\text{-}(+)\text{589}$ - $[\text{Co}(\text{en})_3]^{3+}$. ^c Oxidant: $\Lambda\text{-}(-)\text{546}$ isomer. Product has excess of $\Delta\text{-}(-)\text{589}$ - $[\text{Co}(\text{en})_3]^{3+}$.

Table IV. Effect of Ethylenediamine Concentration on the Rate Constant for Reaction of $[\text{Co}(\text{en})_3]^{2+}$ with $[\text{Co}(\text{edta})]^-$ at 25.0 °C, $\mu = 1.00 \text{ M}$ ^a

$[\text{en}]$, M ^b	$[\text{enH}^+]$, M	$[\text{en}]/[\text{enH}^+]$	$10^3 k_{\text{obsd}}$, ^c s^{-1}	k , ^d $\text{M}^{-1} \text{s}^{-1}$
0.085	0.0974	0.87	2.33	4.66
0.185	0.194	0.95	2.61	5.22
0.485	0.487	1.00	2.63	5.26
0.985	0.974	1.01	2.90	5.79

^a Initial concentration of $\text{K}[\text{Co}(\text{edta})]$ is 2.00 mM; $[\text{CoCl}_2] = 5.00 \text{ mM}$; $[\text{Ca}(\text{NO}_3)_2] = 3.3 \text{ mM}$. ^b Calculated initial free ethylenediamine concentration. ^c Average of three runs. ^d $k_{\text{obsd}}/5.00 \text{ mM}$.

reospecific binding of pdta to $\text{Co}(\text{III})$.¹⁸ The assignment has been extended to $\Delta\text{-}(+)\text{546}$ - $[\text{Co}(\text{cdta})]^-$ by comparison of ORD and CD spectra.^{23,24}

Stereoselectivity Studies. The enantiomeric excess in the $[\text{Co}(\text{en})_3]^{3+}$ product is calculated from the ratio of the rotation at 546 nm to the absorbance at 466 nm in the product solution. Values of $\epsilon_{466} = 83 \text{ M}^{-1} \text{ cm}^{-1}$ for the extinction coefficient²⁵ and $[\text{M}]_{546} = 1680^\circ$ for the molar rotation (based on a literature value²⁶ of $[\alpha]$ for $[\text{Co}(\text{en})_3] \cdot \text{I}_3 \cdot \text{H}_2\text{O}$) were used.

For the reaction of $[\text{Co}(\text{en})_3]^{2+}$ with $[\text{Co}(\text{edta})]^-$ in various solvents, the reaction conditions and observed enantiomeric excesses in the $[\text{Co}(\text{en})_3]^{3+}$ product are presented in Table II. Reactions were performed with both the (+) and (-) forms of $[\text{Co}(\text{edta})]^-$, as a check on precision. In all cases the $\Delta\text{-}(+)\text{546}$ - $[\text{Co}(\text{edta})]^-$ reactant yielded an excess of the $\Lambda\text{-}(+)\text{589}$ - $[\text{Co}(\text{en})_3]^{3+}$ product, and the $\Lambda\text{-}(-)\text{546}$ reactant yielded the $\Delta\text{-}(-)\text{589}$ product, with enantiomeric excesses ranging from 9 to 45% in the separate runs. Except for the reaction in sulfolane, the enantiomeric excesses for the reactions with (+) and (-) forms were in good agreement with each other.

For the reactions of $[\text{Co}(\text{en})_3]^{2+}$ with $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{pdta})]^-$, and $[\text{Co}(\text{cdta})]^-$ in aqueous solution and Me_2SO , the experimental conditions and results are listed in Table III. In all instances, $[\text{Co}(\text{en})_3]^{3+}$ was produced essentially quantitatively. The three oxidants produced almost identical enantiomeric excesses in the $[\text{Co}(\text{en})_3]^{3+}$ product. In water, the observed enantiomeric excesses ranged from 7.3 to 9.0%, and in Me_2SO , the enantiomeric excesses ranged from 31 to 36%.

Kinetic Studies. The effect of the ethylenediamine concentration on the reaction of $[\text{Co}(\text{en})_3]^{2+}$ with $[\text{Co}(\text{edta})]^-$ in aqueous solution at constant ionic strength and constant ratio of $[\text{en}]/[\text{enH}^+]$ was studied at four concentrations of ethylenediamine. In order to scavenge liberated edta^{4-} ligand in the course of the reaction, excess Ca^{2+} ion was present. This measure was necessary to maintain the constant $[\text{Co}(\text{en})_3]^{2+}$ concentrations required for first-order

Table V. Kinetic Data for Oxidations of $[\text{Co}(\text{en})_3]^{2+}$ by $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{pdta})]^-$, and $[\text{Co}(\text{cdta})]^-$ at 25.0 °C, $\mu = 1.00 \text{ M}$ ^a

$[\text{Co}(\text{II})]$, mM	$10^2 k_{\text{obsd}}$, $\text{s}^{-1} \text{ b}$		
	$[\text{Co}(\text{edta})]^-$ ^c	$[\text{Co}(\text{pdta})]^-$ ^c	$[\text{Co}(\text{cdta})]^-$ ^c
10	5.21	5.15	4.7
20	10.81	10.5	9.44
30	15.6	15.7	15.1
k , $\text{M}^{-1} \text{ s}^{-1} \text{ d}$	5.24	5.25	5.00

^a $[\text{en}] = 1.6 \text{ M}$; $[\text{enHCl}] = 0.10 \text{ M}$. ^b Each value is an average of four runs. ^c Oxidant; initial concentration 0.30 mM. ^d Least-squares slope for k_{obsd} vs. $[\text{Co}(\text{II})]$.

kinetics, especially at the lower concentrations of ethylenediamine where free edta^{4-} would have competed for $\text{Co}(\text{II})$. The results are shown in Table IV. The first-order rate constant can be seen to increase from 2.33 to 2.90 s^{-1} , corresponding to second-order rate constants of 4.66 to 5.79 $\text{M}^{-1} \text{ s}^{-1}$, as the free ethylenediamine concentration is raised from 0.085 to 0.985 M.

A comparison of the reaction rates of $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{pdta})]^-$, and $[\text{Co}(\text{cdta})]^-$ with $[\text{Co}(\text{en})_3]^{2+}$ at three concentrations of reductant ($\mu = 1.0 \text{ M}$, $[\text{en}] = 1.6 \text{ M}$, 25.0 °C) is shown in Table V. The first two reactions show second-order kinetic behavior over this range of $[\text{Co}(\text{II})]$, and the rate constants of the two reactions are virtually identical, $k = 5.2 \text{ M}^{-1} \text{ s}^{-1}$. The reaction with $[\text{Co}(\text{cdta})]^-$ shows nearly second-order kinetics; a least-squares analysis of the plot of k_{obsd} vs. $[\text{Co}(\text{II})]$ yields a value of $k = 5.0 \text{ M}^{-1} \text{ s}^{-1}$.

Discussion

Several striking results are apparent in the reactions of $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{pdta})]^-$, and $[\text{Co}(\text{cdta})]^-$ with $[\text{Co}(\text{en})_3]^{2+}$:

(1) The rate constants for the three reactions in aqueous solution are virtually identical: $k \approx 5.2 \text{ M}^{-1} \text{ s}^{-1}$ (25.0 °C, $\mu = 1.0$, $[\text{en}] = 1.6 \text{ M}$).

(2) The degrees of stereoselectivity for the three reactions in aqueous solution or in Me_2SO are virtually identical: $k_{\Delta\Delta}/k_{\Delta\Delta} \approx 1.2$ in aqueous solution, ≈ 2.1 in Me_2SO .

(3) The stereoselectivity of the $[\text{Co}(\text{edta})]^-/[\text{Co}(\text{en})_3]^{2+}$ reaction is strongly solvent dependent, ranging from an enantiomeric excess of 9% in water to an excess between 36 and 45% in sulfolane. However, in all cases, the sense of stereopreference is the same, with the Δ -oxidant reacting more quickly with the Λ -reductant than with the Δ -reductant (and, of course, the Λ -oxidant reacting more quickly with the Δ -reductant).

Before a detailed discussion of the origin of these effects can be made, a question about the basic mechanism of the reaction must be addressed: whether these redox reactions are of the inner- or outer-sphere kind. We have previously assigned the reaction as outer sphere,¹ and we amplify the argument as follows: (1) The substitution inertia of $\text{Co}(\text{III})$ complexes lends support to the outer-sphere mechanism for this reaction, since an inner-sphere mechanism would require initial formation of $[\text{Co}(\text{en-N}, \text{N})_2\text{-}(\text{en-N})(\text{edta-O})]$, which must then lose the carboxylate ligand with subsequent coordination of the dangling amine nitrogen. (2) There is no evidence of a detectable intermediate, and $[\text{Co}(\text{en})_3]^{3+}$ appears to be formed concurrently with loss of $[\text{Co}(\text{edta})]^-$. (3) The work of Alexander and Spillert²⁷ shows that when $[\text{Co}(\text{en-N}, \text{N})_2(\text{enH}^+-\text{N})\text{Cl}]^{3+}$ reacts at high pH, Cl^- is replaced by OH^- without ring closure. (Ring closure is reported in alkaline (piperidine) Me_2SO , but the reaction is quite slow.) By analogy, were the reaction in our system taking place by attack by a carboxylate of the oxidant on a bis(bidentate)-monodentate $[\text{Co}(\text{en})_3]^{2+}$ species, this arrangement of the ethylenediamine groups would be maintained in the immediate $\text{Co}(\text{III})$ products. (4) In our original report¹ and in more recent accounts,^{3,4} cases of stereoselective discrimination in reactions that are unambiguously outer sphere have been reported.

As the discussion to follow shows, these reactions are informative about the relative orientation of the oxidant and reductant in the

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activated complex. Most kinetic studies of redox reactions shed no light on the basic question of how closely the reaction partners approach.

The fact that $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{pdta})]^-$, and $[\text{Co}(\text{cdta})]^-$ all react with $[\text{Co}(\text{en})_3]^{2+}$ with nearly the same rate constant (Table V) and stereoselectivity (Table III) strongly suggests that the molecular orientations in the activated complexes of the three reactions are the same and moreover that the interacting region of the oxidant is restricted to the parts of the oxidant molecule that are in common in the three oxidants. Molecular models of the complexes indicate that roughly one hemisphere of the oxidant complex is taken up by the bound carboxylates and the other by the "ethylenediamine" part of the ligand. Since the "ethylenediamine" part of the molecule is so different in the three complexes, the inescapable conclusion is that, in the activated complex, the "ethylenediamine" part of the oxidant faces away from the reductant. In this configuration, the carboxylate groups on the $[\text{Co}(\text{edta})]^-$ molecule face the reductant and can form hydrogen bonds with the NH groups on the $[\text{Co}(\text{en})_3]^{2+}$ molecule.

Interestingly, a case of stereoselectivity in ion-pair formation which resembles that found here has been observed for Δ - or Λ - $[\text{Co}(\text{en})_3]^{3+}$ with Δ - $[\text{Co}^{\text{III}}(\text{ox})_2(\text{gly})]^{2-}$, in which the Δ - Λ pair is preferred by a relative formation constant of about $1.06 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C , $\mu = 0.01 \text{ M}$.²⁸ A model for the ion pair involving hydrogen bonding between the carboxylate carbonyls and amine NH's was proposed. A similar model was proposed by Osvath and Lappin²⁹ to explain stereoselectivities observed in the reactions of Δ - $[\text{Co}(\text{edta})]^-$ with $[\text{Co}(\text{chxn})_3]^{2+}$ and $[\text{Co}(\text{bn})_3]^{2+}$ (chxn = 1,2-cyclohexanediamine; bn = 2,3-butanediamine).

The effects of solvent on the stereoselectivity of the $[\text{Co}(\text{edta})]^-/[\text{Co}(\text{en})_3]^{2+}$ reaction that we have observed tend to support the hypothesis of hydrogen bonding in the activated complex. The stereoselectivity increases for solvents in the following order: water < ethylene glycol < methanol ~ ethanol ~ formamide < ethylenediamine < DMF < Me_2SO < sulfolane. The reactions in the more protic solvents appear to display lower stereoselectivities than those in the less protic solvents. The formation of hydrogen bonds between the solvent and the reactants could certainly interfere with the hydrogen bonding between the reactants, thereby diminishing the difference in energy between the diastereomeric transition states. It should also be noted that, concurrent with the increase in stereoselectivity upon increasing the ethylenediamine concentration,¹ we see an increase in the rate constant of reaction. That is, the rate constants for both the Δ - Λ and Δ - Δ reactions increase upon raising the ethylenediamine concentration, with the Δ - Λ rate constant increasing at a faster rate than that of the Δ - Δ .

The discussion of the discrimination effects we have observed has been couched in terms of the activated complex itself. Discussion of outer-sphere electron transfer is commonly done in terms of assembling a precursor complex that then undergoes unimolecular decay to products. When the reactants are spherical, if

the issue of the distance of approach is neglected, refinement of the concept is not required. (The definition of precursor complex, which is implicit in the way the concept is used, is that all pre-conditions for reaction have been met except inner- and outer-sphere rearrangement.) Because of the marked asymmetry of the oxidizing agents we have used, it perhaps needs to be pointed out that the precursor complex and the ion-pair complex (that is the total of all the configurations that the 1:1 complex can assume) are not necessarily equivalent. We have concluded that only those 1:1 complexes in which the polar groups of the oxidant face $[\text{Co}(\text{en})_3]^{2+}$ are fruitful for reaction; ion-pair species may exist in which $[\text{Co}(\text{en})_3]^{2+}$ is adjacent to the hydrocarbon face of the reaction partner.

It is noteworthy that there are numerous reports of stereoselective "substitution" reactions in which $[\text{Co}(\text{edta})]^-$ or a relative complex reacts with a chelating ligand, which in fact may be explained by Co(II)-catalyzed stereoselective redox reactions.³⁰⁻³⁷ $[\text{Co}(\text{edta})]^-$ reacts with ethylenediamine to give $[\text{Co}(\text{en})_3]^{3+}$.⁹ The stereoselectivity of this reaction was originally ascribed to a substitution mechanism^{30,37} but was shown¹ to be due to the stereoselective redox reaction of $[\text{Co}(\text{edta})]^-$ with $[\text{Co}(\text{en})_3]^{2+}$. This is an important point, as some attempts to assign absolute configurations of metal complexes have been based on the assumption that the reactions are of a direct substitution mechanism, proceeding with "retention of configuration". In fact, as we have shown here, the Δ - Λ redox reaction may be more favorable. Several attempts had been made to explain solvent effects in stereoselectivity of the "substitution" reaction using complex substitution mechanisms, but all of these effects may now be ascribed to variations in the stereoselectivity of the redox reaction. It should be noted that the report that the reaction of $[\text{Co}(\text{pdta})]^-$ with en proceeds with 100% stereoselectivity,³⁶ with $(-)_546$ - $[\text{Co}((+)\text{-pdta})]^-$ yielding $(+)_589$ - $[\text{Co}(\text{en})_3]^{3+}$, which we noted as interesting,³⁸ is contradicted by our results and those of Doh et al.,³³ who found that Δ - $(+)_546$ - $[\text{Co}((-)\text{-pdta})]^-$ in anhydrous ethylenediamine reacts to give a 34% enantiomeric excess of Λ - $(+)_589$ - $[\text{Co}(\text{en})_3]^{3+}$.

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