70713-70-1; Cu[(naph)$_2$(2,3-DAN)], 70713-72-3; Co[(sal)$_2$en], 36870-54-9; Co[(sal)$_2$DAB], 39836-45-8; Co[(benac)$_2$en], 36802-28-5; Co[(naph)$_2$en], 33271-28-2; Co[(naph)$_2$DAB], 33271-29-3; [Cu-[(sal)$_2$en], 34754-33-1; Cu[(sal)$_2$DAB], 42490-12-0; Cu[(benac)$_2$en], 15277-26-6; Cu[(acac)$_2$en], 36885-37-7; Cu[(naph)$_2$en], 36294-60-7; Cu[(naph)$_2$DAB], 20506-87-0; Co[(sal)$_2$en]$^+$, 66511-70-4; Co-[(sal)$_2$en]$^-$, 26220-77-9; Co[(sal)$_2$DAB]$^+$, 70713-73-4; Co[(sal)$_2$DAB]$^-$, 56811-23-5; Co[(sal)$_2$(3,4-DAEB)]$^+$, 70713-74-5; Co[(sal)$_2$(3,4-DAEB)]$^-$, 70713-75-6; Co[(sal)$_2$(2,3-DAN)]$^+$, 70713-76-7; Co-[(sal)$_2$(2,3-DAN)]$^-$, 70713-77-8; Co[(benac)$_2$en]$^+$, 70713-78-9; Co[(benac)$_2$en]$^-$, 70713-94-9; Co[(naph)$_2$en]$^+$, 70713-79-0; Co-[(naph)$_2$en]$^-$, 70749-45-0; Co[(naph)$_2$DAB]$^+$, 70713-80-3; Co-[(naph)$_2$DAB]$^-$, 70749-61-0; Co[(naph)$_2$(3,4-DAEB)]$^+$, 70713-81-4; Co[(naph)$_2$(3,4-DAEB)]$^-$, 70713-82-5; Co[(naph)$_2$(2,3-DAN)]$^+$, 70713-83-6; Co[(naph)$_2$(2,3-DAN)]$^-$, 70713-84-7; Cu[(sal)$_2$en]$^-$, 70749-46-1; Cu[(sal)$_2$DAB]$^-$, 70713-85-8; Cu[(sal)$_2$(3,4-DAEB)]$^-$, 70713-86-9; Cu[(sal)$_2$(2,3-DAN)]$^-$, 70713-87-0; Cu[(benac)$_2$en]$^-$, 70713-93-8; Cu[(acac)$_2$en]$^-$, 70713-92-7; Cu[(naph)$_2$en]$^-$, 70713-88-1; Cu[(naph)$_2$DAB]$^-$, 70713-89-2; Cu[(naph)$_2$(3,4-DAEB)]$^-$, 70713-90-5; Cu[(naph)$_2$(2,3-DAN)]$^-$, 70713-91-6.

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Circular Dichroism Studies of Some Cobalt(III) Complexes Which Contain Phenyl-Substituted Ethylenediamine-*N*,*N'*-diacetate Analogues

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The contributions from asymmetric nitrogens in cobalt(III) complexes to the rotational strengths can be significant depending upon the homogeneity of the chemical environment about the nitrogen atom. A complex has been prepared, [Co(*l*-sdda)en]$^+$ (*l*-sdda = *l*-stilbenediamine-*N*,*N'*-diacetate ion, en = ethylenediamine), which contains asymmetric nitrogens bonded to a hydrogen and a benzyl group, two substituents known to make opposite contributions to the rotational strength. The complex [Co(edda)(*l*-stien)]$^+$ (edda = ethylenediamine-*N*,*N'*-diacetate ion, *l*-stien = *l*-stilbenediamine) was prepared to estimate the contribution from the asymmetric carbons in *l*-stien. Some stereoselectivity was observed in the preparation of this complex. The carbon-13 NMR spectra for both complexes are reported, verifying that the complexes possess the s-cis geometry. Finally, several para-substituted *N*,*N'*-dibenzylethylenediamine-*N*,*N'*-diacetate (dbedda) cobalt(III) complexes have been prepared to study the electronic effects of substituents on asymmetric nitrogens.

Introduction

Circular dichroism (CD) studies of cobalt(III) complexes which contain edda, *N*,*N'*-dialkyl edda analogues, and *N*,*N'*-dibenzyl edda analogues coordinated in the s-cis geometry have been conducted extensively in the last decade.[1-6] Two important conclusions have been drawn. (1) The rotational strengths of the first ($^1T_{1g}$) CD band are insensitive to changes in the bidentate ligand occupying the non-edda sites.[4,6] This was attributed to the dominant influence of the rigid edda chelate. (2) It was found that the contribution of the asymmetric nitrogens (vicinal effect) to the rotational strength may be comparable in magnitude to that of the configurational effect.[1,2,6]

Maricondi and Maricondi[2] showed that asymmetric nitrogens in edda-type complexes may make opposite contributions to the rotational strength, depending upon whether the substituent on nitrogen is hydrogen or a benzyl group. They reached this conclusion by subtracting the CD curve of [Co(dmedda)en]$^+$ (dmedda = *N*,*N'*-dimethylethylenedi-

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amine-*N,N'*-diacetate) from the CD curves of $[Co(edda)en]^+$. Since three of the groups bonded directly to the nitrogen in $[Co(dmedda)en]^+$ are $-CH_2-$ or $-CH_3$, the environment is rather homogeneous, and the contribution to the rotatory strength might be expected to be negligible. Subtraction of the CD curve for $[Co(dmedda)en]^+$ from that for $[Co(edda)en]^+$ and for $[Co(dbedda)en]^+$ should be equivalent to subtracting the configurational effect, leaving the vicinal effect curves for the asymmetric nitrogens.

In the edda complex, each nitrogen is bonded to a hydrogen, while the dbedda complex contains nitrogens bonded to benzyl groups. We have prepared a novel cobalt(III) complex, $[Co(l\text{-sdda})en]^+$, where each asymmetric nitrogen is bonded to both a hydrogen and a benzyl group, significantly altering the chemical environment about the nitrogen. The complex $[Co(edda)(l\text{-stien})]^+$ was synthesized to estimate the contribution from the asymmetric carbons in *l*-stien. Jordan[7] prepared $[Co(edda)(l\text{-chxn})]^+$ (*l*-chxn = 1,2-diaminocyclohexane) and found that the reaction was completely stereospecific, yielding only the Δ isomer. It was felt that some stereoselectivity of complex formation should be evident in the formation of $[Co(edda)(l\text{-stien})]^+$.

In many of the edda analogues which have been studied, the substituents on the asymmetric nitrogens varied greatly in electron-donating and -withdrawing capabilities. In order to determine if any correlations between CD curves and electronic effects on the asymmetric nitrogens exist, we prepared a series of *N,N'*-dibenzyl edda analogues where the para substituent of the benzene ring was varied from electron-donating to electron-withdrawing groups.

Experimental Section

Preparation of Materials. Two methods are used for the identification of optical isomers: the sign of rotation of plane-polarized light at a specific wavelength, e.g., $(+)_{589}$, and the sign of the low-energy CD peak in the $^1T_{1g}$ region, (+) or (-). Ethylenediamine-*N,N'*-diacetic acid was obtained from LaMont Laboratories, and *d,l*-isoamarine and most organic reagents were obtained from Aldrich Chemical Co. Elemental analyses were performed by Calgon Analytical Laboratories, Pittsburgh, PA, and Integral Microanalytical Laboratories Inc., Raleigh, NC.

Preparation and Resolution of *d,l*-1,2-Diamino-1,2-diphenylethane (*d,l*-Stilbenediamine, *d,l*-stien). The following preparation and resolution are modifications of procedures of Lifschitz and Bos[8] and Williams and Bailar.[9] The *l*-stilbenediamine obtained from the resolution with *d*-tartaric acid gave $[\alpha]_D = -87°$ in ether and $-108°$ in methanol.

Preparation and Resolution of *s-cis*-(Ethylenediamine-*N,N'*-diacetato)(*l*-stilbenediamine)cobalt(III) Chloride Trihydrate, *s-cis*-$[Co(edda)(l\text{-stien})]Cl\cdot 3H_2O$. A mixture of 2.6 g (0.015 mol) of $CoCO_3$ and 1.8 g (0.015 mol) of H_2edda in 50 mL of H_2O was heated at 60 °C until CO_2 evolution ceased. The solution was filtered, and 15 mL of 1 M HCl and 3.2 g (0.015 mol) of *l*-stilbenediamine dissolved in 50 mL of 95% ethanol were added. Air was bubbled through the solution for 24 h to give a red solution and a small amount of a very fine red-purple precipitate. The precipitate was possibly the uns-cis isomer. The filtrate was evaporated in a stream of air to 25 mL, and after it was allowed to stand in a refrigerator overnight, 4.0 g of large red crystals was collected. They were recrystallized to a constant value of $\Delta\epsilon_{520} = 0.29$. Evaporation of the filtrate and recrystallization of the product yielded 2.5 g of a fraction with $\Delta\epsilon_{535} = -5.97$. It appears that the first fraction is racemic with respect to the edda portion of the complex, while the other fraction is the (-) isomer. Thus, the formation of the complex is stereoselective, with the (-) isomer predominating to the extent of approximately 70% (total yield 6.5 g). The preparation of the complex using activated charcoal gave the same ratio of the two isomers.

For isolation of the (+) isomer, the fraction with $\Delta\epsilon_{520} = -0.29$ was resolved. For the resolution, 2.0 g (0.0037 mol) of complex and 1.5 g (0.0037 mol) of silver bis(μ-*d*-tartrato(4-))-diantimonate(III) (silver antimonyl *d*-tartrate) were added to 50 mL of water, and the mixture was stirred and heated at 60 °C for 15 min. Silver chloride was filtered out and the filtrate was concentrated to 20 mL by a stream of air and placed in a refrigerator. After 3 days, a fraction of red needles was obtained. One more recrystallization yielded red needles with a constant $\Delta\epsilon_{535} = +4.63$ (assuming an anhydrous 1:1 diastereoisomer, mol wt 740). Further evaporation yielded another fraction, which after two recrystallizations gave a constant $\Delta\epsilon_{535} = -5.42$. The diastereoisomers were converted to the chloride salt by passing them through a Dowex 1-X8 anion-exchange resin. Recrystallization of the complexes yielded the final products with $\Delta\epsilon_{535} = +5.10$ and -5.98 for the two optical isomers. Anal. Calcd for $[Co(edda)(l\text{-stien})]Cl\cdot 3H_2O$: C, 44.90; H, 5.99; N, 10.48. Found: C, 44.83; H, 6.35; N, 10.46.

Preparation of *s-cis*-Ethylenediamine(*l*-stilbenediamine-*N,N'*-diacetato)cobalt(III) Chloride Trihydrate, *s-cis*-$[Co(l\text{-sdda})en]Cl\cdot 3H_2O$. A solution of 3.2 g (0.015 mol) of *l*-stilbenediamine in 50 mL of methanol was added to a solution of 4.2 g (0.030 mol) of bromoacetic acid in 25 mL of water, which had been neutralized previously with 7 M NaOH while keeping the temperature below 10 °C. The reaction mixture was stirred at 40 °C, keeping the pH at 10-11 by addition of 7 M NaOH. After the reaction was completed, the methanol was removed by rotary evaporation, the pH was adjusted to 7-8, and 3.6 g (0.015 mol) of $CoCl_2\cdot 6H_2O$ was added. The $Co^{II}(l\text{-sdda})$ precipitated immediately (yield 3.7 g). The Co(II) complex was then dissolved in 100 mL of methanol, and 9.6 mL of 1 M HCl and 0.58 g (0.0096 mol) of ethylenediamine were added. After air oxidation for 24 h, the dark red solution was evaporated to dryness, and the product was recrystallized from methanol-water (1:1) (yield 4.2 g). Only one isomer is expected to form from *l*-sdda; however, it was necessary to recrystallize the product six times to obtain a constant $\Delta\epsilon_{528} = +3.22$. Possibly, some racemization of the *l*-stilbenediamine may have occurred during the preparation of *l*-sdda, and many recrystallizations were necessary to remove any of the racemic complex. Also, there may have been some uns-cis isomer present, which was removed during the recrystallizations. Anal. Calcd for $[Co(l\text{-sdda})en]Cl\cdot 3H_2O$: C, 44.90; H, 5.99; N, 10.48. Found: C, 44.84; H, 5.45; N, 10.14.

Preparation of *N,N'*-Bis(*p*-methylbenzyl)ethylenediamine-*N,N'*-diacetic Acid, $dmbH_2edda$. To a 25 mL aqueous solution of 5.28 g (0.03 mol) of H_2edda which had been neutralized with 2.3 g (0.06 mol) of NaOH was added 25 mL of an ethanol solution of 25.4 g (0.18 mol) of *p*-methylbenzyl chloride. This mixture was stirred and heated at 50 °C for 4 h, keeping the pH in the range of 9-10 by adding base. The ethanol was stripped off, and some solid material was filtered. The solution was acidified to pH 2.0 with 6 M HCl, and the white solid was filtered and washed with water, acetone, and ether (yield 5.75 g). Some trace impurities in $dmbH_2edda$ caused the elemental analysis to be in error. However, the identity of this compound was verified by the elemental analysis of the cobalt(III) complex which contained this ligand.

Preparation and Resolution of *s-cis*-(*N,N'*-Bis(*p*-methylbenzyl)-ethylenediamine-*N,N'*-diacetato)(ethylenediamine)cobalt(III) Chloride Hemihydrate, *s-cis*-$[Co(dmbedda)en]Cl\cdot 0.5H_2O$. A 50-mL aqueous solution of 4.2 g (0.011 mol) of $dmbH_2edda$ was neutralized with 0.9 g (0.022 mol) of NaOH. When 2.6 g (0.011 mol) of $CoCl_2\cdot 6H_2O$ was added, a pink precipitate [Co(dmbedda)] formed immediately (yield 4.5 g). This solid was dissolved in 200 mL of methanol, and 0.62 g (0.010 mol) of ethylenediamine, 10.2 mL of a 1 M HCl solution, and 1 g of activated charcoal were added. The solution was air oxidized for 12 h, filtered, and concentrated by using a stream of air to yield red crystals. They were recrystallized from methanol-water (yield 3.7 g).

For the resolution, 3.0 g (0.0055 mol) of complex, 1.0 g (0.0028 mol) of dibenzoyl-*d*-tartaric acid, and 1.6 g (0.0028 mol) of disilver dibenzoyl-*d*-tartrate were stirred at 60 °C for 15 min. The AgCl was filtered, and the solution was evaporated in a stream of air until a pink fluffy solid started to form. After the solution stood in a refrigerator overnight, 1.6 g of product was isolated. This less soluble diastereoisomer was recrystallized from methanol-ethanol (1:1). After two recrystallizations, $\Delta\epsilon_{558} = +1.76$ (assuming an anhydrous 1:1 diastereoisomer, mol wt 859) remained constant. The more soluble diastereoisomer was obtained upon further evaporation and was recrystallized to a constant $\Delta\epsilon_{558} = -1.76$. The diastereoisomers were converted to their chloride salts by ion exchange. The chlorides were recrystallized from a methanol-water mixture, yielding red crystals which gave $\Delta\epsilon_{558} = +1.81$ and -1.81. The CD curves were run in methanol and water, the former having a more concentrated solution. The yields were 1.2 and 0.8 g for the (+) and (-) isomers, respectively. Anal. Calcd for $[Co(dmbedda)en]Cl\cdot 5H_2O$: C, 52.79; H, 6.42; N, 10.26. Found: C, 53.04; H, 6.61; N, 10.24.

Preparation of *N,N'*-Bis(*p*-nitrobenzyl)ethylenediamine-*N,N'*-diacetic Acid, dNO_2bH_2edda. A mixture of 52.8 g (0.03 mol) of H_2edda in 50 mL of water, which had been neutralized with NaOH, and 25.9 g (0.12 mol) of *p*-nitrobenzyl bromide in 150 mL of ethanol was stirred and heated at 60 °C for 3 h. The pH was maintained at 9–10 by adding base intermittently. The ethanol was stripped off, some solid material was filtered, and the solution was acidified to pH 4.0 with 6 M HCl. The yellowish, gummy material could not be recrystallized, although proton NMR indicated that it was the correct product. This product was used for the next preparation.

Preparation and Resolution of *s-cis*-(*N,N'*-Bis(*p*-nitrobenzyl)-ethylenediamine-*N,N'*-diacetato)(ethylenediamine)cobalt(III) Chloride Sesquihydrate, *s-cis*-$[Co(dNO_2bedda)en]Cl\cdot1\cdot5H_2O$. The amount of dNO_2bH_2edda prepared in the preceding preparation was assumed to be quantitative. The ligand was dissolved in 100 mL of H_2O by adding 2.4 g (0.06 mol) of NaOH followed by the addition of 7.14 g (0.03 mol) of $CoCl_2\cdot6H_2O$. A pink precipitate formed immediately and was filtered, washed with water, and air-dried (yield 6.6 g, 37.9%). The pink precipitate, $Co(dNO_2bedda)$, was dissolved in 200 mL of methanol, and 0.66 g (0.011 mol) of ethylenediamine, 11 mL of a 1 M HCl solution, and 1 g of activated charcoal were added. The solution was air oxidized for 12 h, filtered, and evaporated to dryness. The complex was recrystallized by dissolving in methanol, adding an equal volume of water, and allowing the solution to stand overnight. Red-purple crystals separated, leaving only a yellow-brown solution (yield 1.3 g).

For the resolution, a mixture of 1.3 g (0.0021 mol) of complex, 0.6 g (0.001 mol) of disilver dibenzoyl-*d*-tartrate and 0.4 g (0.001 mol) of dibenzoyl-*d*-tartaric acid was stirred and heated at 60 °C for 15 min. The AgCl was filtered, and the solution was evaporated to dryness. It was found that the solubility difference between the two diastereoisomers was so great that the less soluble diastereoisomer could be obtained in almost pure form by simply stirring the entire solid with 50 mL of methanol for 30 min. About 0.6 g of the less soluble diastereoisomer was obtained, which after one recrystallization gave a constant $\Delta\epsilon_{558} = +1.29$ (assuming a 1:1 anhydrous diastereoisomer, mol wt 920). The more soluble diastereoisomer was obtained from the filtrate by evaporation and recrystallization, giving a constant $\Delta\epsilon_{558} = +1.29$ (assuming a 1:1 anhydrous diastereoisomer, mol wt 920). The more soluble diastereoisomer was obtained from the filtrate by evaporation and recrystallization, giving a constant $\Delta\epsilon_{558} = -1.29$ after three recrystallizations. The diastereoisomers were converted to their chloride salts by ion exchange. The compounds were recrystallized by dissolving them in a minimum amount of hot methanol, adding an equal volume of water, and standing the solution overnight. About 0.3 g of the (+) isomer and 0.2 g of the (−) isomer were isolated giving a constant $\Delta\epsilon_{558} = +1.32$ and −1.32, respectively. Anal. Calcd for $[Co(dNO_2bedda)en]Cl\cdot1\cdot5H_2O$: C, 42.2; H, 4.9; N, 13.4. Found: C, 41.9; H, 4.7; N, 13.3.

Preparation of *N,N'*-Bis(*p*-chlorobenzyl)ethylenediamine-*N,N'*-diacetic Acid, $dClbH_2edda$. A 50 mL aqueous solution of 5.28 g (0.03 mol) of H_2edda which had been neutralized with NaOH and 19.3 g (0.12 mol) of *p*-chlorobenzyl chloride in 50 mL of ethanol was stirred and heated at 60 °C for 5 h. The pH was maintained at 9–10 by adding base. The ethanol was stripped off, and the pH was adjusted to 3.0 by adding 6 M HCl. The precipitate was a gummy white solid, but after it was washed with water, ethanol, and ether, a white powder remained (yield 7.1 g). Anal. Calcd for $dClbH_2edda$: C, 56.60; H, 5.19; N, 6.60. Found: C, 56.50; H, 5.10; N, 6.19.

Preparation and Resolution of *s-cis*-(*N,N'*-Bis(*p*-chlorobenzyl)-ethylenediamine-*N,N'*-diacetato)(ethylenediamine)cobalt(III) Chloride Trihydrate, *s-cis*-$[Co(dClbedda)en]Cl\cdot3H_2O$. An aqueous solution of 5.5 g (0.013 mol) of $dClbH_2edda$ was neutralized with 1.04 g (0.026 mol) of NaOH. When 3.1 g (0.013 mol) of $CoCl_2\cdot6H_2O$ was added, a pink precipitate formed immediately (yield 5.8 g). The Co(dClbedda) was dissolved in 200 mL of methanol, and 0.72 g (0.012 mol) of ethylenediamine, 12 mL of 1 M HCl, and 1 g of charcoal were added. The solution was air oxidized for 12 h, filtered, and evaporated to dryness. The red solid was recrystallized by dissolving in a minimal amount of methanol, adding an equal volume of water, and standing the solution overnight (yield 4.2 g).

Since the solubilities of the diastereoisomers are significantly different, a different approach to the resolution was used. A mixture of 4.2 g (0.0066 mol) of the complex and 1.2 g (0.0033 mol) of dibenzoyl-*d*-tartaric acid in 100 mL of methanol gave a pink precipitate (2.4 g). Two recrystallizations of this solid from a methanol–water mixture gave a constant $\Delta\epsilon_{558} = +1.62$ (assuming an anhydrous 1:1 diastereoisomer, mol wt 899). The diastereoisomer was converted to its chloride salt by ion exchange. Two recrystallizations of the chloride salt from aqueous methanol gave a constant $\Delta\epsilon_{558} = +1.79$ (yield 1.1 g). The (−) isomer was isolated directly as the chloride salt from the filtrate by evaporation and recrystallization (yield 0.9 g; $\Delta\epsilon_{558} = -1.79$). Anal. Calcd for $[Co(dClbedda)en]Cl\cdot3H_2O$: C, 41.80; H, 5.38; N, 8.87. Found: C, 41.71; H, 5.11; N, 8.99.

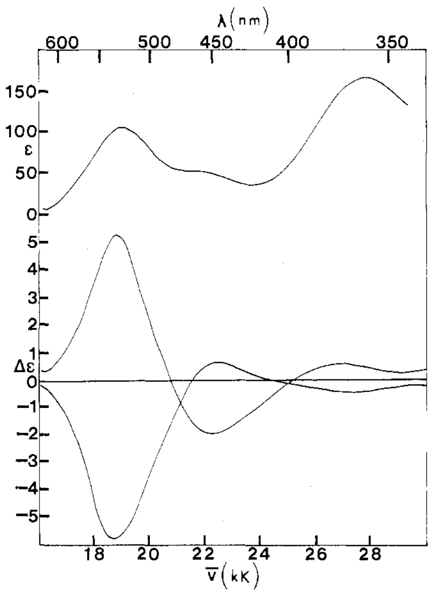

Figure 1. Circular dichroism and absorption spectra of *s-cis*-[Co(edda)(*l*-stien)]$^+$.

Spectral Measurements. The visible absorption spectra were recorded on a Cary recording spectrophotometer, Model 14, using a tungsten lamp. The spectra were measured in 1-cm quartz cells at room temperature in either methanol or water. Sample concentrations were in the range of 10^{-3} M.

The CD spectra were recorded on a Cary Model 61 CD spectropolarimeter using a xenon arc source. Spectra were measured in 1-cm quartz cells in either aqueous or methanol solutions with concentrations in the range of 10^{-3}–10^{-4} M. Carbon-13 nuclear magnetic resonance spectra were recorded on a Jeol, Inc., JNM-FX60 Fourier transform NMR spectrometer operating at approximately 15 MHz in the ^{13}C mode. The spectra were recorded in the broad-band random-noise ^1H decoupling mode, with the field frequency ratio stabilized by locking to the sample solvent, D_2O. Samples were placed in 8–10-mm coaxial tubes with benzene as the external standard in the outer coaxial tube (δ 128.7 downfield from Me_4Si).

Results and Discussion

The characterization of [Co(edda)(*l*-stien)]$^+$ as an s-cis isomer (the oxygens are trans to each other) is based on its absorption and ^{13}C spectra. Related *trans*-N_4O_2 complexes exhibit large splitting of the first absorption band[11,12] (the D_{4h} components), while *cis*-N_4O_2 complexes show only one peak in the $^1T_{1g}$ (O_h) band region, or only very small splitting of the band. Figure 1 indicates that [Co(edda)(*l*-stien)]$^+$ is a *trans*-N_4O_2 complex because of the splitting (shoulder) in the first absorption region. The very simple ^{13}C NMR spectrum (Figure 2) indicates that the complex possesses the symmetric *trans*-N_4O_2 geometry. The assignments made in Figure 2 are based on assignments made by Gailey et al.[13] for related edda complexes.

The absolute configuration has not been established by an X-ray structure determination for any *s-cis*-$[Co(edda)X_2]$ complex, but self-consistent assignments have been made for complexes where X_2 = $(NH_3)_2$,[6] trimethylenediamine,[6] en,[3] *l*-pn,[3] 1,10-phenanthroline,[7] *l*-cyclohexanediamine,[7] L-alanine,[3] carbonate,[4] oxalate,[4] and malonate.[4] These complexes give CD spectra which are remarkably similar, showing little

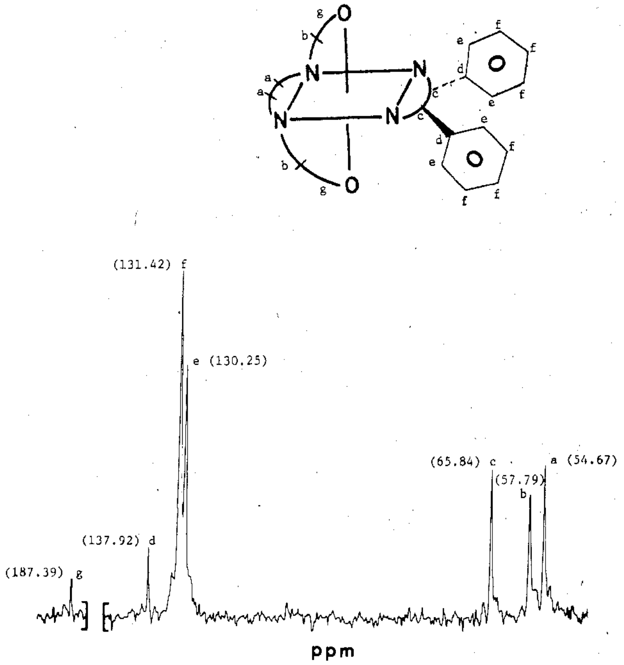

Figure 2. Carbon-13 NMR spectrum of Λ-*s-cis*-[Co(edda)(*l*-stien)]$^+$.

sensitivity to the chemical nature of X_2, the size of the chelate ring, or even the absence of a chelate ring for X_2. The CD curve has been interpreted as being dominated by the rigid edda backbone with a large contribution to intensities from the coordinated asymmetric nitrogen atoms. For bidentate diamines the maximum Δε values fall in the narrow range of 4.46–4.8 except for phen[7] (Δε = 6.6). The high Δε value for the phen complex is expected because ε for the first absorption peak is proportionately higher than those for other diamine complexes. The phen complexes commonly show intense d–d absorption and CD peaks because of borrowing of intensity from allowed bands. The maximum Δε values are also somewhat high for the isomers of [Co(edda)(*l*-stien)]$^+$ (+5.10 and −5.97) in comparison to those of the edda complexes of diamines which contain no phenyl substituents.

The absolute configuration of s-cis complexes of ethylenediamine-*N*,*N*′-di-L-α-propionate ion (LL-eddp) could be determined from NMR studies[10] because of the optically active ligand. This assignment is considered to provide a more direct and reliable basis for assignments of absolute configurations of *s-cis*-[Co(edda)(diamine)]$^+$ complexes than empirical spectral rules related to D_3 complexes (see below). The CD spectrum of (+)-[Co(LL-eddp)en]$^+$ shows the characteristic pattern of (+)-[Co(edda)(diamine)]$^+$ complexes, and these are assigned the Λ configuration.

trans-N_4O_2 complexes are treated as having effective tetragonal (D_{4h}) symmetry. The ordering and separation of the ^1E and $^1A_2$ (D_{4h}) components from the lower energy $^1T_{1g}$ (O_h) absorption band have been discussed by Wentworth and Piper.[14] Where there is a weaker field along the unique axis, as for the *trans*-N_4O_2 case, the ^1E component is lower in energy than the $^1A_2$ component.

Empirical rules have been used for D_3 complexes such as $Co(en)_3^{3+}$ to relate the ^1E component of $^1T_{1g}$ (O_h) parentage to the absolute configuration of the complex.[15] For tetragonal complexes of the type *s-cis*-[Co(edda)(X)$_2$], the sign of the CD peak for the lowest energy ^1E transition is expected to be positive for a Λ configuration, as for [Co(en)$_3$]$^{3+}$. This correlation supports the assignment of the Λ configuration for (+)-[Co(edda)(*l*-stien)]$^+$. Spectral assignments of absolute configurations based on empirical rules for *uns-cis*-[Co(edda)(diamine)]$^+$ complexes[16,17] have been verified by an X-ray structure determination.[18]

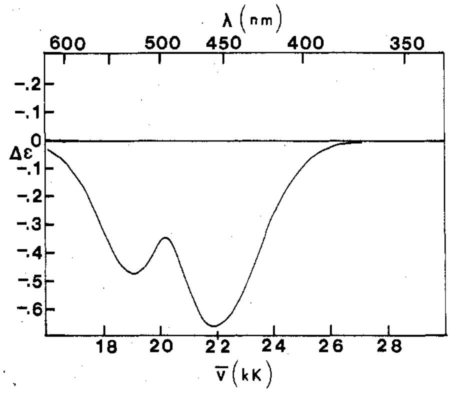

Figure 3. Calculated vicinal effect curve for *s-cis*-[Co(edda)(*l*-stien)]$^+$.

Table I. Circular Dichroism and Absorption Data for *s-cis*-[Co(edda)(*l*-stien)]$^+$ and *s-cis*-[Co(*l*-sdda)en]$^+$

	absorption		CD	
compd[a]	$cm^{-1} \times 10^3$	ε	$cm^{-1} \times 10^3$	Δε
(+)-*s-cis*-[Co(edda)-(*l*-stien)]Cl·3H_2O	18.87	102	18.69	+5.10
	22.22[b]	49	22.32	−1.97
	27.93	158	26.67	+0.43
(−)-*s-cis*-[Co(edda)-(*l*-stien)]Cl·3H_2O	18.87	102	18.69	−5.97
	22.22[b]	49	22.47	+0.69
	27.93	158	26.67	−0.40
(+)-*s-cis*-[Co(*l*-sdda)en]-Cl·3H_2O	18.42	89	18.94	+3.22
	21.74[b]	37	22.12	−0.64
	27.40	117	27.40	−0.23

[a] The optically active isomers are designated (+) or (−), the sign of the low-energy CD band in the $^1T_{1g}$ region. [b] Shoulder on main absorption band.

There had been some controversy[19-22] over the assignment of the absolute configuration for *l*-stien, but a recent X-ray determination[23] has finally established that coordinated *l*-stien has the δ(*S*,*S*) absolute configuration. The formation of [Co(edda)(*l*-stien)]$^+$ was stereoselective, with the (−) isomer favored by the same ratio (7:3) for the preparation carried out in the presence or absence of activated charcoal. The (−) isomer is assigned the Δ configuration. Models prepared by using the δ conformation for (*S*,*S*)-stien show somewhat more favorable steric interaction for the Δ isomer, particularly for the amine hydrogens which are staggered in the Δ isomer but opposed in the Λ isomer.

The combined vicinal and conformational contribution from *l*-stien can be calculated by the established procedure[24] of adding the CD curves of the (+) and (−) isomers and dividing by 2. The result is shown in Figure 3. It appears that *l*-stien makes a negative contribution to the rotational strength in the visible region, but the edda portion of the complex is still dominant in determining the overall shape and intensity of the curve. The evaluation of the CD contributions of the asymmetric C atoms of *l*-stien is needed for the interpretation of the contribution of *l*-sdda which contains coordinated asymmetric N atoms in addition to the asymmetric C atoms.

The absorption and CD spectra of [Co(*l*-sdda)en]$^+$ are shown in Figure 4 (see also Table I). The s-cis geometry for [Co(*l*-sdda)en]$^+$ was verified by its absorption spectrum (Figure 4) and ^{13}C NMR spectrum (Figure 5), as for [Co(edda)(*l*-stien)]$^+$. The one isomer of [Co(*l*-sdda)en]$^+$ shows a positive dominant CD peak and an overall CD curve similar to that of Λ(+)-*s-cis*-[Co(edda)(diamine)]$^+$ complexes as noted above and hence also might be expected to have the Λ configuration. However, the Λ-s-cis configuration would require the *l*-stilbenediamine backbone to have the λ conformation, forcing the large substituents into unfavorable axial positions. Since only one isomer was obtained, the favored δ conformation

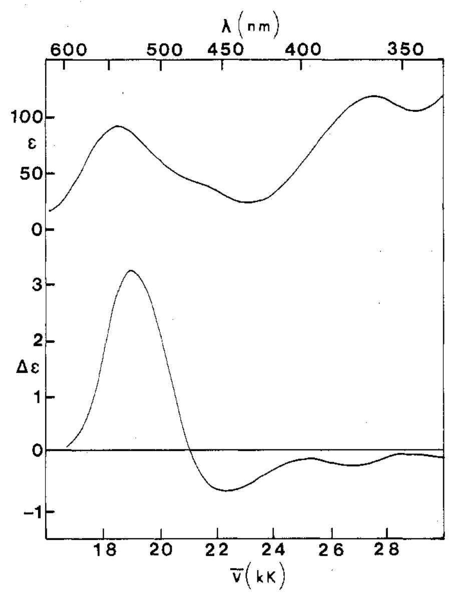

Figure 4. Circular dichroism and absorption spectra of *s-cis*-[Co(*l*-sdda)en]$^+$.

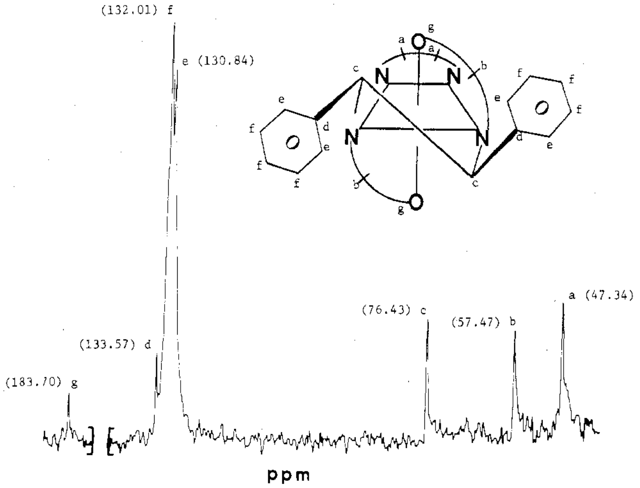

Figure 5. Carbon-13 NMR spectrum of *s-cis*-[Co(*l*-sdda)en]$^+$.

is expected, requiring that the isomer of [Co(*l*-sdda)en]$^+$ have the Δ configuration. Previous studies[1,2] have shown that the difference between the CD curves for Δ-(−)-[Co(edda)en]$^+$ ($\Delta\epsilon_{\max} = -4.49$) and the *N,N'*-Et$_2$edda complex is about −3.4 for the ^1E component and about +2.0 for the A_2 component. Since the maximum CD value for (+)-[Co(*l*-sdda)en]$^+$ is +3.22 and the contribution of the asymmetric carbons in *l*-stien is small, but negative, there must be a very large positive contribution to the rotational strength for the ^1E transition from the coordinated asymmetric N atoms in *l*-sdda for the complex to have the expected Δ configuration.

The homogeneity of the chemical environment of the asymmetric nitrogen is important in determining the contribution to the rotational strength.[1,2] In the case of [Co(dbedda)en]$^+$ for which the substituents on the asymmetric nitrogens are the methylenes of the ethylenediamine and glycinate rings and a benzyl group, Maricondi and Maricondi[2] have shown that the contributions to the rotational strength for the major peak are opposite the contribution from the configurational effect. The asymmetric nitrogens in [Co(edda)en]$^+$, which are bonded to two methylenes and a hydrogen, make contributions of the same sign as that for the configurational effect. The substituents on the asymmetric nitrogens of [Co(*l*-sdda)en]$^+$ (methylene of the glycinate ring, hydrogen, and benzyl) are very dissimilar, and this might cause the large contribution. It should be noted that the formal designations of absolute configurations for nitrogens with the same overall arrangements of substituents are *R,R* for the s-cis isomers of Δ-[Co(edda)en]$^+$ and *S,S* for Δ-[Co(dbedda)en]$^+$ and Δ-[Co(*l*-sdda)en]$^+$. The differences result from changes in priorities of substituents on N.

The examination of additive contributions[24] such as configurational, conformational, and vicinal effects of optically active ligands has been useful in the correlation of stereochemical effects and CD spectra. The ligand-polarization model[25-28] of optical activity depends upon the polarizability of the perturbing groups which constitute the dissymmetric environment around the symmetric chromophore. Phenyl substituents which have large anisotropic polarizability can make contributions with signs reversed from those expected.[25]

The optical activity induced by substituents on the ligand can be significant, and many empirical and theoretical treatments have been developed which relate stereochemical configuration with the signs and magnitudes of CD curves. These are commonly referred to as regional or sector rules.[19,29-34] The major difficulty with applying regional rules results from assumptions which must be made about the electrostatic or polarizable nature of the perturbing groups. Bosnich and Harrowfield[19] have pointed out the uncertainty concerning the sign of the potential of hydrogen atoms which are bonded to donor nitrogens. The acidity of the hydrogen atoms may cause the hydrogens to have an opposite potential of an *N*-alkyl group, even though both the hydrogen and the alkyl group might lie in the same sector of space. Also, anisotropic perturbing groups, such as benzene rings, can make contributions which are not readily predictable.[25]

Maricondi and Maricondi[2] have shown that Mason's hexadecadal regional rule can be applied to predict the experimentally observed sign of the low-energy CD transition for *s-cis*-[Co(dbedda)en]$^+$ where the nitrogens are substituted with benzyl groups. Mason[34] assumed that the effect on the sign and magnitude of the rotational strength produced by N-substitution is large, while the effect from *C*-alkyl substitution is small.

In both complexes, [Co(edda)(*l*-stien)]$^+$ and [Co(*l*-sdda)en]$^+$, attempts to apply regional rules (which have been questioned[19,35]) can be very ambiguous because the complexes contain substituents which differ significantly. Also, both complexes contain a nitrogen which is bonded to a hydrogen and carbons which are bonded to benzene rings. Neither the signs nor the magnitudes of these particular substituents are known or readily predictable.

The complex [Co(*l*-sdta)]$^-$ (*l*-sdta = *l*-stilbenediaminetetraacetate ion) is formed stereospecifically. The one isomer obtained[36] has a CD curve of the same form as those of the $(-)_{546}$ isomers of [Co(edta)]$^-$ and [Co(1,3-pdta)]$^-$ (1,3-pdta = 1,3-propanediaminetetraacetate ion). The absolute configurations of both of these complexes are known to be ΛΔΛ.[37,38] The ΛΔΛ isomer of [Co(*l*-sdta)]$^-$ permits the (*S,S*)-stilbenediamine backbone ring to adopt the stable δ conformation with both phenyl groups equatorial. If one removes the "in-plane" or G acetate rings to give a *sym*-sdda complex, the absolute configuration is Δ (the rings retained are those which give the Δ chiral pair for ΛΔΛ-[Co(*l*-sdta)]$^-$). This gives strong support for the Δ configuration assigned above for the one isomer obtained for [Co(*l*-sdda)en]$^+$.

The signs and magnitude of the CD curve of [Co(edda)(*l*-stien)]$^+$ agree with previously studied Co^{III}–edda complexes,[1,2,6] indicating that the edda portion of the complex dominates and that the benzene substitution on the carbons has little effect. However, for [Co(*l*-sdda)en]$^+$, the signs of the low-energy peaks in the CD spectrum are the opposite of those expected from the stereospecificity of [Co(*l*-sdta)]$^-$ and

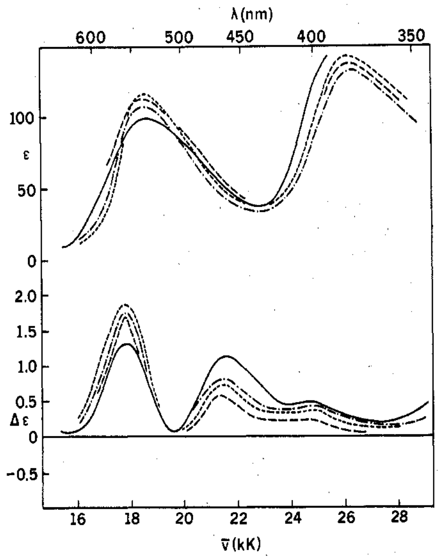

Figure 6. Cirular dichroism and absorption spectra of *s-cis*-[Co(dbedda)en]$^+$ (- - -), *s-cis*-[Co(dNO$_2$bedda)en]$^+$ (—), *s-cis*-[Co(dClbedda)en]$^+$ (- · -), and *s-cis*-[Co(dMebedda)en]$^+$ (· · ·).

Table II. Circular Dichroism and Absorption Data for *s-cis*-[Co(dNO$_2$bedda)en]$^+$, *s-cis*-[Co(dmbedda)en]$^+$, *s-cis*-[Co(dClbedda)en]$^+$, and *s-cis*-[Co(dbedda)en]$^+$

	absorption		CD	
compd[a]	cm^{-1} × 10^3	ε	cm^{-1} × 10^3	Δε
(+)-*s-cis*-[Co(dmbedda)en]-Cl·0.5H$_2$O	18.69	115	17.92	+1.81
	21.28[b]	52	21.55	+0.68
	26.32	139	25.00	+0.29
(+)-*s-cis*-[Co(dNO$_2$bedda)en]-Cl·1.5H$_2$O	18.69	97	17.92	+1.32
	21.28[b]	61	21.50	+1.12
			24.69	+0.49
(+)-*s-cis*-[Co(dClbedda)en]-Cl·3H$_2$O	18.69	107	17.92	+1.79
	21.28[b]	52	21.50	+0.75
	26.32	132	25.00	+0.36
(+)-*s-cis*-[Co(dbedda)en]-Cl·4H$_2$O	18.45	116	17.95	+1.70
	21.10[b]	58	21.15	+0.65
	26.85	150	24.55	+0.21

[a] The optically active isomers are designated (+), the sign of the low-energy CD band in the $^1T_{1g}$ region. [b] Shoulder on main absorption band.

[Co(*l*-sdda)en]$^+$. There is a clear choice between two conclusions. (1) (+)-[Co(*l*-sdda)en]$^+$ has the Λ configuration based on the CD sign pattern similar to those other Λ-(+)-[Co(edda)(diamine)]$^+$ complexes. There would be little contribution from the asymmetric N atoms in this case. This assignment requires the phenyl groups to occupy very unfavorable axial positions, contrary to the case of [Co(stien)$_3$]$^{3+}$ for which the structure is known. The complete stereospecificity of [Co(*l*-sdta)]$^-$ and [Co(*l*-sdda)en]$^+$ argues against this assignment. (2) (+)-[Co(*l*-sdda)en]$^+$ has the Δ configuration based on the steric requirements of *l*-(*S*,*S*)-sdda. It is consistent with the conformation of stien in Co(*l*-stien)$_3$$^{3+}$ and the results for [Co(*l*-sdta)]$^-$ and [Co(edda)(*l*-stien)]$^+$. It requires very large contributions from the coordinated asymmetric N atoms in the region of the first absorption band. Such a large contribution might be expected from previous studies of substituted edda and ed3a type complexes.[1,2]

The latter choice is preferred, but only an X-ray structure determination can settle the question with certainty.

A series of para-substituted dbedda analogues was prepared to study any possible electronic effects on asymmetric nitrogens which might be manifested in the CD spectra. The substituted dbedda complexes which were prepared were the para methyl, chloro, and nitro derivatives. These were compared to the dbedda complex[2] which contains a hydrogen in the para position. The absorption and CD data are shown in Figure 6, and the corresponding data are collected in Table II. As shown in Figure 6, substitution of different groups in the para position of the benzene ring has no effect on the position of the maxima for the low-energy (^{1}E) component and very little effect on the intensities. Only the nitro-substituted dbedda complex has a maximum which can be considered to be significantly different. However, small shifts in the positions of two adjacent CD peaks can result in changes in peak intensities. Although the extent of overlap of peaks is difficult or impossible to evaluate, it may be reasonable that the nitro-substituted dbedda complex may show a larger tetragonal splitting than the other complexes. Generally, substitution at the para position is probably too far removed from the chromophore to produce any significant changes. The para position was selected to avoid steric effects.

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Registry No. (+)-*S-cis*-[Co(edda)(*l*-stien)]Cl, 70812-16-7; (−)-*S-cis*-[Co(edda)(*l*-stien)]Cl, 70728-63-1; (+)-*S-cis*-[Co(*l*-sdda)en]Cl, 70728-64-2; (+)-*S-cis*-[Co(dmbedda)en]Cl, 70728-65-3; (−)-*S-cis*-[Co(dmbedda)en]Cl, 70774-43-5; (+)-*S-cis*-[Co(dNO$_2$bedda)en]Cl, 70811-67-5; (−)-*S-cis*-[Co(dNO$_2$bedda)en]Cl, 70728-66-4; (+)-*S-cis*-[Co(dClbedda)en]Cl, 70811-68-6; (−)-*S-cis*-[Co(dClbedda)en]Cl, 70728-67-5; (+)-*S-cis*-[Co(dbedda)en]Cl, 70774-44-6; dmbH$_2$edda, 70728-68-6; dNO$_2$bH$_2$edda, 70728-69-7; dClbH$_2$edda, 70728-70-0; H$_2$edda, 5657-17-0.

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