Chiral Induction in the Inner-Sphere Reduction of [Co(ox)$_3$]$^{3-}$ by [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and Derivatives

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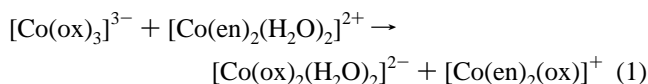
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The reductions of [Co(ox)$_3$]$^{3-}$ by [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and derivatives are rapid inner-sphere electron transfer reactions which proceed through a doubly chelated oxalate bridge. The second-order rate constants for the reactions are 1.6×10^4 M^{-1} s^{-1} and 3.6×10^4 M^{-1} s^{-1} respectively for [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$. Hydrolysis of the complexes inhibits the reaction and reflects the need to form a chelate bridge in the electron transfer precursor complex. The primary products in the reaction with [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ are Λ,Δ-*cis-β*-(*SR,RS*)-[Co(2,2,2-tet)(ox)]$^+$ (15%) and Λ,Δ-*cis-β(SS,RR)*-[Co(2,2,2-tet)(ox)]$^+$ (85%) and they have been characterized by X-ray crystallography. Λ,Δ-*cis-β*-(*SR,RS*)-[Co(2,2,2-tet)(ox)]ClO$_4$ crystallizes in *Pna*2$_1$ with Z = 4, a = 15.126(1) Å, b = 7.9468(4) Å, c = 11.603(1) Å, and R = 0.021 for 1882 reflections. Λ,Δ-*cis-β*-(*SS,RR*)-[Co(2,2,2-tet)(ox)]Cl·3H$_2$O crystallizes in $P\bar{1}$, with Z = 2, a = 7.636(3) Å, b = 8.468(2) Å, c = 13.456-(3) Å, α = 107.45(2)°, β = 102.00(3)°, γ = 99.62(3)°, and R = 0.045 for 1784 reflections. A single cis-β product, Λ,Δ-*cis-β(SS,RR)*-[Co(2,3,2-tet)(ox)]$^+$ is formed with the [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$ as reductant, and reaction with [Co(5(*R,S*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ gives three products, all with the cis-β geometry. Two of these products have been characterized by X-ray crystallography. Λ,Δ-*cis-β(SR,RS)-exo*-[Co(5(*S,R*)-Me-2,2,2-tet)(ox)](ClO$_4$)·2NaClO$_4$·H$_2$O crystallizes in $P\bar{1}$, with Z = 2, a = 8.796(1) Å, b = 11.479(1) Å, c = 12.632(2) Å α = 107.59(1)°, β = 90.21(1)°, γ = 106.43(1)°, and R = 0.049 for 2790 reflections. Λ,Δ-*cis-β(SS,RR)-endo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]Cl·2H$_2$O crystallizes in $P\bar{1}$, with Z = 2, a = 8.2143(9) Å, b = 8.2572(9) Å, c = 11.755(1) Å, α = 80.845(9), β = 84.621(9)°, γ = 75.912(9)°, and R = 0.040 for 2527 reflections. When optically active Δ-[Co-(ox)$_3$]$^{3-}$ is used, chiral induction is observed in the products. The sense of the induction is dependent on the configuration of the polydentate amine ligand. When it is bound as cis-β(*SS,RR*), a Δ-product results. When it is bound as cis-β(*SR,RS*), a Λ-product results. The induction is small, typically <10% enantiomeric excess, but can be correlated with the fluxionality of the amine.

Introduction

Over the past decade, there has been interest in the study of chiral induction in inner-sphere electron transfer reactions involving metal ion complexes.[1−6] The problems associated with the design of such studies are well documented. While rigid stereochemistry is essential for understanding any structural role in the process, lability is required in at least one of the reactants in order to promote inner-sphere interactions. In addition, the reactions are complex and involve a number of primary steps: outer-sphere association, precursor-complex formation, successor-complex formation as a result of the electron transfer process itself, and successor-complex dissociation. Any one of these steps can contribute to the stereoselectivity. On the other hand, the precursor complex geometry in the inner-sphere reaction is in general much better defined than in outer-sphere reactions, and this may provide an advantage in interpretation.

One approach used in this laboratory has been the study of inner-sphere reactions involving oxalate as a bridging ligand,

taking advantage of the number of optically stable chiral species with this bidentate ligand. In the electron transfer reaction, formation of a double bridge with oxalate is well recognized[7−9] and transfer of the bridging ligand has been demonstrated in earlier work.[3] Studies of the reactions with [Co(en)$_2$(OH$_2$)$_2$]$^{2+}$, eq 1, and a variety of substituted derivatives led to the suggestion

$$[\text{Co(ox)}_3]^{3-} + [\text{Co(en)}_2(\text{H}_2\text{O})_2]^{2+} \rightarrow$$
$$[\text{Co(ox)}_2(\text{H}_2\text{O})_2]^{2-} + [\text{Co(en)}_2(\text{ox})]^+ \quad (1)$$

that formation of the precursor involves substantial changes in geometry.[4] However, subsequent work with a range of oxidants pinpointed more subtle effects of hydrogen bonding with groups surrounding the oxalate bridge as an alternative explanation.[6] In this work, the nonbridging ligand 3,6-diaza-1,8-octanediamine (2,2,2-tet) and its derivatives 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 5(*R,S*)-methyl-3,6-diaza-1,8-octanediamine (5(*R,S*)-Me-2,2,2-tet) have been used to reduce the fluxional instability while maintaining the hydrogen-bonding abilities in an attempt to differentiate between the two proposed mechanisms.

Oligodentate ligands such as 2,2,2-tet can bind to metal ions in a variety of ways: trans, Λ,Δ-*cis-α(RR,SS)*, Λ,Δ-*cis-β*-(*SS,RR*), and Λ,Δ-*cis-β(SR,RS)*, Figure 1.[10] The inner-sphere reactions involving chelating oxalate bridges, eq 1, are such that the formation of trans-products is not favored. While the distribution of these different isomers in the cobalt(II) complex

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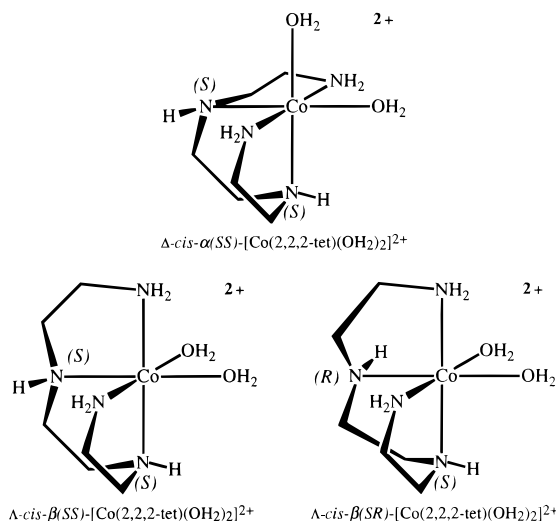
Figure 1. Representative cis-binding modes of (2,2,2-tet) in [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$.

is not known, detailed molecular mechanics calculations for [Co^{III}(2,2,2-tet)(gly)]$^{2+}$ complexes reveal that the Λ,Δ-*cis-β-*(*SS,RR*) isomer is the most stable.[11,12] All three cis isomers of the cobalt(III) oxalato species have been identified, and the distribution of isomers varies with the preparation.[13]

In this paper, the reductions of [Co(ox)$_3$]$^{3-}$ by [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$, [Co(5-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and [Co(2,3,2-tet)-(OH$_2$)$_2$]$^{2+}$ are examined in some detail, and stereoselectivities in the reaction products are determined. The crystal structures of the two products, Λ,Δ-*cis-β*(*SR,RS*)-[Co(2,2,2-tet)(ox)]$^+$ and Λ,Δ-*cis-β*(*SS,RR*)-[Co(2,2,2-tet)(ox)]$^+$, from the reaction with [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and two products, Λ,Δ-*cis-β*(*SR,RS*)-*exo*-[Co(5(*S,R*)-Me-2,2,2-tet)(ox)]$^+$ and Λ,Δ-*cis-β*(*SS,RR*)-*endo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$, from the reaction with [Co-(5(*R,S*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ are also reported. The effects of changes in the pattern of hydrogen bonding between the reactants are noted.

Experimental Section

K$_3$[Co(ox)$_3$]·3H$_2$O was prepared[14] and resolved[15] by literature methods (ϵ_{605} = 165 M^{-1} cm^{-1} and $\Delta\epsilon_{622}$ = 3.80 M^{-1} cm^{-1} for Λ-(−)$_{589}$-[Co(ox)$_3$]$^{3-}$). The ligand 3,6-diaza-1,8-octanediamine, (Aldrich, triethylenetetramine, 2,2,2-tet) was distilled under reduced pressure prior to use, while 3,7-diaza-1,9-nonanediamine (2,3,2-tet) was used as purchased (Aldrich, *N,N'*-bis(2-aminoethyl)-1,3-propanedi-amine). 5(*R*)-methyl-3,6-diaza-1,8-octanediamine (5(*R*)-Me-2,2,2-tet) and its racemate were prepared according to Yoshikawa,[16] and distilled prior to use. The ligands were characterized by ^{1}H and ^{13}C NMR.

(10) The nomenclature used is adapted from that of Buckingham et al.[11] Thus (*SR*) in cis-β(*SR*)- refers to the absolute configurations of the angular and planar secondary nitrogen atoms respectively. The designations *endo*- and *exo*- refer to the position of the 5-Me substituent with respect to the folded cis-β tetradentate ligand (Mulqui, M. W.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1984,** *88,* 183−192). Designation of chelate ring conformation in the cis-β isomers is in the following order: terminal apical ring, central planar ring, and terminal planar ring.
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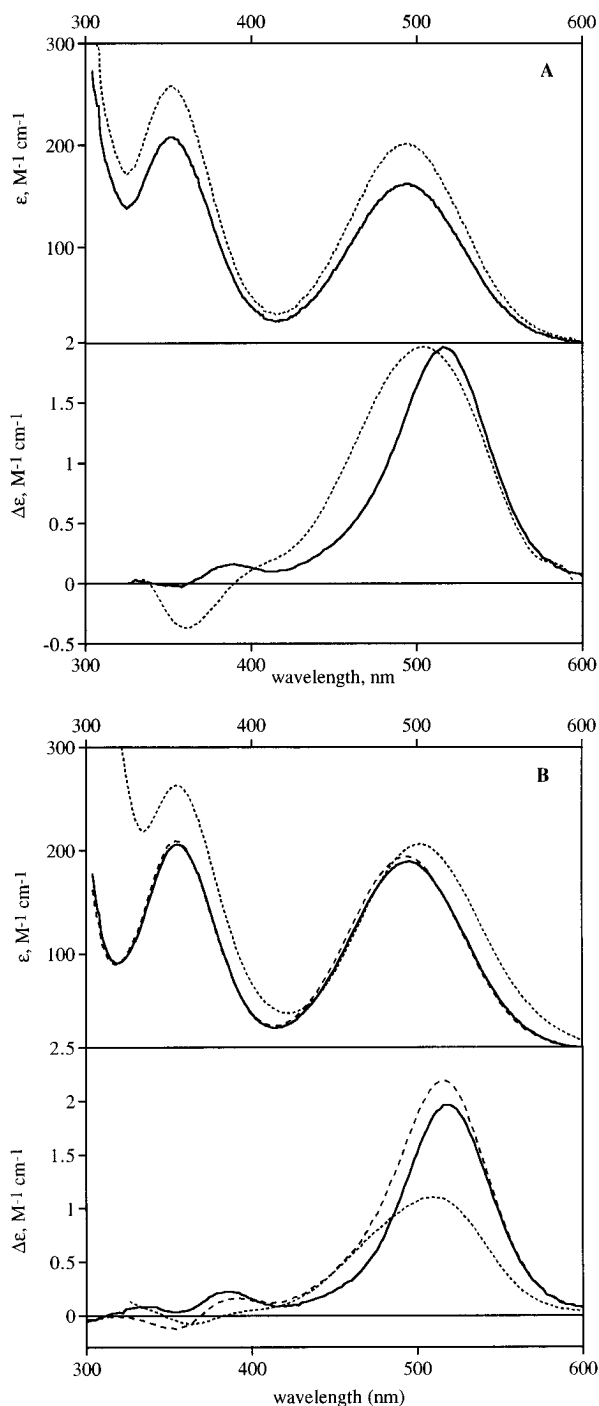(16) Goto, M.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1969,** *8,* 358−366.

Figure 2. (A) Visible and circular dichroism spectra for Λ-*cis-β*(*SR*)-[Co(2,2,2-tet)(ox)]$^+$ (−) and Λ-*cis-β*(*SS*)-[Co(2,2,2-tet)(ox)]$^+$ (− −) in aqueous solution at 25 °C. (B) Visible and circular dichroism spectra for Λ-*cis-β*(*SS*)-*endo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ (−), Λ-*cis-β*(*SS*)-*exo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ (− −) and Λ-*cis-β*(*SR*)-*exo*-[Co(5(*S*)-Me-2,2,2-tet)(ox)]$^+$ (- -) in aqueous solution at 25 °C.

Solutions of [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$, [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$, and [Co(5(*R,S*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ complexes were prepared immediately before use by addition of deoxygenated solutions containing 5% excess of the respective amine to solutions of either cobalt(II) nitrate (Baker Analyzed) or cobalt(II) triflate[17] which were purged of oxygen by sparging with argon.

cis-α-[Co(2,2,2-tet)(ox)]$^+$ and *cis*-β(*SS,RR*)-[Co(2,2,2-tet)(ox)]$^+$ were prepared from the corresponding *cis*-α- and *cis*-β-[Co(2,2,2-tet)(CO$_3$)]$^+$ complexes[18] and resolved with lithium hydrogen (2*R*,3*R*)-tartrate

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Table 1. Visible and Circular Dichroism Spectroscopic Parameters for Cobalt(III) Product

complex	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))		λ (nm) ($\Delta\epsilon$ (M^{-1} cm^{-1}))
Λ-*cis*-β(*SS*)-[Co(2,2,2-tet)(ox)]$^+$	494 (179)	356 (179)	515 (+2.09)[a]
	494 (161)	356 (167)	
Λ-*cis*-β(*SR*)-[Co(2,2,2-tet)(ox)]$^+$	498 (201)	353 (226)	510 (+1.96)
Λ-*cis*-α(*SS*)-[Co(2,2,2-tet)(ox)]$^+$	493 (110)	357 (123)	515 (+2.95)[a]
Λ-*cis*-β(*SS*)-[Co(2,3,2-tet)(ox)]$^+$	500 (140)	360 (175)	535 (+1.47)[a]
	498 (135)	356 (186)	
Λ-*cis*-β(*SS*)-*endo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$	496 (189)	355 (194)	518 (+1.96)
Λ-*cis*-β(*SS*)-*exo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$	492 (194)	352 (206)	515 (+2.19)
Δ-*cis*-β(*RS*)-*exo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$	500 (206)	355 (239)	512 (−1.04)

[a] Reference 19.

dibenzoate.[19] The complex *cis*-β(*SR,RS*)-[Co(2,2,2-tet)(ox)]$^+$ for mutarotation studies was obtained from the reaction between stoichiometric amounts of [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and [Co(ox)$_3$]$^{3-}$ under an atmosphere of argon. Subsequent elution of the product mixture with 0.2 M HCl from a 15 × 1.5 cm column (DOWEX 50X2-200) yields 15% of the (*SR,RS*) isomer as the first eluted isomer and 85% of *cis*-β-(*SS,RR*)-[Co(2,2,2-tet)(ox)]$^+$ as the second eluted isomer. Attempts to resolve the *cis*-β(*SR,RS*)-[Co(2,2,2-tet)(ox)]$^+$ isomer were not successful with lithium hydrogen (2*R*,3*R*)-tartrate dibenzoate or with ammonium 3-bromocamphor-8-sulfonate.

Stoichiometry and stereoselectivity studies were carried out at 0.10 M ionic strength (KCl) in the presence of 0.010 M buffer. The buffers used were MES (2-[*N*-morpholino]ethanesulfonic acid), Tris (tris-(hydroxymethyl)aminomethane), HEPES (*N*-[2-hydroxyethyl]piperazine-*N*′-2 ethanesulfonic acid), CAPS (3-[cyclohexylamino]-1-propanesulfonic acid), and CAPSO (3-[cyclohexylamino]-2-hydroxy-1-propanesulfonic acid). Reactions were run with the labile reductant in excess by reacting solutions of [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ or [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$ (typically 20 mL of 0.02 M) with solutions of [Co(ox)$_3$]$^{3-}$ (typically 20 mL of 0.005 M) under argon. The reactions are rapid, and efficient mixing is required to ensure reproducibility. The reaction mixtures were quenched with 2 M HCl (typically 10 mL) within 30 s of mixing, and the product mixture, containing an excess of unreacted cobaltous complex, was diluted with deaerated distilled water to 1 L and loaded onto a 25 × 3.5 cm column (DOWEX 50X2-200). The adsorbed complexes were subsequently washed with distilled water and eluted with 0.2 M HCl. In order to check the effect of quenching with acid on the reaction products, experiments were carried out in which the products from unquenched reactions were separated anaerobically by hplc with use of a Waters 501 pump with LC-481 detector and a Protein Pak SP-5PW Sephadex ion exchange column with 0.10 M NaNO$_3$ as eluent. Similar anaerobic conventional ion-exchange analyses were also carried out.

The quenching, separation, and analyses were performed under argon to minimize formation of μ-peroxo, μ-hydroxo dimers and other oxidation products. Only the oxalato-containing products, identifiable by their lower charges, were examined in any detail. For [Co(2,2,2-tet)(ox)]$^+$, elution with 0.2 M HCl resulted in three major bands, identified in the order of elution as *cis*-β(*SR,RS*)-[Co(2,2,2-tet)(ox)]$^+$, *cis*-β(*SS,RR*)-[Co(2,2,2-tet)(ox)]$^+$, and unreacted [Co(aq)]$^{2+}$. Elution of the product mixture of [Co(2,3,2-tet)(ox)]$^+$ system resulted in *cis*-β(*SS,RR*)-[Co(2,3,2-tet)(ox)]$^+$ as the sole oxalate-containing product. Three isomers of [Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ were isolated by initial elution of the reaction mixture with 0.2 M HCl on a DOWEX 50X2-200 column, separating the *cis*-β(*SR,RS*)-*exo*-[Co(5(*S,R*)-Me-2,2,2-tet)-(ox)]$^+$ as the first eluted band from the rest of the product mixture. Absorption of the remaining product mixture on to a 55 × 1.5 cm DOWEX 50X2-200 column and elution with acidic 0.1 M Na$_2$SO$_4$ (H$_2$SO$_4$, pH 2.5) resulted in separation of the two remaining isomers, with the elution of *cis*-β(*SS,RR*)-*exo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ prior to that of *cis*-β(*SS,RR*)-*endo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$. The product bands were collected, concentrated under reduced pressure and characterized by ^{1}H, ^{13}C NMR, and UV−visible spectroscopic analysis.

Identification of the cobalt(III)-containing products was facilitated by ^{1}H and ^{13}C NMR. The spectroscopic characteristics are given in Table 1, and ^{13}C NMR data are available as Supporting Information. Visible and circular dichroism spectra for the complexes are shown in

Figure 2. Stoichiometry was determined by visible spectrophotometry, and the stereoselectivity was determined from the optical purity of the products by circular dichroism spectroscopy. Extinction and circular dichroism coefficients for Λ-*cis*-β(*SS*)-[Co(2,3,2-tet)(ox)]$^+$ (ϵ_{500} = 140 M^{-1} cm^{-1}, $\Delta\epsilon_{535}$ = 1.47 M^{-1} cm^{-1}) have been reported previously.[19,20] Of the two reaction products in the reaction with [Co(2,2,2-tet)-(OH$_2$)$_2$]$^{2+}$, only the major product, Λ-*cis*-β(*SS*)-[Co(2,2,2-tet)(ox)]$^+$ (ϵ_{497} = 179 M^{-1} cm^{-1}, $\Delta\epsilon_{515}$ = 2.09 M^{-1} cm^{-1}), has been resolved to optical purity.[19] The extinction coefficient for the minor *cis*-β(*SR,RS*)-[Co-(2,2,2-tet)(ox)]$^+$ isomer was determined by ICP emission spectroscopy measurements as ϵ_{498} = 201 M^{-1} cm^{-1}. The optical purity of partially resolved samples of the minor isomer, Λ-*cis*-β(*SR*)-[Co(2,2,2-tet)(ox)]$^+$, was determined by mutarotation of the samples to the major isomer, Λ-*cis*-β(*SS*)-[Co(2,2,2-tet)(ox)]$^+$, with 0.1 M NaOH for 30 s. Samples were quenched with HCl and the products separated by ion exchange chromatography and analyzed as described above. The optical purity of the Λ-*cis*-β(*SR*)-[Co(2,2,2-tet)(ox)]$^+$ isomer was assumed to be the same as that of the mutarotated product, giving $\Delta\epsilon_{510}$ = 1.96 for Λ-*cis*-β(*SR*)-[Co(2,2,2-tet)ox]$^+$. Extinction coefficients for the [Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ compounds were also determined by ICP emission spectroscopy and are presented in Table 1. Optically pure diastereomers of *cis*-β-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ were obtained by using optically active [Co(5(*R*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ in the electron transfer reaction in order to form one enantiomer of each of the three products stereospecifically. The NMR analyses confirm the presence of only one diastereomer in each case. Absolute configurations for these compounds were determined by X-ray analysis and by comparisons of CD spectra.

Structural assignments of the [Co(2,2,2-tet)(ox)]$^+$ isomers were confirmed by X-ray crystallography. Orange rod-shaped crystals of racemic Λ,Δ-*cis*-β(*SS,RR*)-[Co(2,2,2-tet)(ox)]Cl·3H$_2$O, synthesized by literature methods, and burgundy platelike crystals of Λ,Δ-*cis*-β(*SR,RS*)-[Co(2,2,2-tet)(ox)]ClO$_4$, isolated from the electron transfer reaction, were obtained by vapor diffusion of 2-propanol into slightly acidic aqueous solutions. Over time, interconversion of the two isomers was observed entailing mechanical separation of the crystalline samples. Microanalysis of the two crystalline samples gave 26.65% C, 6.25% H, and 15.50% N (theoretical: 25.11% C, 6.32% H, and 14.64% N) for Λ,Δ-*cis*-β(*SS,RR*)-[Co(2,2,2-tet)(ox)]Cl·3H$_2$O and 25.04% C, 5.01% H, and 14.26% N (theoretical: 24.47% C, 4.62% H, and 14.27%N) for Λ,Δ-*cis*-β(*SR,RS*)-[Co(2,2,2-tet)(ox)]ClO$_4$. The discrepancies are thought to reflect the presence of differently hydrated forms of the isomers and the inefficiency of the mechanical separations. Two of the isomers of [Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ were also structurally characterized. Burgundy platelike crystals of Λ,Δ-*cis*-β(*SR,RS*)-*exo*-[Co(5(*S,R*)-Me-2,2,2-tet)(ox)](ClO$_4$)·2NaClO$_4$·H$_2$O and burgundy block-shaped crystals of Λ,Δ-*cis*-β(*SS,RR*)-*endo*-[Co(5(*R,S*)-Me-2,2,2-tet)-(ox)]Cl·2H$_2$O were also obtained by vapor diffusion of 2-propanol into slightly acidic aqueous solutions of the separated electron transfer products. Suitable crystals of the four complexes were examined at 20 °C on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator using Mo Kα radiation (λ = 0.710 73 Å). Further details are avaiable as Supporting Information.

UV−visible measurements were made on an Varian DMS-100 spectrophotometer. Circular dichroism spectra were obtained with an

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Aviv Model 62DS Circular Dichroism Spectrophotometer (Aviv Associates, Lakewood, NJ). Atomic emission measurements were made with a Perkin-Elmer Plasma 400 ICP spectrometer.

Kinetics of the electron transfer reactions were monitored at 605 nm for the disappearance of $[Co(ox)_3]^{3-}$ using a Durrum D-110 stopped-flow spectrophotometer, modified to permit the handling of solutions under nitrogen atmosphere and thermostatted at 25.0(1) °C. Pseudo-first-order conditions with the concentration of cobalt(II) solutions at least in 10-fold excess over $[Co(ox)_3]^{3-}$ solutions were used, and excellent first-order kinetics were observed under most of the experimental conditions. The ionic strength of solutions was maintained at 0.10 M with NaNO$_3$. The pH of the reaction mixtures was determined with a Corning 240 pH meter equipped with a Corning combination electrode on aliquots maintained under an atmosphere of Ar immediately after the kinetic measurements. It should be noted that considerable difficulties were experienced with competing reactions with trace amounts of O$_2$, particularly under conditions where the electron transfer process is slow. The reaction with O$_2$ leads to the formation of highly colored $\{[Co(2,2,2-tet)]_2(O_2)\}$, $\{[Co(2,3,2-tet)]_2-(O_2)\}$, and $\{[Co(2,2,2-tet)]_2(O_2)(OH)\}$ absorbing maximally between 340−380 nm,[21] and these processes interfere with the reactions under study. Fortunately, the electron transfer reaction is much faster than the reactions with O$_2$ in the pH range 7−9, but the complications at pH 9−11 limit the accuracy of the kinetic data in the present study. Kinetics of the mutarotation process of *cis-β(SR,RS)*-[Co(2,2,2-tet)-ox]$^+$ were monitored at 520 nm on a CARY 3 spectrophotometer, thermostated at 25.0(2) °C.

Results

At pH 8.0, under conditions of excess reductant, the reaction of $[Co(ox)_3]^{3-}$ with $[Co(2,2,2-tet)(OH_2)_2]^{2+}$ results in the quantitative formation of a mixture of the two structurally possible *cis-β* isomers of $[Co(2,2,2-tet)(ox)]^+$ in the ratio $(SS,RR):(SR,RS) = 85:15$. This same ratio is found over the pH range 6−10, but the recovery of the products is less than quantitative at higher and lower pH. At higher pH, this may be the result of formation of small amounts of the products of the outer-sphere reaction with $[Co(ox)_3]^{3-}$. This product appears as a yellow, highly charged band in the chromatographic separations and was not further investigated.

The identities of the two reaction products were confirmed by X-ray crystallography. The minor product, Λ,Δ-*cis-β*-(SR,RS)-[Co(2,2,2-tet)(ox)]$^+$, was isolated chromatographically as a perchlorate salt from a product mixture while the major isomer, Λ,Δ-*cis-β*(SS,RR)-[Co(2,2,2-tet)(ox)]$^+$ was obtained by a previously published procedure[19] as a chloride salt and was shown to be identical to the major reaction product by ^{1}H and ^{13}C NMR.

The X-ray structures of the two complexes are very similar, differing in the configuration at the in-plane secondary nitrogen atom and the complex ions are not exceptional. The isomers shown in Figures 3 and 4 are $\Lambda\Lambda\Lambda\Lambda$ abbreviated to Λ. In both complexes, the shortest Co−N bond length is found at the in-plane secondary nitrogen, reflecting ring strain in the consecutive five-membered chelate ring structure.[11,12]

The minor isomer *cis-β(SR,RS)*-[Co(2,2,2-tet)(ox)]$^+$ converts to a mixture of *cis-β*-(SS,RR)-[Co(2,2,2-tet)(ox)]$^+$ and *cis-β*-(SR,RS)-[Co(2,2,2-tet)(ox)]$^+$ (85:15), and a limited study of the kinetics of this process was undertaken. The reaction rate is first-order in the complex concentration and is dependent on pH, obeying a rate law of the type in eq 2. The second-order

$$\frac{-\text{d}[cis\text{-}\beta(RS,SR)\text{-}[Co(2,2,2\text{-tet})(ox)]^+]}{\text{d}t} =$$

$$(k_f + k_r)[cis\text{-}\beta(RS,SR)\text{-}[Co(2,2,2\text{-tet})(ox)]^+][OH^-] \quad (2)$$

rate constant, $(k_f + k_r)$, is 490 M^{-1} s^{-1} at 0.10 M ionic strength

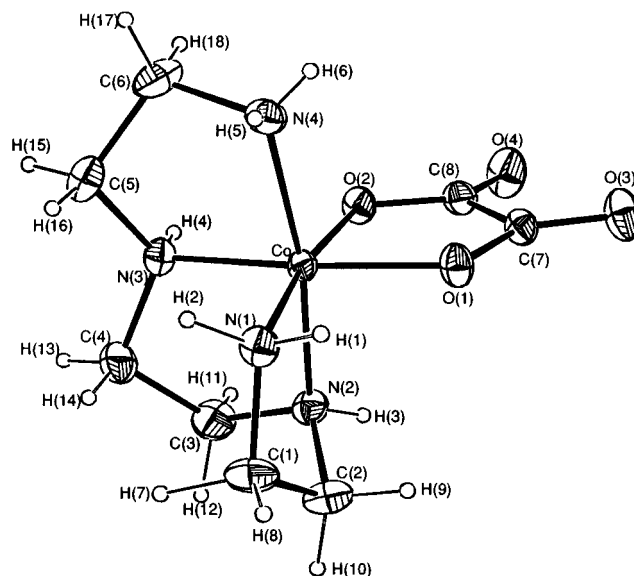(21) Miller, F.; Wilkins, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 2687−2691.

Figure 3. Ortep drawing of $\Lambda(\lambda\delta\lambda)$-*cis-β*(SR)-[Co(2,2,2-tet)(ox)]$^+$ illustrating the numbering scheme. Important bond lengths (Å) and angles (deg) are as follows: Co−O(1) = 1.906(2), Co−O(2) = 1.909-(2), Co−N(1) = 1.950(2), Co−N(1) = 1.950(2), Co−N(2) = 1.949-(2), Co−N(3) = 1.925(2), Co−N(4) = 1.964(2); O(1)−Co−N(1) = 86.62(8). The thermal ellipsoids are drawn at the 50% level.
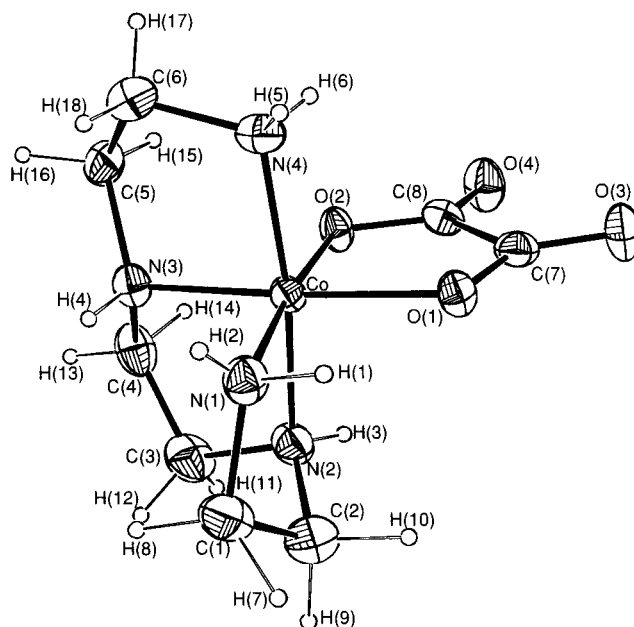

Figure 4. Ortep drawing of $\Lambda(\lambda\lambda\delta)$-*cis-β*(SS)-[Co(2,2,2-tet)(ox)]$^+$ illustrating the numbering scheme. Important bond lengths (Å) and angles (deg) are as follows: Co−O(1) = 1.924(3), Co−O(2) = 1.898-(2), Co−N(1) = 1.928(3), Co−N(2) = 1.944(4), Co−N(3) = 1.914-(4), Co−N(4) = 1.949(4); O(1)−Co−N(1) = 90.1(1). The thermal ellipsoids are drawn at the 50% level.

and 25.0 °C and compares with values of 390 M^{-1} s^{-1} and 1110 M^{-1} s^{-1} for the corresponding process for conversion of *cis-β$_2$(SR,RS)*-[Co(2,2,2-tet)(glyO)]$^{2+}$ to *cis-β$_2$(SS,RR)*-[Co(2,2,2-tet)(glyO)]$^{2+}$ and *cis-β$_1$(SR,RS)*-[Co(2,2,2-tet)(glyO)]$^{2+}$ to *cis-β$_1$(SS,RR)*-[Co(2,2,2-tet)(glyO)]$^{2+}$ at 25 °C and 1.0 M ionic strength.[11,12]

Under pseudo-first-order conditions with an excess of reductant, $[Co(2,2,2-tet)(OH_2)_2]^{2+}$, at higher pH, the loss of $[[Co(ox)_3]^{3-}]$ obeys a first-order rate law. The pseudo-first-order rate constants, k_{obsd}, are linearly dependent on the $[[Co-(2,2,2-tet)(OH_2)_2]^{2+}]$ concentration with a second-order rate constant, k_{so}, of 1.48×10^4 M^{-1} s^{-1} at pH 9.9. The reaction is dependent on pH in a complex manner. Over the pH range
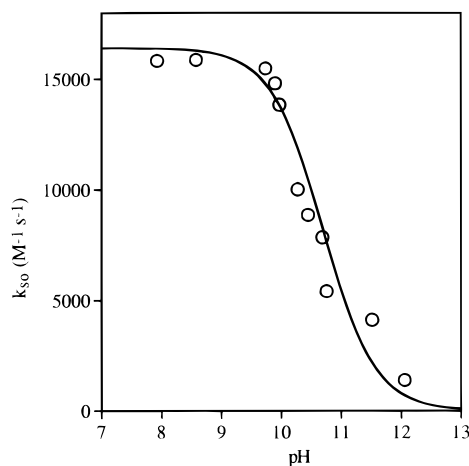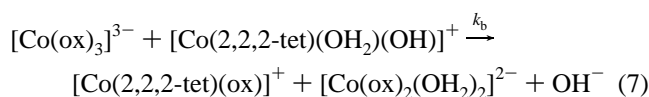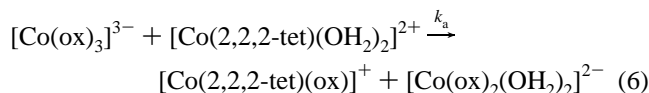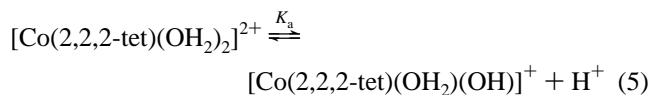
Figure 5. Plot of the second-order rate constant, k_{so}, as a function of pH for the reduction of [Co(ox)₃]³⁻ by [Co(2,2,2-tet)(OH₂)₂]²⁺ at 25.0 °C and 0.10 M ionic strength.

6−8, the second-order rate constant increases with increasing pH but above pH 10, the rate decreases. The dependence at higher pH can be described by the expression shown in eq 3.

$$k_{so} = \frac{k_a[\text{H}^+] + k_b K_a}{[\text{H}^+] + K_a} \quad (3)$$

The limiting second-order rate constant at higher pH, $k_b \leq 1000$ M⁻¹ s⁻¹, zero within experimental error. With this parameter fixed at zero, $K_a = 2.5(4) \times 10^{-11}$ M and $k_a = 1.63(4) \times 10^4$ M⁻¹ s⁻¹, and the fit of the data to these values is shown in Figure 5. A general mechanism consistent with this rate law is shown in eqs 4−7. Hydrolysis of the coordinated water in the

$$[\text{Co}_{aq}]^{2+} + (2,2,2\text{-tet}) \overset{K}{\rightleftharpoons} [\text{Co}(2,2,2\text{-tet})(\text{OH}_2)_2]^{2+} \quad (4)$$

$$[\text{Co}(2,2,2\text{-tet})(\text{OH}_2)_2]^{2+} \overset{K_a}{\rightleftharpoons}$$
$$[\text{Co}(2,2,2\text{-tet})(\text{OH}_2)(\text{OH})]^+ + \text{H}^+ \quad (5)$$

$$[\text{Co}(\text{ox})_3]^{3-} + [\text{Co}(2,2,2\text{-tet})(\text{OH}_2)_2]^{2+} \overset{k_a}{\rightarrow}$$
$$[\text{Co}(2,2,2\text{-tet})(\text{ox})]^+ + [\text{Co}(\text{ox})_2(\text{OH}_2)_2]^{2-} \quad (6)$$

$$[\text{Co}(\text{ox})_3]^{3-} + [\text{Co}(2,2,2\text{-tet})(\text{OH}_2)(\text{OH})]^+ \overset{k_b}{\rightarrow}$$
$$[\text{Co}(2,2,2\text{-tet})(\text{ox})]^+ + [\text{Co}(\text{ox})_2(\text{OH}_2)_2]^{2-} + \text{OH}^- \quad (7)$$

reductant has been noted previously in a study of the reactions of [Co(2,2,2-tet)]²⁺ with O₂, and a value for K_a, 6.3×10^{-12} M, at 25 °C [21] is within a factor of 5 of the value determined in the present work.

The decrease in rate with decreasing pH below pH 8 is quantitatively explained by a thermodynamic effect, the result of dissociation on protonation of the 2,2,2-tet ligand from the metal center. The stability constant for association of 2,2,2-tet is 1.23×10^{11} M⁻¹. Acidity constants for the ligand are reported as $K_{a1} = 1.82 \times 10^{-10}$, $K_{a2} = 8.32 \times 10^{-10}$, $K_{a3} = 2.75 \times 10^{-7}$, and $K_{a4} = 5.62 \times 10^{-4}$ for 2,2,2-tet.[22] Protonation of the coordinated ligand has been noted below pH 5.37 in the case of [Co(2,2,2-tet)(OH₂)₂]²⁺;[23] however, such protonated species are unlikely to participate in the reaction.

Table 2. Stereoselectivity Observed in the Electron Transfer Reactions between [Co(2,3,2-tet)(H₂O)₂]²⁺ and [Co(ox)₃]³⁻ as a Function of pH

pH (buffer)	% enantiomeric excess	pH (buffer)	% enantiomeric excess
6.0 (MES)	8.6(7)	9.0 (CAPSO)	5.8(1)
7.0 (HEPES)	6.7(7)	10.0 (CAPS)	5.6(1)
8.0 (Tris)	4.8(4)	11.0 (CAPS)	4.8(2)

The distribution of the reaction products remains largely unchanged over the pH range 6−10, consistent with the proposed mechanism. Only two oxalate-containing products are identified: the major product, *cis-β(SS,RR)*-[Co(2,2,2-tet)-(ox)]⁺, and the minor product, *cis-β(SR,RS)*-[Co(2,2,2-tet)(ox)]⁺. At lower pH, although the distribution of these products is very similar to the thermodynamic distribution obtained after base equilibration, this distribution is determined by the kinetics of the electron transfer reaction since, under the reaction conditions at pH 8.0, there is insufficient time for equilibration. When optically active [Co(ox)₃]³⁻ is used as oxidant, the product mixture is weakly optically active. Below pH 8, the optical activity is found predominantly in the minor *cis-β(SR,RS)*-[Co-(2,2,2-tet)(ox)]⁺ isomer, amounting to 1.4% with a ΔΛ preference. Optical activity in the major isomer is negligible and is estimated to be less than 0.1%. At higher pH where [Co(2,2,2-tet)(OH₂)(OH)]⁺ is the predominant reagent, problems of the competing mutarotation reaction interfere with measurement of the chiral induction.

In the reaction with [Co(2,3,2-tet)(OH₂)₂]²⁺, a single oxalate-containing product, identified as *cis-β(SS,RR)*-[Co(2,3,2-tet)-(ox)]⁺, was isolated in 80% yield. This less than quantitative recovery is puzzling but may be due to the presence of products of singly bridged reactions which hydrolyze in the subsequent separation and analysis. The rate law found is similar to that for [Co(2,2,2-tet)(OH₂)₂]²⁺, and an identical mechanism is proposed. The value for k_a was determined to be $3.58(8) \times 10^4$ M⁻¹s⁻¹, but an accurate value for k_b was not obtained as a result of complications from precipitation at higher pH. As in the reaction with [Co(2,2,2-tet)(OH₂)₂]²⁺, the value of k_b was set to zero which gives $K_a = 1.25 \times 10^{-12}$. The decrease in rate at lower pH can be described by the thermodynamic dissociation of the 2,3,2-tet ligand, $K_1 = 1.58 \times 10^{12}$ M⁻¹, with acidity constants for the ligand $K_{a1} = 6.91 \times 10^{-11}$, $K_{a2} = 5.89 \times 10^{-10}$, $K_{a3} = 1.32 \times 10^{-7}$, and $K_{a4} = 3.24 \times 10^{-6}$.[23] Protonation has not been noted above pH 5.17 in the case of [Co(2,3,2-tet)(OH₂)₂]²⁺, and in any case the protonation should occur at lower pH than with [Co(2,2,2-tet)(OH₂)₂]²⁺. In this reaction, the oxalate-containing product is *cis-β(SS,RR)*-[Co-(2,3,2-tet)(ox)]⁺ exclusively and the chiral induction is larger, amounting to 5% with a ΔΔ preference. Unlike the reaction with [Co(2,2,2-tet)(OH₂)₂]²⁺, there is some evidence that the stereoselectivity increases, by almost 50%, with decreasing pH, Table 2. Although kinetic evidence for additional acid- or buffer-catalyzed pathways in this reaction was not obtained, minor changes in rate may be swamped by the larger thermodynamic effects which occur in this pH range.

The kinetics of the reaction with [Co(5(*R,S*)-Me-2,2,2-tet)-(OH₂)₂]²⁺ were not examined. The ligand is noted to bind stereospecifically to metals, but this has been shown to be an oversimplification.[16,24] However, reaction products obtained when optically active ligand is used are diastereomers and when isolated are as optically pure as the starting ligand. Stoichiometry studies reveal the presence of only three oxalate-containing isomers as products in the reaction, identified by

(22) Smith, R. M.; Martell, A. E. *Critical Stability Constants, Vol. 2;* Plenum: New York, 1975; pp 105−106.

(23) Anderegg, G. A.; Blauenstein, P. *Helv. Chim. Acta* **1982**, *65*, 162− 169. Anderegg, G. A.; Blauenstein, P. *Helv. Chim. Acta* **1982**, *65*, 913−923

(24) Saburi, M.; Sawai, T.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1086−1092.
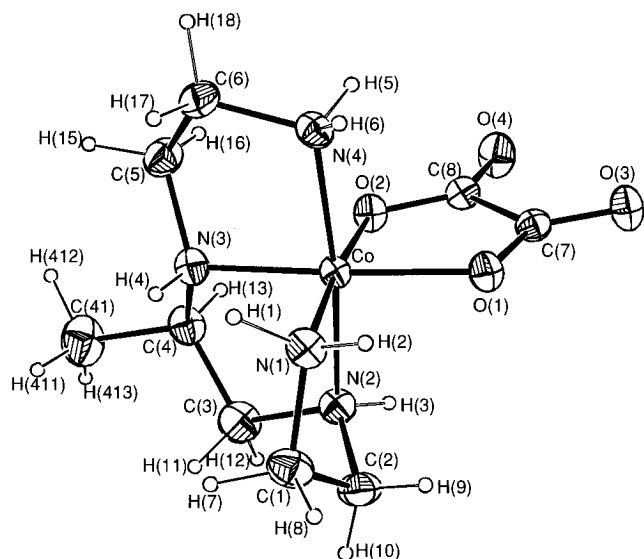
Figure 6. Ortep drawing of $\Lambda(\lambda\lambda\delta)$-*cis-$\beta$(SS)-endo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ illustrating the numbering scheme. Important bond lengths (Å) and angles (deg) are as follows: Co−O(1) = 1.922(1), Co−O(2) = 1.910(2), Co−N(1) = 1.945(2), Co−N(2) = 1.950(2), Co−N(3) = 1.924(2), Co−N(4) = 1.947(2); O(1)−Co−N(1) = 90.37(7). The thermal ellipsoids are drawn at the 50% level.
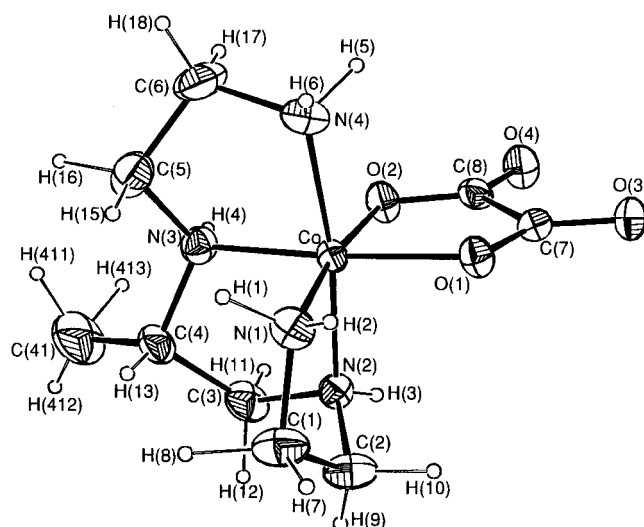

Figure 7. Ortep drawing of $\Lambda(\lambda\delta\lambda)$-*cis-$\beta$(SR)-exo*-[Co(5(*S*)-Me-2,2,2-tet)(ox)]$^+$ illustrating the numbering scheme. Important bond lengths (Å) and angles (deg) are as follows: Co−O(1) = 1.915(3), Co−O(2) = 1.909(3), Co−N(1) = 1.962(3), Co−N(2) = 1.956(4), Co−N(3) = 1.913(4), Co−N(4) = 1.959(5); O(1)−Co−N(1) = 87.9(1). The thermal ellipsoids are drawn at the 50% level.

X-ray crystallography and NMR as *cis-β(SS,RR)-endo*-[Co-(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$, *cis-β(SS,RR)-exo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ and *cis-β(SR,RS)-exo*-[Co(5(*S,R*)-Me-2,2,2-tet)-(ox)]$^+$ in the ratios 35%, 30%, and 35% respectively. Crystal structures were obtained for *cis-β(SS,RR)-endo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ and *cis-β(SR,RS)-exo*-[Co(5(*S,R*)-Me-2,2,2-tet)-(ox)]$^+$ and these are illustrated in Figures 6 and 7, respectively. The structures of the complex ions closely resemble those of the corresponding unmethylated derivatives. The identity of *cis-β(SS,RR)-exo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ was deduced from experiments performed with 5(*R*)-Me-2,2,2-tet as ligand. The absolute configuration at the metal center under these conditions is Λ and the complex does not mutarotate to give the known Λ-*cis-β(SS)-endo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ so that Λ-*cis-β(SR)-endo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ can be ruled out as a possible structure. This leaves only Λ-*cis-β(SS)-exo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ and Λ-*cis-β(SR)-exo*-[Co(5(*R*)-

Me-2,2,2-tet)(ox)]$^+$ or the α isomer as reasonable possibilities. The NMR, UV−visible, and circular dichroism spectroscopic parameters are more consistent with the former assignment, and the similarity of the chromatographic behavior with that of Λ-*cis-β(SS)-endo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ leads one to the conclusion that the third isomer is Λ-*cis-β(SS)-exo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$.

Stereoselectivity in the reaction between [Co(ox)$_3$]$^{3-}$ and [Co-(5(*R,S*)-Me-2,2,2-tet)]$^{2+}$ was examined in two different experiments. With use of optically active [Co(5(*R*)-Me-2,2,2-tet)]$^{2+}$, reactions were examined under conditions of excess racemic [Co(ox)$_3$]$^{3-}$. At the termination of the reaction, the remaining [Co(ox)$_3$]$^{3-}$ was isolated and optical activity induced in this reagent was determined. From this measurement, an average selectivity, weighted in the relative proportions of the product forms, of 0.67% with a Δ preference is obtained for the reaction. The [Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ products isolated from the reaction mixtures are optically pure. Absolute configurations, determined from the circular dichroism spectra are Λ, Λ, and Δ respectively for the *cis-β(SS)-endo*-[Co(5(*R*)-Me-2,2,2-tet)-(ox)]$^+$, *cis-β(SS)-exo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ and *cis-β-(RS)-exo*-[Co(5(*R*)-Me-2,2,2-tet)(ox)]$^+$ isomers. The second method yields information on the stereoselectivity for the formation of each of the isomeric species. In this case, the reaction is run with optically active [Co(ox)$_3$]$^{3-}$ and an excess of [Co(5(*R,S*)-Me-2,2,2-tet)]$^{2+}$. The oxalate-containing reaction products are isolated, and the individual optical purity can be determined by comparison with optically pure samples. All three complexes reveal chiral induction. When Δ-[Co(ox)$_3$]$^{3-}$ is used, two of the complexes, *cis-β(SS,RR)-endo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ and *cis-β(SS,RR)-exo*-[Co(5(*R,S*)-Me-2,2,2-tet)(ox)]$^+$ show a 2.8% and 1.7% enantiomeric excess of the Δ- forms while *cis-β(SR,RS)-exo*-[Co(5(*S,R*)-Me-2,2,2-tet)(ox)]$^+$ shows a 6.5% excess of the Λ-form. The selectivities are small, comparable with the selectivities for the unmethylated derivatives. The two methods, with excess reductant and with excess oxidant, give satisfactory agreement when both isomer distribution and selectivity are combined.

Discussion

The reactions under study are inner-sphere electron transfer processes in which ox^{2-} is transferred from the oxidant [Co(ox)$_3$]$^{3-}$ to the labile cobalt(II)−amine reductant. Kinetic studies show that the rates are first order in both reactants and there is no evidence for the formation of a long-lived bridged intermediate. The rates of the reactions for [Co(2,2,2-tet)-(OH$_2$)$_2$]$^{2+}$ and [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$ may be compared, Table 3, with that for [Co(en)$_2$(OH$_2$)$_2$]$^{2+}$ reported previously.[3] An order of magnitude increase in rate is found for the tetradentate chelate ligands, and the reasons for this are not immediately obvious. Some consideration of the nature of the rate-limiting step is merited.

Structural information including species distribution is not available for [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$, [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$, and their substituted analogues; however, the ligands and the complexes are expected to be fluxional. For [Co(2,2,2-tet)-(OH$_2$)$_2$]$^{2+}$, there have been two studies of the ligand dissociation process. The mechanism involves rate limiting rupture of a Co−N bond. Pulse radiolytic reduction of [Co(2,2,2-tet)Cl$_2$]$^+$ gives a value of 2.1 × 10^3 s^{-1} at 25 °C for this process[25,26] while a stopped-flow study gives a value which is 4-orders of

(25) Lilie, J.; Shinohara, N.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6516−6520.
(26) Shinohara, N.; Lilie, J.; Simic, M. G. *Inorg. Chem.* **1977**, *16*, 2809−2813.

Table 3. Second-Order Rate Constants and Observed Stereoselectivities for Inner-Sphere Electron Transfer Reactions of Cobalt(II) Complexes with Optically Active [Co(ox)$_3$]$^{3-}$

reductant	% enantiomeric excess	k_{so} (M^{-1}s^{-1})
cis-β(*SR,RS*)-[Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$	1.7(1), ΔΛ	1.6×10^4
cis-β(*SS,RR*)-[Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$	<0.1(1)	
cis-β(*SS,RR*)-[Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$	5.5(7), ΔΛ	3.6×10^4
cis-β(*SS,RR*)-*exo*-[Co(5(*R,S*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$	1.7(2), ΔΛ	
cis-β(*SS,RR*)-*endo*-[Co(5(*R,S*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$	2.8(5), ΔΛ	
cis-β(*SR,RS*)-*exo*-[Co(5(*S,R*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$	6.5(3), ΔΛ	
[Co(en)$_2$(OH$_2$)$_2$]$^{2+}$	1.5, ΔΛ[a]	3.3×10^{3} [a]
[Co(*N,N*′-Me$_2$en)$_2$(OH$_2$)$_2$]$^{2+}$	8.0, ΔΛ[b]	
[Co(*N,N*-Me$_2$en)$_2$(OH$_2$)$_2$]$^{2+}$	4.3, ΔΛ[b]	
[Co(bpy)$_2$(OH$_2$)$_2$]$^{2+}$	19, ΔΛ[c]	1.6×10^{2} [c]
[Co(phen)$_2$(OH$_2$)$_2$]$^{2+}$	63, ΔΛ[c]	9.4×10^{1} [c]

[a] Reference 3. [b] Reference 4. [c] Reference 5.

magnitude slower[27] and most likely relates to a subsequent process. Thus, within the constraints of the present study, isomerization of the reductant can take place quite readily on the time scale of the electron transfer reaction.

The coordinated water molecules in [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ are labile with solvent exchnge rates estimated to be ≈10^8 s^{-1}.[28] Substitution rates for complexation reactions of [Co(2,2,2-tet)-(OH$_2$)$_2$]$^{2+}$ with 2,2′-bipyridine,[28] pada,[29] and 5-nitrosalicylate-(−2)[30] are 2.3 × 10^5 M^{-1} s^{-1}, 2.1 × 10^4 M^{-1} s^{-1}, and 6.2 × 10^7 M^{-1} s^{-1}. The oxidant [Co(ox)$_3$]$^{3-}$ has a −3 charge and might be expected to react faster than the ligands of lower charge so that a substitution-controlled mechanism can be eliminated. Rate-determining ring closure is a possibility. It can be argued that ring closure of the oxalato chelate must take place before electron transfer since ring closure of monodentate oxalate is slow for species such as *cis*-[Co(en)$_2$Hox]$^+$, with k = 4.6 × 10^{-5} s^{-1} at pH 5, increasing to k = 1.6 × 10^{-4} s^{-1} at pH 1.[31] However, there is no evidence for rate-limiting ring closure in other studies of substitution reactions with [Co(2,2,2-tet)-(OH$_2$)$_2$]$^{2+}$.

The trend in rates observed in Table 3 is most readily explained by rate-limiting electron transfer within a preformed doubly bridged precursor complex. The stronger ligand field of the secondary nitrogen donors favors the higher oxidation state of the reductant with [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and [Co-(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$ and the resultant change in the driving force for the reactions gives rise to a higher rate. There is one other redox process with which comparisons might be made, the reactions of [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ with O$_2$.[21] The rate constant for this process which also involves inner-sphere electron transfer is 2.5 × 10^4 M^{-1} s^{-1} at 25 °C and 0.10 M ionic strength.

In both of the reactions in which rate studies were examined, the rate decreases with increasing pH as a result of hydrolysis of one of the coordinated water molecules on the reductant to give a less reactive aqua−hydroxo species. The decrease in reactivity $k_{H2O}/k_{OH}-$ is >50 for both [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$. The acidity constant for [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ obtained in the present study is a factor of 4 larger than that obtained spectrophotometrically and kinetically for the reaction with O$_2$ reported in the literature.[21] Although this may reflect differences in the conditions of the two studies and some

of the uncertainties of working with very oxygen sensitive solutions, it also to be expected that the observed hydrolysis constant will vary with the nature of the reactant species. Solutions of [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ contain an unknown distribution of isomers. Only the cis-β-isomers react with [Co(ox)$_3$]$^{3-}$, and the major pathways in the oxidation by O$_2$ involve participation of both cis-α and cis-β isomers.[32]

Interestingly the reaction with O$_2$ shows an increase in rate with decreasing pH[21] whereas a decrease is observed with [Co(ox)$_3$]$^{3-}$. This is believed to be a reflection of the requirement for chelate formation in the latter reaction and may indicate a change in mechanism from rate-limiting electron transfer to rate-limiting ring closure as a result of the requirement to cleave the stronger Co−OH bond. The presence of an intermediate of the type [Co(2,2,2-tet)(OH)(ox)Co(ox)$_2$]$^{2-}$ where the [Co(ox)$_3$]$^{3-}$ "ligand" is attached in a monodentate fashion would also provide an explanation for the difference in the observed acidity constants for the two reactions.

The distribution of products in these reactions reflects both the composition and relative reactivities of the reactant species. There is no information on species distribution among the labile cobalt(II) reactants although in the case of [Co(2,3,2-tet)-(OH$_2$)$_2$]$^{2+}$, the trans isomer is suggested as the most stable species.[33] The isolated oxalato-chelated products are necessarily, cis and interconversions between the isomers must take place prior to the electron transfer process since interconversions among the reaction products are generally sluggish. It is of considerable interest that only cis-β isomers are isolated from all three reaction mixtures. In part the explanation may be that the cis-α forms of [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and [Co(2,3,2-tet)-(OH$_2$)$_2$]$^{2+}$ are not thermodynamically favored. In the case of [Co(2,2,2-tet)(gly)]$^{2+}$, the cis-β isomers predominate on thermodynamic equilibration at 25 °C to the extent of 49:1.[12] The predominance of the β(*SS,RR*) isomers over the β(*SR,RS*) isomers in the present case also reflects a similar result with [Co(2,2,2-tet)(gly)]$^{2+}$ complexes. Molecular mechanics studies on the latter species suggest[11,12] that this is due to the balance of unfavorable intramolecular interactions within the (2,2,2-tet) ligand in the case of the β(*SR,RS*) isomer and unfavorable interactions between the ternary ligand and the (2,2,2-tet) ligand in the case of β(*SS,RR*). No molecular mechanics study was carried out in the present work, but a similar result might be anticipated. In addition, the structures of *cis*-β-(oxalato)-((4*R*,6*R*)-dimethyl-3,7-diazanonane-1,9-diamine)cobalt(III) per-

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chlorate[34] and its N-methylated derivative *cis-β*-(oxalato)-((6*R*,8*S*)-dimethyl-2,5,9,12-tetraazatridecane)cobalt(III) perchlorate[35] are related to *cis-β(SS,RR)*-[Co(2,3,2-tet)(ox)]$^+$ and reflect the same isomeric forms.

There is a large amount of structural data on oxalato–tetramine complexes of cobalt(III)[4,36–40] in part because of intense interest in the formation of conglomerate crystals by these species.[36] In all four structures examined, the complexes are racemic mixtures. Although racemic Λ,Δ-*cis-β(SR,RS)*-[Co-(2,2,2-tet)(ox)]ClO$_4$ crystallizes in a chiral space group, the chirality is the result of the spatial distribution of the complex ions with respect to the polar axis. In all cases except Λ,Δ-*cis-β(SS,RR)-endo*-[Co(5(*R*,*S*)-Me-2,2,2-tet)(ox)]Cl·2H$_2$O, there is an extensive network of hydrogen bonds between the complexes in the crystal. The absence of three-point contacts is notable, and this may preclude the chiral recognition required for conglomerate formation.[36]

The mutarotation of *cis-β(SR,RS)*-[Co(2,2,2-tet)(ox)]$^+$ to *cis-β(SS,RR)*-[Co(2,2,2-tet)(ox)]$^+$ has a second-order rate constant of 490 M^{-1} s^{-1}. The rate is base catalyzed, and conversion from one isomer to the other is believed to proceed by proton abstraction at the planar secondary nitrogen, followed by an inversion and reprotonation at that site at a rate which is close to diffusion.[12] Base catalysis in this epimerization presents a problem for the detection of stereoselectivity since the reactions themselves are carried out in weakly basic media. Unless precautions are taken, isomerization can take place during the separation and analysis, particularly if strongly acidic conditions are not used to quench the reaction.

Spectroscopic parameters have been determined for three derivatives of [Co(5-Me-2,2,2-tet)(ox)]$^+$. The spectra are very similar to the corresponding spectra for derivatives of [Co(2,2,2-tet)(ox)]$^+$ determined previously. It should be pointed out that in general, the *cis-β(SR)*-[Co(2,2,2-tet)(ox)]$^+$ isomers have larger extinction coefficients in the visible region than the corresponding *cis-β(SS)*-[Co(2,2,2-tet)(ox)]$^+$ isomers, while the extinction coefficient of *cis-α(SS)*-[Co(2,2,2-tet)(ox)]$^+$ is smaller than the corresponding cis-β isomer. This feature can be useful for assigning structure.[41] The use of 5(*R*)-Me-2,2,2-tet allows the assignment of absolute configuration to the complexes. The similarity in the spectroscopic parameters of the 5(*R*)-Me-2,2,2-tet derivatives which are optically pure and those for 2,2,2-tet

gives credence to both the values for Δε and the structural assignments.[19]

Stereoselectivity in the reactions was investigated with use of optically active [Co(ox)$_3$]$^{3-}$ as oxidant, and the results are summarized in Table 3. In the reaction with [Co(2,2,2-tet)-(OH$_2$)$_2$]$^{2+}$ at pH 6–8, the minor, (*SR*,*RS*) isomer is the only one which shows significant (1.7% ΔΛ) optical activity. Selectivity in the reaction with *cis-β(SR,RS)-exo*-[Co(5(*S*,*R*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ is significantly larger but in the same sense (6.5% ΔΛ). In contrast, with [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$ the sole (*SS*,*RR*) product has a 5.5% ΔΔ preference and the reactions with *cis-β(SS,RR)-endo*-[Co(5(*R*,*S*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and *cis-β(SS,RR)-exo*-[Co(5(*R*,*S*)-Me-2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ also show a ΔΔ preference. The change in stereoselectivity with the change in the configuration of the in-plane nitrogen is of significant interest and suggests that it is the pattern of hydrogen bonding which surrounds the bridging ligand which determines the sense of the stereoselectivity.

The magnitude of the selectivity can be correlated with the conformational lability of the reactant complexes. The central six-membered chelate ring in [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$ is conformationally more rigid than the five-membered ring in [Co-(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ while the addition of a methyl group on the ligand backbone also reduces conformational freedom. However, in comparison with the significantly more rigid [Co-(bpy)$_2$(OH$_2$)$_2$]$^{2+}$ and particularly [Co(phen)$_2$(OH$_2$)$_2$]$^{2+}$, the selectivities shown by these amines are very small. Thus, while the pattern of hydrogen bonding serves to direct the stereochemical preference in the reaction, the energetic consequences of this interaction are modest.

In summary, the reductions of [Co(ox)$_3$]$^{3-}$ by [Co(2,2,2-tet)-(OH$_2$)$_2$]$^{2+}$ and derivatives are inner-sphere processes in which electron transfer through a doubly chelated oxalate bridge is rate limiting. The stereochemical course of the reactions is such that cis-β isomers are produced. The pattern of hydrogen bonding around the open coordination sites of the reductant determines the sense of the chiral induction, and the magnitude of the induction is related to the fluxionality of the amine backbone.

Supporting Information Available: Text describing the structure solution and tables giving crystal data and details of structure determinations, fractional atom coordinates and *B* values, bond lengths, bond angles, anisotropic thermal parameters, ^{13}C NMR data for the comlex ions, pseudo-first-order rate constants and final product distributions for the mutarotation of *cis-β(SR,RS)*-[Co(2,2,2-tet)(ox)]$^+$ to an equilibrium mixture of *cis-β(SS,RR)*-[Co(2,2,2-tet)(ox)]$^+$ and *cis-β(SR,RS)*-[Co(2,2,2-tet)(ox)]$^+$, and pseudo-first-order rate constants for the oxidations of [Co(2,2,2-tet)(OH$_2$)$_2$]$^{2+}$ and [Co(2,3,2-tet)(OH$_2$)$_2$]$^{2+}$ by [Co(ox)$_3$]$^{3-}$ (35 pages). Ordering information is given on any current masthead page.

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