chemistry of Ru(III)–DMSO derivatives. The mechanism of the synthesis of *cis*-$RuCl_2(DMSO)_4$ from hydrated $RuCl_3$ has been partially elucidated, and a detailed picture of the relationships between the redox state of the ruthenium atom and the composition and stability of its coordination sphere has been obtained. Comparison of the structures and vibrational spectra of Ru(III)– and Ru(II)–DMSO derivatives has allowed one to draw an analysis of the relative importance of σ-donor and π-acceptor properties of the DMSO ligand.

In view of our results and of those reported in ref 40, all the previous literature on this subject should be reconsidered. In our opinion, most of the complexes described as Ru(III)–DMSO derivatives are actually either Ru(II)–DMSO or Ru(III)–DMS species. In the absence of magnetic moment measurements, a careful examination of the complexes' NMR or visible spectra (extinction coefficients of Ru(III)–DMSO complexes are about 1 order of magnitude greater than those of Ru(II) derivatives) should allow an easy determination of the metal oxidation state. On the other hand, the systematic synthesis of the corresponding hexadeuterated derivatives should allow unambiguous IR assignments, avoiding confusion between DMSO and DMS complexes. Finally, in agreement with the trend of the complex reduction potentials versus the number of coordinated DMSO's, we believe that the existence of stable Ru(III) complexes with more than three DMSO ligands, such as $[Ru(DMSO)_5Cl]Cl_2$ and $[Ru(DMSO)_6]Cl_3$, is rather improbable.

New perspectives in the chemistry of the reported complexes can be easily envisaged. For example, due to the rather unfavorable situation of the two trans S-bonded DMSO's in both **1** and **2**, substitution of at least one of them with a stronger σ-donor ligand should be a relatively easy task.

As to their potential biological properties, the activities of **1** and **2** will be compared to that of the halogen–DMSO–Ru(II) derivatives against metastasizing tumor models. It is worthy of note that complex **1** is isoelectronic and isostructural with the imidazole (Im) derivative $[(Im)H][$*trans*-$Ru(Im)_2Cl_4]$, which shows very good activity toward the chemically induced colorectal murine tumor (a model against which cisplatin is completely inactive)[55–58] and is presently entering phase-one clinical trials.[56] Comparison between the biological and chemical properties (in particular kinetic and redox) of these complexes will help to understand the influence of the axial ligands on their antitumor properties. Interestingly enough, in view of the "activation by reduction mechanism" proposed for Ru(III) complexes as antitumor agents,[59–61] both **1** and **2** have biologically accessible reduction potentials.[61]

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Supplementary Material Available: For **1** and **2**, tables of anisotropic temperature factors for non-hydrogen atoms and positional and thermal parameters for hydrogen atoms (4 pages); tables of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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Inner-Sphere Electron-Transfer Stereoselectivities in the Oxidation of Bis(1,2-diaminoethane)cobalt(II) Derivatives by $[Co(ox)_3]^{3-}$

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$[Co(N,N\text{-}Me_2en)_2(ox)]^+$ (N,N-Me_2en = N,N-dimethyl-1,2-diaminoethane, ox^{2-} = oxalate(2−)) is the sole product in the inner-sphere reduction of $[Co(ox)_3]^{3-}$ by cobalt(II) in solutions of N,N-Me_2en and is formed stereoselectively with an enantiomeric excess of 4.3% ΔΛ. The structure of this product has been determined by X-ray crystallography. $[\Delta\text{-}Co(N,N\text{-}Me_2en)_2(ox)]I$ crystallizes in the orthorhombic space group *Pbca* (No. 61) with $Z = 8$, $a = 15.206$ (2) Å, $b = 12.523$ (2) Å, $c = 16.999$ (2) Å, and $R = 0.039$ for 2681 reflections. Four inner-sphere products are isolated in the corresponding reaction with N,N'-Me_2en (N,N'-Me_2en = N,N'-dimethyl-1,2-diaminoethane). The structure of the major product $[\Lambda(RS,RS)/\Delta(SR,SR)\text{-}Co(N,N'\text{-}Me_2en)_2(ox)]^+$ (40%) has been determined by X-ray crystallography. $[\Delta(SR,SR)\text{-}Co(N,N'\text{-}Me_2en)_2(ox)]I\cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1$ (No. 4) with $Z = 2$, $a = 8.260$ (2) Å, $b = 7.735$ (1) Å, $c = 13.697$ (3) Å, $\beta = 101.96$ (1)°, and $R = 0.088$ for 2434 reflections. Two isomers $\Lambda(RR,SS)/\Delta(RR,SS)$ (24%) and $\Lambda(SS,RS)/\Delta(RR,SR)$ (22%) are also formed as products. Stereoselectivities are 7.8% ΔΔ, 8.1% ΔΔ, and 7.7% ΔΔ, respectively. The fourth, minor product is also formed stereoselectively but is not unambiguously characterized. Stereoselectivities reflect hydrogen bonding in outer-sphere intermediates in the formation of the inner-sphere precursor complexes.

Introduction

Reduction of $[Co(ox)_3]^{3-}$ (ox^{2-} = oxalate(2−)) by the labile $[Co(en)_3]^{2+}$ (en = 1,2-diaminoethane) occurs[1] by two parallel pathways, an outer-sphere pathway leading to $[Co(en)_3]^{3+}$ and an inner-sphere pathway leading to $[Co(en)_2(ox)]^+$. When $[\Delta\text{-}Co(ox)_3]^{3-}$ is used, both products show chiral induction, and in particular, that for the inner-sphere pathway shows an enantiomeric excess of 1.5% of the Δ isomer, a 1.5% ΔΔ process. There are few other reports of stereoselectivity in inner-sphere reactions,[2,3] and further study of this system is warranted. The small chiral induction in the formation of $[Co(en)_2(ox)]^+$ is proposed to be a consequence of the bidentate oxalate bridge, which prevents intimate contact of the discriminating, nonbridging ligands. In

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this report, *N*,*N*-dimethyl-1,2-diaminoethane and *N*,*N′*-dimethyl-1,2-diaminoethane have been used as bidentate ligands for the cobalt(II) reductant to investigate the effect of increased steric bulk on the chiral discrimination in the reaction. The expected inner-sphere products, $[Co(N,N\text{-}Me_2en)_2(ox)]^+$ and $[Co(N,N'\text{-}Me_2en)_2(ox)]^+$, are not well described in the literature,[4,5] and a more complete characterization of these complexes has been undertaken.

Experimental Details

Preparation[6] and resolution[7,8] of $[\Lambda\text{-}(-)_{589}\text{-}Co(ox)_3]^{3-}$ ($\epsilon_{605} = 165$ M^{-1} cm^{-1}, $\Delta\epsilon_{622} = 3.80$ M^{-1} cm^{-1}) were carried out as described previously. Preparation and resolution of $[Co(en)_2(ox)]Cl \cdot H_2O$ ($\epsilon_{500} = 103$ M^{-1} cm^{-1}) were achieved by literature methods;[9] the absolute configuration is $[\Lambda\text{-}(+)\text{-}Co(en)_2(ox)]^+$ ($\Delta\epsilon_{520} = 2.65$ M^{-1} cm^{-1}).[10] The preparation of $[Co(N,N\text{-}Me_2en)_2(ox)]Cl \cdot 3.5H_2O$ was similar to that for $[Co(en)_2(ox)]Cl \cdot H_2O$ with minor modifications, since the product is more sensitive to thermal decomposition. Spectroscopic characteristics are consistent with those reported in the literature[4] ($\epsilon_{547} = 132$ M^{-1} cm^{-1}, $\epsilon_{390} = 148$ M^{-1} cm^{-1}). $[Co(N,N\text{-}Me_2en)_2(ox)]I$ was prepared by adding excess NaI to a saturated solution of the chloride salt at 4 °C, and crystals of the iodide salt suitable for X-ray analysis were obtained in this manner. Partial resolution of $[Co(N,N\text{-}Me_2en)_2(ox)]^+$ was accomplished by addition of a stoichiometric amount of silver (−)-3-bromocamphor-8-sulfonate to a solution of the cobalt(III) salt in 1% HNO_3 at 45–55 °C. After 15 min, the mixture was cooled in an ice bath ($\Delta\epsilon_{558}(\max) = -0.15$ M^{-1} cm^{-1}). Repeated recrystallization from water gave improvements in optical purity, but even after seven recrystallizations, no indication of a limiting value was reached. The absolute configuration of this isomer is assigned as $[\Delta\text{-}(-)\text{-}Co(N,N\text{-}Me_2en)_2(ox)]^+$ by comparison with $[\Lambda\text{-}(+)\text{-}Co(en)_2(ox)]^+$.

The preparations of $[Co(N,N'\text{-}Me_2en)_2(ox)]I$ and $[Co(N,N'\text{-}Me_2en)_2(ox)]ClO_4$ were carried out in the dark, using a procedure similar to that for $[Co(en)_2(ox)]Cl$. Slow crystallization from a saturated solution of the iodide salt at 4 °C produced long, thin plates of the dihydrate, $[Co(N,N'\text{-}Me_2en)_2(ox)]I \cdot 2H_2O$, suitable for X-ray analysis. The ^1H NMR spectrum for the $[Co(N,N'\text{-}Me_2en)_2(ox)]^+$ product is identical with that reported previously[5] and is referred to as the Λ(*RS*,*RS*)/Δ-(*SR*,*SR*) isomer.[11] Absorption maxima are at 522 nm ($\epsilon_{522} = 125$ M^{-1} cm^{-1}) and 372 nm ($\epsilon_{372} = 161$ M^{-1} cm^{-1}). Complete resolution of $[Co(N,N'\text{-}Me_2en)_2(ox)]^+$ was achieved with silver (−)-3-bromocamphor-8-sulfonate by the procedure described above for the $N,N\text{-}Me_2en$ derivative. Recrystallization from water gave the optically pure isomer, $\Delta\epsilon_{555} = -2.04$ M^{-1} cm^{-1}, which was isolated as the chloride salt by ion-exchange on Dowex 50x2-400 resin (H^+ form) and eluted with 0.25 M HCl. The absolute configuration of this isomer is assigned as $[\Delta\text{-}(-)\text{-}Co(N,N'\text{-}Me_2en)_2(ox)]^+$.[5]

Examination of crystals of $[Co(N,N\text{-}Me_2en)_2(ox)]I$ and $[Co(N,N'\text{-}Me_2en)_2(ox)]I \cdot 2H_2O$ was carried out on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal incident beam monochromator. A summary of the crystal data and intensity collection parameters is presented in Table I. All calculations were performed on a VAXstation 3200 computer.

Table I. Summary of Crystal Data and Intensity Collection Parameters for $[Co(N,N\text{-}Me_2en)_2(ox)]I$ and $[Co(N,N'\text{-}Me_2en)_2(ox)]I \cdot 2H_2O$

complex	$[Co(N,N\text{-}Me_2en)_2(ox)]I$	$[Co(N,N'\text{-}Me_2en)_2(ox)]I \cdot 2H_2O$
chem formula	$[CoO_4N_4C_{10}H_{24}]I$	$[CoO_6N_4C_{10}H_{28}]I$
fw	450.2	486.2
cryst dimens, mm	0.30 × 0.52 × 0.27	0.06 × 0.19 × 1.44
color	dark purple	red violet
space group	*Pbca* (No. 61)	$P2_1$ (No. 4)
T, K	293	293
a, Å	15.206 (2)	8.620 (2)
b, Å	12.523 (2)	7.735 (1)
c, Å	16.999 (2)	13.697 (3)
β, deg		101.96 (1)
V, $Å^3$	3237.0	893.4
Z	8	2
ρ_{calc}, g/cm^3	1.85	1.81
ρ_{obsd}, g/cm^3	1.87	
radiation (λ, Å)	Mo Kα (0.71073)	Cu Kα (1.5418)
scan technique	$\theta-2\theta$	$\theta-2\theta$
maximum 2θ, deg	54.9	125.4
μ(Mo Kα), cm^{-1}	29.7	219.1
transm coeff	0.75–0.99	0.213–0.995
no. of data measd	4038	3938
no. of unique obsd data	2681	2434
criterion for obsd data	$F_o > 3.0\sigma(F_o)$	$F_o > 3.0\sigma(F_o)$
data/variable ratio	13.0	12.3
$R_1 = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.039	0.088
$R_2 = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w F_o^2]^{1/2}$	0.034	0.098
EOF	1.67	2.67

For $[Co(N,N\text{-}Me_2en)_2(ox)]I$, a total of 4038 reflections were measured. The intensity of four standard reflections, measured every 60 min, showed no significant trends. Data reduction[12] included Lorentz, polarization, and empirical absorption[13] corrections. The structure was solved by direct methods.[14,15] After three cycles of least-squares refinement, a difference electron density Fourier map revealed alternative positions for three carbon atoms of one *N*,*N*-dimethylethylenediamine ligand (C(7), C(81), and C(82)) with occupancy factors 0.60 and 0.40. The final cycles of least-squares refinement based on the 2681 observed reflections included hydrogen atoms as idealized fixed contributors.[16] All non-hydrogen atoms were assumed to vibrate anisotropically. The highest residual peak (1.4 e/$Å^3$) in the final difference electron density Fourier map is near the iodide anion.

Crystals of $[Co(N,N'\text{-}Me_2en)_2(ox)]I \cdot 2H_2O$ formed as needles that were extremely susceptible to mechanical fracture. All samples that were examined exhibited high mosaic spread across the narrow directions. The best crystal obtained still had full widths at half-heights for the Ω scans of 0.85°. A total of 3691 reflections were measured from this sample. Four standard reflections, measured every 90 min, showed significant decline in intensity. Data reduction[16] included Lorentz, polarization, linear decay (correction factors 1.000–1.210), and empirical absorption[13] corrections. The structure was solved by the Patterson heavy-atom method.[17] Final cycles of least-squares refinement based on the 2434 observed reflections included hydrogen atoms as idealized fixed contributors.[16] All non-hydrogen atoms were assumed to vibrate anisotropically. The highest peaks (up to 5.0 e/$Å^3$) in the final difference electron density Fourier map were associated with the iodide anion. A difference electron density Fourier map calculated with the iodide atom removed did not reveal disorder. It is presumed that the high discrepancy indices for this structure result from the low quality of the data crystal and the decomposition during data collection.

Stoichiometry and product analysis in the oxidations of $[Co(N,N\text{-}Me_2en)_2]^{2+}$ and $[Co(N,N'\text{-}Me_2en)_2]^{2+}$ by $[Co(ox)_3]^{3-}$ were investigated by HPLC and conventional ion-exchange chromatography. Free-base ligands $N,N\text{-}Me_2en$ (Aldrich, 95%) and $N,N'\text{-}Me_2en$ (Aldrich, 97%) were distilled before use. NMR analysis indicated that $N,N'\text{-}Me_2en$ was contaminated with a small amount (~2%) of *N*-Meen. In general, argon-purged solutions of cobalt(II) (~0.02 M) containing the appro-

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Table II. Reaction Conditions, Stoichiometry, and Stereoselectivity in the Reduction of $[Co(ox)_3]^{3-}$ by $[Co(N,N'\text{-}Me_2en)_2]^{2+}$ and $[Co(N,N\text{-}Me_2en)_2]^{2+}$ in Aqueous Solution at 23.0 ± 0.5 °C

	$10^3[Co^{III}]$, M	$10^2[Co^{II}]$, M	10^2[ligand],[a] M	product	reacn stoich, %	stereosel,[b] % ee
Λ	1.68	1.90 (Cl^-)	4.08 (*N,N*)		91[c]	3.17 ΔΛ
Λ	5.66	1.81 ($CF_3SO_3^-$)	4.13 (*N,N*)		40	3.43 ΔΛ
Δ	5.65	1.81 ($CF_3SO_3^-$)	4.03 (*N,N*)		38	3.36 ΔΛ
	1.92	1.82 ($CF_3SO_3^-$)	3.79 (*N,N*)		36[c]	
Δ	1.81	1.82 ($CF_3SO_3^-$)	3.74 (*N,N'*)		69	
				A[d]	(23.4)	7.47 ΔΔ
				B	(16.3)	7.68 ΔΔ
				C	(20.2)	8.00 ΔΔ
				D	(40.1)	7.02 ΔΔ
Δ	5.52	1.81 ($CF_3SO_3^-$)	3.94 (*N,N'*)		71	
				A	(25.0)	8.53 ΔΔ
				B	(16.9)	8.67 ΔΔ
				C	(21.4)	7.34 ΔΔ
				D	(36.6)	8.56 ΔΔ
Λ	5.66	1.81 ($CF_3SO_3^-$)	3.89 (*N,N'*)		74	
				A	(24.3)	8.23 ΛΛ
				B	(16.5)	8.03 ΛΛ
				C	(21.0)	7.69 ΛΛ
				D	(38.3)	7.86 ΛΛ

[a] *N,N* = *N,N*-dimethyl-1,2-diaminoethane (95%, Aldrich); *N,N'* = *N,N'*-dimethyl-1,2-diaminoethane (97%, Aldrich). [b] CD analysis before and after product separation indicates a loss of 15% product optical activity during the separation process for the *N,N'* complex. No loss of optical activity of the *N,N* product is observed. Circular dichroism parameters for the isomers of $[Co(N,N'\text{-}Me_2en)_2(ox)]^+$ are assumed similar to those for $[Co(N,N\text{-}Me_2en)_2(ox)]^+$. [c] Reaction Mixture is not filtered prior to quenching with HCl. [d] A = Λ(*RR,SS*)/Δ(*RR,SS*); B = uncharacterized product; C = Λ(*SS,RR*)/Δ(*RR,SR*); D = Λ(*RS,RS*)/Δ(*SR,SR*).

priate amine ligand (~0.04 M) were added to rigorously argon-purged solutions of $[Co(ox)_3]^{3-}$ and aliquots of each resulting solution were filtered and analyzed by HPLC by using a Waters Protein Pak SP-5Pw Sephadex ion-exchange column and 0.01 M $NaNO_3$ as eluent. For conventional chromatographic analysis, product solutions were filtered and quenched in argon-purged HCl to pH 1, diluted (×10) with distilled water, and loaded onto a Dowex 50×2-400 (1 × 20 cm) cation-exchange column, which was subsequently washed with water. The products were separated by elution with 5×10^{-2} M HCl, and the resulting solutions were evaporated to dryness under reduced pressure at 35–40 °C. Stoichiometries of the reactions were determined by comparing the amount of cobalt(III) product with the amount of $[Co(ox)_3]^{3-}$ reactant. Concentrations were determined spectrophotometrically and isomeric distributions determined by HPLC. The results are summarized in Table SI, available as supplementary material.

Stereoselectivity experiments were carried out by using both Λ and Δ isomers of the $[Co(ox)_3]^{3-}$ oxidant, and the products were isolated as described for the stoichiometry experiments. Samples were prepared in 10 cm path length cells at $\sim 10^{-4}$ M as chloride salts for circular dichroism analysis. Product optical activities were measured immediately after reaction and following product separation by chromatographic methods (Table II). Circular dichroism spectra were measured on an Aviv circular dichroism spectropolarimeter, Model 60DS, and UV–visible spectra were measured on a Varian DMS 100 spectrophotometer. Extinction coefficients for the reaction products were determined by atomic absorption measurements. ^1H and ^{13}C NMR spectra were run on a General Electric GN-300 system with reference to the downfield peak of DSS, 3-(trimethylsilyl)-1-propanesulfonate (0 ppm), and 1,4-dioxane (0 ppm) for ^1H and ^{13}C spectra, respectively.

Results and Discussion

Conditions for the electron-transfer reactions were chosen to optimize inner-sphere reduction of $[Co(ox)_3]^{3-}$ by $[Co(N,N'\text{-}Me_2en)_2]^{2+}$ and $[Co(N,N\text{-}Me_2en)_2]^{2+}$. The reactions are rapid and, in both instances, are followed by the formation of fine green precipitates. These precipitates do not contain the products of the inner-sphere pathway, which involves a doubly bridged oxalate intermediate, and were not examined in detail.[18] However, as a consequence of the precipitation, kinetic studies are not possible.

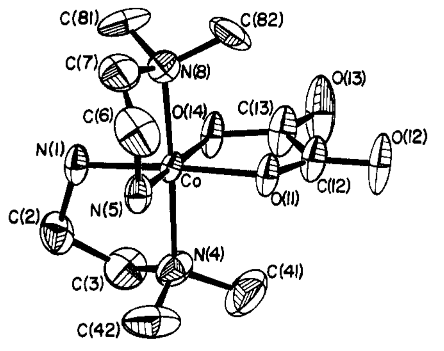

Figure 1. ORTEP diagram of the $[Co(N,N\text{-}Me_2en)_2(ox)]^+$ ion, illustrating the numbering scheme. The thermal ellipsoids are drawn at the 50% level.

There are three possible structural isomers of $[Co(N,N\text{-}Me_2en)_2(ox)]^+$. Two have cis arrangements of the substituted nitrogen atoms, the third has a trans arrangement. Only this latter isomer is found by HPLC from the reaction between $[Co(N,N\text{-}Me_2en)_2]^{2+}$ and $[Co(ox)_3]^{3-}$, presumably because of steric constraints. In Cl^- media, isolated yields in excess of 90% are obtained, but in triflate ($CF_3SO_3^-$) media, preferred because of the larger solubility range for the reductant, the yield is much lower, around 40%. Stereoselectivity in the isolated product, however, is independent of the anion used. UV-visible and ^1H NMR parameters for the purple $[Co(N,N\text{-}Me_2en)_2(ox)]^+$ product are identical with those obtained for this complex generated by alternative routes.[4] The complex has an absorption maximum at 547 nm (ϵ_{547} = 132 M^{-1} cm^{-1}). The ^1H NMR spectrum consists of a single N–*H* signal (δ 5.26 (relative intensity 2)), two methylene multiplets (δ 2.59 (2), 2.87 (2)), and two N–C*H*$_3$ singlets (δ 1.77 (3), 2.20 (3)), which confirms the C_2 symmetry of the ion. The upfield N–C*H*$_3$ groups on each bidentate ligand are positioned over the plane of the oxalate ring.

The X-ray structure of this product was undertaken to confirm the assignment and is shown in Figure 1. Fractional coordinates of $[Co(N,N\text{-}Me_2en)_2(ox)]I$ are presented in Table III. In this structure there is evidence from bond-length data (Table IV) for distortions due to the presence of the bulky methyl groups. In particular, the Co–N bond lengths from the dimethyl-substituted nitrogens of both chelate rings are approximately 0.1 Å longer than the corresponding bond lengths for the unsubstituted nitrogens. These are respectively longer and shorter than the

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(18) However, they dissolve in acid and show only trace contamination by the major cis-inner-sphere products, and when optically active $[Co(ox)_3]^{3-}$ was used, no optical activity was detected in the redissolved precipitate. In general, the precipitate was removed by millipore filtration before subsequent product analyses. It is likely that the precipitate is a neutral *trans*-bis(diamine)cobalt(III) species, containing a monodentate oxalate and a counterion in the trans positions. Such a product might be expected from an alternative inner-sphere pathway made more favorable by the bulky methyl substituents on the amine nitrogens. The chemistry of these species has been investigated extensively (Miskelly, G. M.; Clark, C. R.; Simpson, J.; Buckingham, D. A. *Inorg. Chem.* **1983**, *22*, 3237–3241).

Table III. Fractional Coordinates for the Non-Hydrogen Atoms[a]

atom	*x*	*y*	*z*
	[Co(*N*,*N*-Me$_2$en)$_2$(ox)]I		
I	0.72940 (2)	0.00819 (3)	0.51314 (2)
Co	0.89572 (4)	−0.24380 (5)	0.33888 (4)
O(11)	0.87308 (23)	−0.09845 (24)	0.31480 (22)
O(12)	0.92933 (29)	0.03177 (27)	0.24136 (29)
O(13)	1.0410 (3)	−0.1200 (3)	0.1761 (3)
O(14)	0.98514 (23)	−0.23614 (25)	0.26190 (22)
N(1)	0.93236 (28)	−0.3889 (3)	0.36507 (26)
N(4)	0.9850 (3)	−0.2007 (3)	0.42400 (29)
N(5)	0.79552 (27)	−0.2418 (3)	0.40962 (26)
N(8)	0.8078 (3)	−0.2943 (4)	0.25613 (28)
C(2)	0.9986 (4)	−0.3916 (5)	0.4294 (4)
C(3)	1.0488 (4)	−0.2885 (5)	0.4262 (4)
C(6)	0.7125 (4)	−0.2586 (6)	0.3655 (4)
C(7)	0.7315 (8)	−0.3287 (10)	0.3024 (7)
C(7′)	0.7197 (10)	−0.2483 (12)	0.2824 (9)
C(12)	0.9261 (4)	−0.0615 (4)	0.2638 (4)
C(13)	0.9902 (4)	−0.1432 (4)	0.2279 (4)
C(41)	0.9466 (5)	−0.1858 (6)	0.5022 (4)
C(42)	1.0357 (5)	−0.1008 (6)	0.4073 (5)
C(81)	0.8454 (11)	−0.3908 (13)	0.2131 (9)
C(82)	0.7863 (12)	−0.2171 (15)	0.1988 (8)
C(81′)	0.7983 (13)	−0.4136 (18)	0.2453 (17)
C(82′)	0.8192 (21)	−0.2453 (28)	0.1708 (13)
	[Co(*N*,*N*′-Me$_2$en)$_2$(ox)]I·2H$_2$O		
Co	0.3747 (3)	0.1664 (3)	0.7302 (2)
I	0.1462 (1)	0.000	0.30530 (8)
O(1)	0.346 (1)	0.023 (1)	0.8352 (7)
O(2)	0.387 (1)	−0.038 (1)	0.6560 (7)
O(3)	0.322 (2)	−0.260 (1)	0.8671 (9)
O(4)	0.381 (1)	−0.325 (1)	0.6759 (9)
N(1)	0.604 (1)	0.167 (2)	0.7859 (9)
N(2)	0.364 (1)	0.370 (1)	0.8174 (9)
N(3)	0.401 (1)	0.307 (2)	0.6142 (8)
N(4)	0.144 (1)	0.178 (2)	0.673 (1)
C(1)	0.341 (2)	−0.144 (2)	0.810 (1)
C(2)	0.369 (2)	−0.185 (2)	0.7059 (9)
C(3)	0.694 (2)	−0.005 (3)	0.798 (1)
C(4)	0.623 (2)	0.257 (2)	0.885 (1)
C(5)	0.527 (2)	0.417 (2)	0.870 (1)
C(6)	0.269 (2)	0.347 (2)	0.893 (1)
C(7)	0.494 (2)	0.225 (2)	0.545 (1)
C(8)	0.242 (2)	0.358 (2)	0.557 (1)
C(9)	0.127 (2)	0.211 (2)	0.562 (1)
C(10)	0.039 (2)	0.029 (2)	0.683 (1)
O(1s)	0.073 (2)	−0.066 (4)	−0.055 (2)
O(3s)	0.083 (4)	0.152 (6)	0.059 (2)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

corresponding values in [Co(en)$_2$(ox)]$^+$ (1.98 ± 0.01 Å).[19] Bond lengths and angles for the ligand structures are within normal limits once allowance is made for the disorder in the structure. The chelate ring incorporating N(1), N(4) has an envelope conformation (*ob*) with C(3) out of the plane of the other atoms. Although the other chelate ring incorporating N(5), N(8) has a dominant skew conformation (*lel*), it exhibits disorder, and the minor form also has the envelope conformation (*ob*). The dominant isomer, illustrated in Figure 1, is denoted Δ(δ,λ).

Attempts to resolve the [Co(*N*,*N*-Me$_2$en)$_2$(ox)]$^+$ complex with a variety of reagents and methods met with only partial success,[20] and circular dichroism parameters for the [Co(*N*,*N*-Me$_2$en)$_2$(ox)]$^+$ product are assumed to be similar to those for the [Δ-(−)-Co(*N*,*N*′-Me$_2$en)$_2$(ox)]$^+$ complex. Chiral induction around 4.3% ΔΛ is observed in the oxidation of [Co(*N*,*N*-Me$_2$en)$_2$]$^{2+}$ by optically active [Co(ox)$_3$]$^{3-}$, in the opposite sense from that detected in [Co(en)$_2$(ox)]$^+$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for [Co(*N*,*N*-Me$_2$en)$_2$(ox)]I[a]

	Distances		
Co–O(11)	1.897 (3)	N(8)–C(7)	1.467 (13)
Co–O(14)	1.890 (3)	N(8)–C(7′)	1.526 (16)
Co–N(1)	1.952 (4)	C(12)–C(13)	1.539 (7)
Co–N(4)	2.056 (5)	C(2)–C(3)	1.501 (8)
Co–N(5)	1.941 (4)	C(6)–C(7)	1.416 (14)
Co–N(8)	2.041 (5)	C(6)–C(7′)	1.422 (16)
O(11)–C(12)	1.271 (6)	N(4)–C(41)	1.464 (8)
O(14)–C(13)	1.302 (6)	N(4)–C(42)	1.496 (8)
O(12)–C(12)	1.230 (6)	N(8)–C(81)	1.524 (17)
O(13)–C(13)	1.207 (6)	N(8)–C(82)	1.411 (17)
N(1)–C(2)	1.487 (7)	N(8)–C(81′)	1.512 (21)
N(4)–C(3)	1.466 (7)	N(8)–C(82′)	1.584 (24)
N(5)–C(6)	1.483 (8)		
	Angles		
O(11)CoO(14)	86.13 (14)	CoN(5)C(6)	110.7 (4)
O(11)CoN(4)	91.13 (17)	CoN(8)C(7′)	104.8 (6)
O(11)CoN(5)	88.80 (16)	CoN(8)C(7)	103.8 (5)
O(11)CoN(8)	91.70 (17)	O(11)C(12)O(12)	125.6 (5)
O(14)CoN(1)	89.99 (15)	O(11)C(12)C(13)	115.5 (4)
O(14)CoN(4)	89.93 (18)	O(12)C(12)C(13)	118.9 (5)
O(14)CoN(8)	90.55 (19)	O(14)C(13)O(13)	125.3 (5)
N(1)CoN(4)	84.00 (18)	O(13)C(13)C(12)	122.3 (5)
N(1)CoN(5)	95.43 (17)	O(14)C(13)C(12)	112.4 (5)
N(1)CoN(8)	93.19 (19)	N(1)C(2)C(3)	107.3 (4)
N(4)CoN(5)	94.54 (19)	N(4)C(3)C(2)	108.0 (5)
N(5)CoN(8)	85.24 (20)	N(5)C(6)C(7)	107.3 (6)
CoO(11)C(12)	112.4 (3)	N(5)C(6)C(7′)	115.1 (8)
CoO(14)C(13)	113.3 (3)	N(8)C(7)C(6)	112.6 (8)
CoN(1)C(2)	112.4 (3)	N(8)C(7′)C(6)	108.9 (10)
CoN(4)C(3)	104.9 (3)	CoN(8)C(81)	109.4 (7)
CoN(4)C(41)	114.1 (4)	CoN(8)C(82)	114.5 (8)
CoN(4)C(42)	115.2 (4)	C(7)N(8)C(81)	108.7 (8)
C(3)N(4)C(41)	109.7 (5)	C(7)N(8)C(82)	112.8 (10)
C(3)N(4)C(42)	106.9 (5)	C(81)N(8)C(82)	107.4 (10)
C(41)N(4)C(42)	105.7 (6)	C(7′)N(8)C(81′)	108.9 (10)
CoN(8)C(81′)	116.9 (10)	C(7′)N(8)C(82′)	102.6 (13)
CoN(8)C(82′)	116.1 (12)	C(81′)N(8)C(82′)	106.4 (16)

[a] The estimated standard deviations of the least significant digits are given in parentheses. Primed and unprimed symbols denote a pair of disordered atoms.

A single structural isomer of [Co(*N*,*N*′-Me$_2$en)$_2$(ox)]$^+$ is possible. However, in addition to the metal center, each of the four ligand nitrogen atoms is chiral, resulting in 10 diastereomers. Many of these are unlikely through steric constraints. Reduction of [Co(ox)$_3$]$^{3-}$ with [Co(*N*,*N*′-Me$_2$en)$_2$]$^{2+}$ results in four different products with isolated yields that total 71%. These products were separated in bulk by conventional chromatographic methods. Identification of the product isomers is readily accomplished by ^{1}H and ^{13}C NMR spectroscopy, including appropriate decoupling experiments, and in one instance, by X-ray crystallography. The major product (40 ± 3%) has an absorption maximum at 522 nm (ϵ_{522} = 125 M^{-1} cm^{-1}). The ^{1}H NMR spectrum indicates two N-*H* environments (δ 5.19 (1), 5.80 (1)) and two N-C*H*$_3$ environments (δ 1.91 (3), 2.26 (3)), suggesting that the complex has C_2 symmetry and that there are two methyl groups above and below the plane of the oxalate ring. Consistent with this, only one ^{13}C oxalate peak is observed. These characteristics are identical with those for the Λ(*RS*,*RS*)/Δ(*SR*,*SR*) isomer obtained by the published synthesis,[5] and this is confirmed by the structure of the cobalt(III) complex derived from X-ray analysis (Figure 2). Fractional coordinates are also presented in Table III. Bond lengths and angles for the ligands are within normal limits (Table V), and the Co–N bond lengths average 1.99 Å in good agreement with those in [Co(en)$_2$(ox)]$^+$ although the Co–O bond lengths are somewhat shorter. The chelate ring incorporating N(1), N(2)

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(19) Aoki, T.; Matsumoto, K.; Ooi, S.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 159–162.

(20) Attempts to determine the optical purity of the partially resolved [Δ-(−)-Co(*N*,*N*-Me$_2$en)$_2$(ox)]$^+$ complex by NMR spectroscopy with the aqueous chiral shift reagent [Eu(*R*-pdta)(D$_2$O)$_3$]$^-$ (Kabuto, K.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1650–1652), have been carried out. Addition of a 5-fold excess of the europium salt resolves the four AA′BB′ methylene protons on the amine backbone, but no evidence for enantiomeric resolution is observed. This suggests that the europium complex preferentially interacts with the amine protons of the ethylenediamine ligands on the cobalt(III) complexes. This is most likely the result of a hydrogen-bonding interaction that is not selective enough for detection of enantiomeric discrimination.

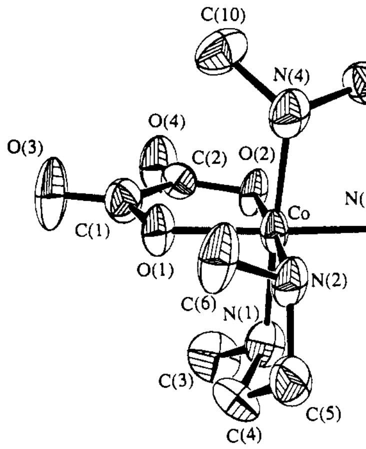

Figure 2. ORTEP diagram of the $[Co(N,N'\text{-}Me_2en)_2(ox)]^+$, illustrating the numbering scheme. The thermal ellipsoids are drawn at the 50% level.

has a skew conformation (*ob*), while that incorporating N(3), N(4) has an envelope conformation (*ob*) with C(9) out of the plane. The isomer shown is $\Delta(SR(\lambda),SR(\lambda))$.

Two minor isomers are obtained in similar proportions. The first (24 ± 4%) has an absorption maximum at 523 nm (ϵ_{523} = 125 M^{-1} cm^{-1}). The ^1H NMR spectrum indicates four nonequivalent N–*H* environments (δ 5.15 (1), 5.49 (1), 5.77 (1), 6.18 (1)) and four distinct N–CH_3 environments (δ 1.92 (3), 2.27 (3), 2.33 (3), 2.34 (3)), only one of which is over the plane of the oxalate ring. Two ^{13}C oxalate peaks are observed. The isomer is identified as $\Lambda(RR,SS)/\Delta(RR,SS)$. The second minor isomer (22 ± 2%) has an absorption maximum at 525 nm (ϵ_{525} = 119 M^{-1} cm^{-1}). The ^1H NMR spectrum indicates four nonequivalent N–*H* environments (δ 5.37 (1), 5.50 (1), 5.93 (1), 5.96 (1)) and two distinct N–CH_3 environments (δ 1.92 (6), 2.28 (6)), one of which is over the plane of the oxalate ring. Two ^{13}C oxalate peaks are observed. The isomer is identified as $\Lambda(SS,RS)/\Delta(RR,SR)$. A fourth product, which has somewhat different characteristics with an absorption maximum at 515 nm (ϵ_{515} = 122 M^{-1} cm^{-1}), is also obtained, in low yield (14 ± 4%). The ^1H NMR spectrum indicates four nonequivalent N–*H* environments (δ 5.15 (1), 5.35 (1), 5.52 (1), 6.12 (1)) and only three distinct N–CH_3 environments (δ 1.96 (3), 2.24 (3), 2.33 (3)), only one of which is over the plane of the oxalate ring. The absence of a fourth well-defined methyl peak strongly suggests that this product is a mixed-ligand complex, $[Co(N,N'\text{-}Me_2en)(N\text{-}Meen)(ox)]^+$, formed by incorporation of the ubiquitous *N*-Meen impurity in *N,N'*-Me_2en. The UV–visible spectroscopic data, with a shift in wavelength to 515 nm, are also consistent with this explanation. However, the complex appears readily interconvertible with the isomers of $[Co(N,N'\text{-}Me_2en)_2(ox)]^+$ under basic conditions and an alternative explanation is that one methyl group is subject to hindered rotation and the peak is difficult to detect. Unfortunately, ^{13}C NMR spectra that could answer this point were inconclusive due to the very low yields of this species, its instability, and the fact that it was not isolated in a pure form. The exact nature of this derivative remains open to debate. The order of elution of these isomers by the HPLC method is $\Lambda(RR,SS)/\Delta(RR,SS)$, $\Lambda(SS,RS)/\Delta(RR,SR)$, and $\Lambda(RS,RS)/\Delta(SR,SR)$. The unidentified minor product is eluted before $\Lambda(SS,RS)/\Delta(RR,SR)$ and is invariably contaminated with $\Lambda(RR,SS)/\Delta(RR,SS)$ and $\Lambda(SS,RS)/\Delta(RR,SR)$. The same order is observed for the conventional chromatography except that the minor product is eluted after $\Lambda(SS,RS)/\Delta(RR,SR)$.

Under mildly basic conditions (HPO_4^{2-}, pH ~8), isomers $\Lambda(RS,RS)/\Delta(SR,SR)$, $\Lambda(RR,SS)/\Delta(RR,SS)$, and $\Lambda(SS,RS)/\Delta(RR,SR)$ are readily interconverted to identical mixtures of all four isolated products in the percentage ratios 45 ± 2% $\Lambda(RS,RS)/\Delta(SR,SR)$, 22 ± 2% $\Lambda(RR,SS)/\Delta(RR,SS)$, 23 ± 2% $\Lambda(SS,RS)/\Delta(RR,SR)$, and 10 ± 3% for the unidentified minor product (Table SII (supplementary material)). This distribution is similar to that obtained in the electron-transfer reaction, also under mildly basic conditions, from which it is concluded that it represents an equilibrium mixture. For the minor product interconversion is slower and more complex, and a substantial amount (15%) of an uncharacterized decomposition product is noted.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Co(N,N'\text{-}Me_2en)_2(ox)]I\cdot 2H_2O^a$

	Distances		
Co–O(1)	1.876 (7)	N(3)–C(8)	1.49 (1)
Co–O(2)	1.900 (6)	N(4)–C(9)	1.51 (1)
Co–N(1)	1.967 (9)	N(4)–C(10)	1.49 (1)
Co–N(2)	1.996 (8)	C(1)–C(2)	1.53 (1)
Co–N(3)	1.979 (8)	C(4)–C(5)	1.48 (2)
Co–N(4)	1.988 (9)	C(8)–C(9)	1.52 (2)
O(1)–C(1)	1.34 (1)		
O(2)–C(2)	1.36 (1)	O(1s)–H(1sa)	1.09
C(1)–O(3)	1.23 (1)	O(1s)–H(1sb)	1.19
C(2)–O(4)	1.18 (2)	O(3s)–H(2sb)	1.06
N(1)–C(3)	1.54 (1)	O(3s)–H(1sa)	1.51
N(1)–C(4)	1.50 (1)	O(3s)–H(3sa)	1.50
N(2)–C(5)	1.48 (1)	I–H(1n)	2.97
N(2)–C(6)	1.47 (1)	I–H(4n)	2.88
N(3)–C(7)	1.50 (1)	I–H(2sb)	2.77
	Angles		
O(1)CoO(2)	87.1 (3)	O(3)C(1)C(2)	120 (1).
O(1)CoN(1)	89.3 (3)	O(1)C(1)C(2)	116.0 (9)
O(1)CoN(2)	88.7 (3)	O(2)C(2)C(1)	111 (1)
O(1)CoN(3)	176.8 (3)	O(2)C(2)O(4)	124.7 (9)
O(1)CoN(4)	92.8 (3)	O(4)C(2)C(1)	124 (1)
O(2)CoN(1)	92.6 (3)	C(3)N(1)C(4)	110.4 (8)
O(2)CoN(2)	175.7 (3)	N(1)C(4)C(5)	107.7 (9)
O(2)CoN(3)	89.9 (3)	N(2)C(5)C(4)	108.4 (9)
O(2)CoN(4)	89.4 (3)	C(5)N(2)C(6)	107.5 (9)
N(1)CoN(2)	86.1 (3)	C(7)N(3)C(8)	109.7 (9)
N(1)CoN(3)	92.0 (4)	N(3)C(8)C(9)	108.1 (9)
N(1)CoN(4)	177.1 (4)	N(4)C(9)C(8)	104.6 (9)
N(2)CoN(3)	94.3 (3)	C(9)N(4)C(10)	107.3 (9)
N(2)CoN(4)	92.0 (4)		
N(3)CoN(4)	85.9 (4)	H(1sa)O(1s)H(1sb)	90
CoO(1)C(1)	112.2 (6)	H(2sb)O(3s)H(1sa)	75
CoO(2)C(2)	113.8 (6)	H(2sb)O(3s)H(3sa)	101
CoN(1)C(3)	118.9 (7)	H(1sa)O(3s)H(3sa)	105
CoN(1)C(4)	105.5 (6)		
CoN(2)C(5)	108.9 (7)	H(1n)IH(4n)	89
CoN(2)C(6)	115.5 (6)	H(1n)IH(2sb)	103
CoN(3)C(7)	116.2 (6)	H(4n)IH(2sb)	105
CoN(3)C(8)	109.0 (7)	IH(1n)N(1)	148
CoN(4)C(9)	106.4 (7)	IH(4n)N(4)	139
CoN(4)C(10)	120.3 (7)	IH(2sb)O(3s)	128
O(1)C(1)O(3)	124 (1)	O(1s)H(1sa)O(3s)	159

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Chiral induction is observed in the oxidation of $[Co(N,N'\text{-}Me_2en)_2]^{2+}$ by optically active $[Co(ox)_3]^{3-}$. The $\Lambda(RS,RS)/\Delta(SR,SR)$ isomer has been fully resolved, and circular dichroism spectra for the other isomers are almost identical and are assumed to have similar $\Delta\epsilon$ values. There is a reduction (~15%) in the total optical activity summed after isolation of the individual isomeric products from that measured immediately after reaction. Under the acidic conditions of the workup procedures, racemization over a 10-day period is insignificant (<5%); however, isomeric interconversion is observed.[21] This is consistent with Jackson and Sargeson,[22] who have shown that racemization in *cis*-(bis-1,2-diaminoethane)cobalt(II) complexes is due to cis–trans isomerization, with rate constants on the order of 10^{-5} M^{-1} s^{-1} under dilute acidic conditions. Also, at pH 8.5, rapid deuteration and isomerization at the asymmetric nitrogens of $[Co(N,N'\text{-}Me_2en)(ox)_2]^-$ take place with no Δ to Λ interconversion, the result of proton exchange[23-25] that is inhibited under acidic conditions.

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(21) Marusak, R. A. Thesis, University of Notre Dame, 1990.
(22) Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348–1362.
(23) Larson, K. W.; Ryan, A. A.; Brushmiller, J. G. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 991–995.
(24) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 825–830.

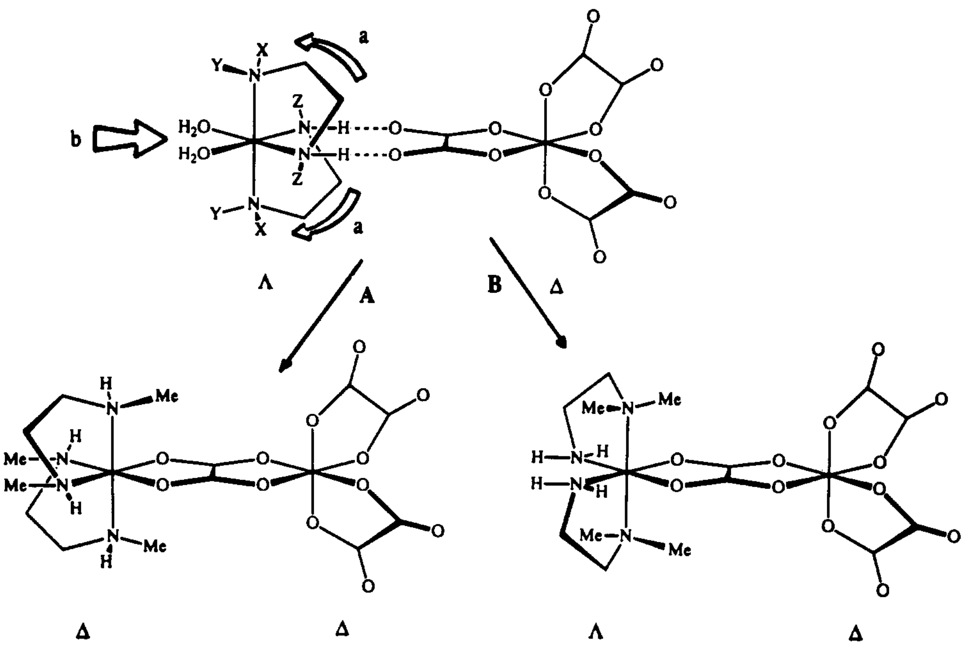

Figure 3. Formation of the bridged binuclear intermediate from a hydrogen-bonded outer-sphere precursor in the reduction of $[Co(ox)_3]^{3-}$ by $[Co(en)_2]^{2+}$ and its derivatives. The outer-sphere precursor has a ΔΛ preference. When X = H and Y, Z = H, CH_3, inner-sphere association proceeds by solvent loss and inversion of configuration (arrows a) at the cobalt(II) center, pathway A, but this is prevented when X, Y = CH_3 and Z = H, and the reaction proceeds by attack on the reverse side of the reductant (arrow b), with retention, pathway B.

Significantly, interconversion in all cases occurs with a resulting increase in the Λ(*RR*,*SS*)/Δ(*RR*,*SS*) isomer. It is suspected that there is loss of product during the column separation procedures resulting in the small reduction in optical activity.

The observed stereoselectivities for each isomer are as follows: 8.1 ± 0.6% ΛΛ, Λ(*RR*,*SS*)/Δ(*RR*,*SS*); 7.7 ± 0.4% ΛΛ, Λ-(*SS*,*RS*)/Δ(*RR*,*SR*); 7.8 ± 0.8% ΛΛ, Λ(*RS*,*RS*)/Δ(*SR*,*SR*). Though larger, the sense of the stereoselectivity is identical with that obtained by using the $[Co(en)_2]^{2+}$ reductant, suggesting that the interactions of the two reductants with $[Co(ox)_3]^{3-}$ are similar. The lack of sensitivity of the chiral induction to isomer structure need not imply that discrimination for each isomer is the same. It can be explained by the rapid, subsequent interconversion between the diastereomers in the basic conditions of the electron-transfer reactions. Consequently, it is not possible to define a structure for the discriminating intermediate in the reaction.

The extent of chiral induction in the three related inner-sphere electron-transfer reactions is as follows: $[Co(en)_2]^{2+}$, 1.5% ΔΔ; $[Co(N,N'\text{-}Me_2en)_2]^{2+}$, 7.9% ΔΔ; $[Co(N,N\text{-}Me_2en)_2]^{2+}$, 4.3% ΔΛ. In all three reactions the geometry of the inner-sphere electron-transfer precursor is defined by a doubly bound oxalate bridge that maintains the metal–metal distance around 5 Å. Although the presence of methyl substituents on the amine nitrogen atoms has a small but measurable effect, strong interactions between the nonbridging ligands that dictate the chirality are prevented, resulting in the low enantiomeric excesses detected in the reactions. In attempting to rationalize the trends in the data, it is important to note that this inner-sphere intermediate need not be the sole source of the chiral discrimination. During the formation of the bridged intermediate, it is likely that weaker, outer-sphere complexes are involved, and these provide an attractive explanation for the change in the sense of the stereoselectivity with $[Co(N,N\text{-}Me_2en)_2]^{2+}$. For example, a possible configuration for an outer-sphere complex, stabilized by hydrogen bonding between the carboxylate oxygen atoms of $[Co(ox)_3]^{3-}$ and amine protons on the reductant, is shown in the scheme in Figure 3 and is proposed to have a ΔΛ preference.[26] Progression from this outer-sphere complex to the bridged inner-sphere complex is readily accomplished for both the unsubstituted and *N*,*N'*-dimethyl complexes by solvent loss and *inversion* of configuration at the labile cobalt(II) center to give the observed ΔΔ preference, whereas for the *N*,*N*-dimethyl complex, such a rearrangement is prevented on steric grounds. The intermediate is thus a "dead-end" complex in the formation of the binuclear intermediate, $[(N,N\text{-}Me_2en)_2Co(ox)Co(ox)_2]^-$, which must take place by substitution on the reverse side of the ion pair, with *retention* of configuration, a ΔΛ preference. Differences in the sense of the stereoselectivity can be rationalized on this basis.

Acknowledgment. The generous support of the National Science Foundation (Grant No. 87-02012) is gratefully acknowledged.

Supplementary Material Available: Listings of reaction conditions and product isomer distributions in the reduction of $[Co(ox)_3]^{3-}$ by $[Co(N,N'\text{-}Me_2en)_2]^{2+}$ (Table SI), isomer distributions for $[Co(N,N'\text{-}Me_2en)_2(ox)]^+$ complexes in the presence of hydrogen phosphate ion (Table SII), and general atomic displacement parameter expressions (B_{ij}'s) and fractional coordinates and isotropic thermal parameters for hydrogen atoms for $[Co(N,N\text{-}Me_2en)_2(ox)]I$ and $[Co(N,N'\text{-}Me_2en)_2(ox)]I\cdot 2H_2O$ (Tables SIII, SIV, SVI, and SVII) (6 pages); listings of observed and calculated structure factors for the two complexes (Tables SV and SVIII) (19 pages). Ordering information is given on any current masthead page.

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(25) Halpern, B.; Sargeson, A. M.; Turnbull, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 4630–4636.

(26) Consistent with this, the outer-sphere ion pair formed between $[Co(ox)_3]^{3-}$ and $[Co(en)_3]^{2+}$ is proposed to have a ΔΛ preference.[1]